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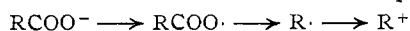
The Formation of Carbonium Ions by Oxidative Decarboxylation of Carboxylic Acids with Lead Tetraacetate

BY E. J. COREY AND J. CASANOVA, JR.¹

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The bisdecarboxylation of *meso*- or *d,l*-1,2-diphenylsuccinic acid by lead(IV) or anodic oxidation produces *trans*-stilbene, a result which excludes a concerted *cis* elimination for this system. The intervention of a cationic intermediate is indicated as an alternative by the behavior of α,β,β -triphenyl- β -hydroxypropionic acid (I) which undergoes oxidative decarboxylation to form chiefly phenyl benzhydryl ketone (II). The reaction of lead tetraacetate with either optically active *exo*- or *endo*-norbornane-2-carboxylic acid leads to *exo*-norbornyl acetate as principal product with the same degree of retention of optical activity in each case. The relatively minor effect of solvent on the stereochemistry of this reaction suggests that the enantiomeric products are formed *via* a common intermediate, probably a classical norbornyl cation associated with the anion $\text{Pb}(\text{OAc})_3^-$ or AcO^- ; the norbornyl free radical is definitely excluded as a precursor of inverted (rearranged) *exo*-norbornyl acetate on the basis of previous studies which indicate that this intermediate rearranges only at relatively high temperatures. Other examples of oxidative decarboxylation by lead(IV) are discussed in which the products seem to be formed predominantly from cations rather than free radicals. The possible significance of this reaction in the study of electron transfer, ion-pairing phenomena or questions of carbonium ion structures is noted.

It has recently been shown that under certain conditions the anodic oxidative decarboxylation of carboxylic acids can produce cationic species by a process which appears to be an extension of the Kolbe sequence²



At higher voltages with those systems in which carbonium ion stability can be inferred from rapid solvolytic ionization of halides or sulfonates the formation of cations is actually favored. This is evidenced by the correspondence of products from electrolysis and solvolysis reactions and the absence of those reaction products to be expected from free radicals. The intermediacy of cations in anodic oxidation has been noted in a number of instances including the epimeric norbornane- and 5-norbornene-2-carboxylic acids, cyclobutane carboxylic acid, cholesteryl- 3β -carboxylic acid and various α -, β - and γ -hydroxy acids and appears to be a broadly observable phenomenon. Of course the possibility that in certain systems or under certain intermediate conditions cations and radicals may be involved *simultaneously* in an electrolytic reaction must be considered.

During the course of the electrolysis studies it became apparent that the oxidative decarboxylation³ effected by lead(IV) salts might be comparable mechanistically to anodic decarboxylation and it seemed of interest to study the products of the lead(IV) reaction in the same systems. We were especially conscious of the possibility that such an investigation might serve to reconcile the conflicting views which have been expressed regarding the importance of free radical^{3c} and cationic^{3d} intermediates. A brief outline of the formal mechanistic possibilities is presented in Fig. 1. A more detailed interpretation of the decarboxylation step is purposely omitted since there is really no clear evidence on this point (including, for example, tests relative to the intermediacy of species such as $\text{RCO}_2\cdot$ or RCO_2^+). Also unspecified is the possibility of some degree of covalent interaction in the radical or ion pairs. The formulation of carbonium ion-anion ($(\text{R}-$

$\text{CO}_2)_3\text{Pb}^-$ or RCO_2^-) pairs may occur by electron transfer at the radical pair stage or by a more direct process.

Previous investigations of product distribution in the lead(IV) oxidative decarboxylation reaction have yielded results which are suggestive of a mechanistic spectrum. Thus, it seems likely that for lead tetraacetate^{3a,b,c} the ultimate products are formed from methyl radicals, whereas for lead tetrapivalate^{3d} the products come mainly from the tertiary butyl cation. Of particular significance to the theme of the present work is the fact that in the decomposition of lead tetraacetate no methyl acetate, the product expected for an ionic pathway, could be detected.^{3c} This datum raises the question of whether in general the formation of carboxylic ester from the radical pair, $(\text{RCO}_2)_3\text{Pb}\cdot\text{RCOO}\cdot$ can occur competitively. In some instances, e.g., α -hydroxy acids,⁴ α -acylamino acids⁵ and formic acid,^{3d} it is probable that the oxidative decarboxylation is a two-electron process which does not involve intermediate radicals.

One of the first objectives of this study was a comparison of 1,2-bis-decarboxylation by anodic⁶ and lead(IV)^{7,8} oxidation with respect to stereochemistry. It was found that both the anodic (134 volts, smooth platinum) and lead(IV) (using carboxylate exchange with lead tetraacetate according to ref. 8) bisdecarboxylations of *meso*- and *d,l*-1,2-diphenylsuccinic acids afforded the same product, *trans*-stilbene. Under the conditions of these experiments *cis*-stilbene is stable to isomerization and hence cannot be an intermediate. On the basis of these results it seems likely that this bisdecarboxylation reaction is not concerted and that a labile monocarboxylic intermediate is involved. The data on anodic oxidation in other systems and the evidence which follows directly below implicate the cation $\text{C}_6\text{H}_5\text{C}^+\text{H}-\text{CH}(\text{C}_6\text{H}_5)\text{COOH}$ (or the corresponding carboxylate dipolar ion) for both anodic and lead(IV) reactions. How generally this will be true for other examples of bisdecarboxylation cannot yet be specified. However, it would hardly be surprising if the concerted cyclic elimination mechanism were generally unimportant in view of the unfavorable ring geometry of the lead(IV)-dicarboxylate structure

(1) U. S. Public Health postdoctoral fellow 1959-1961. This research was also supported in part by the Higgins Fund of Harvard University and a grant (G-9999) from the National Science Foundation. Presented at the 142nd Meeting of the American Chemical Society, September, 1962.

(2) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(3) Cf. (a) L. F. Fieser and F. C. Chang, *ibid.*, **64**, 2043 (1942); (b) L. F. Fieser and Richard C. Clapp and W. H. Daudt, *ibid.*, **64**, 2052 (1942); (c) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951); (d) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

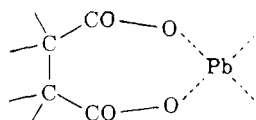
(4) R. Criegee in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 16.

(5) O. Süss, *Ann.*, **564**, 137 (1949).

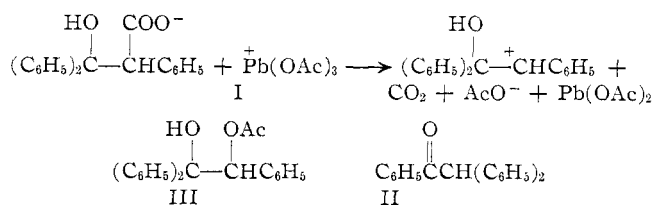
(6) F. Fichter and A. Petrovich, *Helv. Chim. Acta*, **24**, 549 (1941).

(7) W. von E. Doering, M. Farber and A. Sayigh, *J. Am. Chem. Soc.*, **74**, 4371 (1952).

(8) C. A. Grob, M. Ohta, E. Renk and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).



The lead tetraacetate oxidation of the acid I was studied to test for a cationic intermediate in this and the related 1,2-diphenylsuccinic acid cases. Cationic de-



composition would be expected to produce the ketone II as a rearrangement product and the acetate III in the absence of rearrangement. In actuality the rearranged ketone II was formed as the major product in both benzene (71% yield) and acetonitrile (76% yield) with the acetate III in much smaller amount (yields 14% and 8%, respectively). These data indicate a cationic intermediate for the ketone II. That this cation is also a precursor of the acetate III (rather than the radical) follows from the relatively small influence

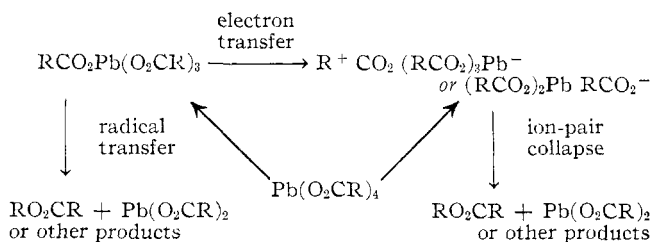


Fig. 1.

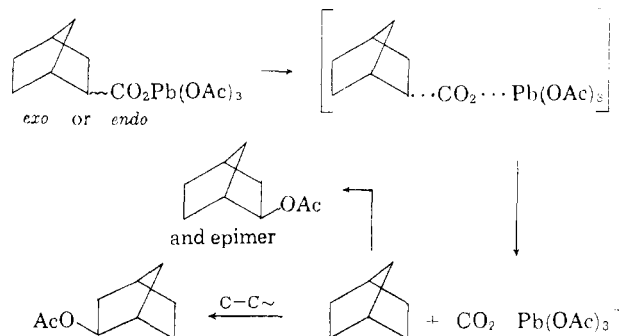
of solvent polarity on product distribution. It might be expected that the more polar solvent acetonitrile would greatly favor the electron transfer from $\text{R}\cdot$ to $\text{Pb}(\text{OAc})_3$ (charge separation). The rather modest solvent effect is more likely due to small differences in the collapse time of the ion pair R^+AcO^- (there being relatively more time for competing rearrangement in the more polar solvent).⁹

The next objective in this investigation was the study of oxidative decarboxylation by lead tetraacetate in the norbornyl and cyclobutyl series since the behavior of these cations had been investigated previously in solvolysis, amine deamination and electrolysis.² Both *endo*- and *exo*-norbornane-2-carboxylic acids underwent smooth conversion to predominantly *exo*-norbornyl acetate (24–67% yield) upon treatment with lead tetraacetate–pyridine in benzene. The acetate from the *endo*-acid was essentially pure *exo* isomer uncontaminated by appreciable amounts of *endo*-acetate, whereas the product from the *endo*-acid consisted of ca. 97% *exo*- and 3% *endo*-acetates. When either the optically active *exo*- or *endo*-acid was subjected to oxidative decarboxylation in benzene solution, the *exo*-acetate which resulted was optically active with a rotation corresponding in each case to 43% net retention of optical purity. In acetonitrile as solvent, optically active *exo*- and *endo*-norbornane-2-carboxylic acids again afforded *exo*-acetate each with the same

(9) In addition it might be noted that the total yield of product is essentially the same in acetonitrile as in benzene. If the carbon radical is an intermediate, its lifetime would have to be less than the time required for collision with solvent since acetonitrile is an excellent hydrogen atom donor. In this case it is difficult and perhaps unrewarding to try to distinguish between *direct* carbonium ion generation and *indirect* formation *via* an $\text{R}\cdot\text{Pb}(\text{OAc})_3$ radical pair.

net retention of optical purity, 33%, somewhat less than observed for benzene as solvent. The invariance of the optical result with the *exo*- and *endo*-isomers is striking, all the more so because it holds in two solvents of widely different polarity. These facts set severe interpretive limits; moreover, we suggest that they provide a uniquely plausible mechanistic hypothesis which can be constructed in the following way.

First of all, since the occurrence of any type of stereospecific, concerted displacement of carboxyl can be excluded, one or more norbornyl intermediates lacking the carboxyl are required; obviously the extant possibilities are the norbornyl radical, the norbornyl cation or both of these. It is known that the 2-norbornyl radical is not subject to carbon rearrangement in the temperature range of the present studies and, indeed, that significant rearrangement does not set in until far higher temperatures.¹⁰ Thus, the racemic *exo*-norbornyl acetate, the major product of reaction, must come from a carbonium ion precursor,¹¹ and it remains only to explain the occurrence of the optically active product. There are two possibilities: (1) both rearranged and non-rearranged acetate are derived from the classical norbornyl cation– AcO^- (or alternatively throughout this discussion $\text{Pb}(\text{OAc})_3^-$) ion-pair in a close competition between rearrangement and ion-pair collapse as formulated in Fig. 2, and (2) rearrangement occurs *via* a cation and non-rearrangement *via* the norbornyl free radical. Of these, the latter explanation seems untenable since the observed solvent effect (factor of 1.2 between benzene–dielectric constant at 20° = 2.28— and acetonitrile–dielectric constant at 20° = 37.5) is hardly compatible with the



assumption of competing processes, one of which does and one of which does not involve charge separation. In our view, therefore, *all* the norbornyl acetate is formed from cation; in the case of the optically active acetate the precursor must be the classical cation (as distinguished from the bridged, symmetrical cation¹¹). Further, the evidence for a common behavior of *exo*- and *endo*-acids argues that the classical ion serve as a precursor for rearranged acetate as well.¹¹ This conclusion is identical with that reached previously for the deamination reaction of the *exo*- and *endo*-2-norbornylamines.¹² It is also in agreement with the observation that the rates of oxidative decarboxylation of *exo*- and *endo*-norbornane-2-carboxylic acids are qualitatively the same, indicating the absence of strong participation effects in the generation of cation. It would seem reasonable to suppose that the norbornyl skeleton does not carry appreciable positive charge in the transition state for decarboxylation. In the (not improbable) extreme the mechanism might be represented as homolytic decarboxylation followed by very fast

(10) Cf. J. A. Berson, D. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960).

(11) S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).

(12) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry and R. Winter, *ibid.*, **84**, 169 (1962).

electron transfer from the norbornyl radical to $\text{Pb}(\text{OAc})_2$,^{12a} (Certainly, a more detailed study of this point is in order.) Lastly, mention should be made again of the absence of methyl acetate as a product in the decomposition of lead tetraacetate,^{3c} a reaction which probably proceeds *via* the radical pathway without intervention of carbonium ions.

If a classical norbornyl cation is presumed to be the intermediate for both rearranged and unrearranged acetate in oxidative decarboxylation of the norbornane-2-carboxylic acids in benzene or acetonitrile and in the deamination of the norbornylamines in acetic acid,¹¹ comment is required on the relatively greater fraction of rearrangement in the latter case. A reasonable explanation would seem to be that the cation produced in the oxidative decarboxylation is necessarily paired with a neighboring anion in a solvent which is relatively less polar than acetic acid, the medium for deamination. Consequently, one would expect a longer lifetime for the cation from deamination in acetic acid, and hence more rearrangement, granting even that this reaction also produces cation-acetate pairs exclusively (which seems extreme).

During the course of our work we learned of an independent study of the reaction of lead tetraacetate with carboxylic acids in the laboratories of Prof. G. Büchi¹³ and in private discussions it was agreed that the investigation of the cyclobutanecarboxylic acid case would be made by the M.I.T. group. These studies have now revealed a reasonably close similarity in the acetate mixture (cyclobutyl, cyclopropylcarbonyl and allylcarbonyl) formed with lead tetraacetate with the product mixtures previously obtained by sulfonate solvolysis and amine deamination.¹³ The case for a cationic intermediate in this instance is quite compelling.

In addition to these results several other examples of oxidative decarboxylation with lead tetraacetate are recorded in recent papers^{14,15} which are most readily interpreted in terms of the cationic pathway. Of special interest is the conversion of α,β -diphenylglutaric acid (either diastereomer) to β,γ -diphenyl- γ -butyrolactone (probably *trans*).¹⁶

There can now be little doubt that the oxidation of carboxylic acids by lead(IV) can lead to carbonium ion intermediates and also that this reaction is of both theoretical and practical significance. The rather unusual circumstances under which carbon cations can be generated will doubtless be of value in the development of a broader understanding of carbonium ion behavior. For example, the oxidative decarboxylation may allow the generation of classical cations in systems for which a bridged ion is formed by solvolytic ionization. Since such a cation would doubtless be produced together with an anion, there is a reasonable chance that these may unite to form a stable product without complete rearrangement. Finally, it is clear that the reactions discussed herein are connected in a general sense with the problem of ligand *vs.* electron transfer mechanisms in organic reactions.¹⁷ A spectrum of reaction mechanisms is indicated: cationic intermediates are to be expected when these are

relatively stable, otherwise free radical or ligand transfer processes should dominate.

Experimental¹⁸

Electrolysis of *meso*-2,3-Diphenylsuccinic Acid.¹⁹—A solution of 540.6 mg. (2.0 mmoles) of *meso*-2,3-diphenylsuccinic acid, m.p. 242–245°, and 1.12 ml. (8.0 mmoles) of triethylamine in 10 ml. of 90% pyridine–water, was maintained at reflux under nitrogen in an electrolysis apparatus consisting of smooth platinum electrodes, nitrogen inlet tube, dropping funnel and magnetic stirrer in a 300-ml. glass vessel. Electrolysis was conducted for 550 minutes at 134 volts, during which time the current fell from 0.14 ampere to 0.10 ampere and held constant. The dark reaction mixture was evaporated on a steam-bath at 10 mm., treated with 50 ml. of ether, and extracted with 2 \times 20 ml. of *N* hydrochloric acid, 2 \times 5 ml. of saturated salt, 2 \times 20 ml. of *N* sodium hydroxide and 1 \times 10 ml. of saturated salt. The remaining pale yellow ether solution was dried over anhydrous magnesium sulfate and evaporated, leaving an amber-colored oily crystalline solid; 810.0 mg. after drying in high vacuum. Infrared analysis (CCl_4) showed all absorptions characteristic of *trans*-stilbene, with the characteristic 10.89 μ absorption of *cis*-stilbene entirely absent. A carbonyl absorption at 5.85 μ was present. Quantitative ultraviolet analysis (95% ethanol) demonstrated the presence of *trans*-stilbene of 49.5% purity in the crude neutral product and also showed the presence of a second ultraviolet absorber (λ_{max} 255). Separation of components of this mixture was effected by chromatography on alumina, activity grade 2. Elution with 1:1 petroleum ether–benzene afforded 170.4 mg. (68% by weight) of a white oily solid, m.p. 96–112°, essentially identical in infrared with authentic *trans*-stilbene. Crystallization of this material from ethanol gave *trans*-stilbene, m.p. 119.5–121.0°, undepressed in melting point on admixture with an authentic sample. Elution of the chromatogram with benzene gave 18 mg. (7.2% by weight) of oily solid, which exhibited carbonyl absorption at 5.85 μ , but failed to give a 2,4-dinitrophenylhydrazone by the usual procedure.²¹ The over-all yield of *trans*-stilbene was 35.5% based on quantitative ultraviolet analysis.

Electrolysis of *d,l*-2,3-Diphenylsuccinic Acid.²²—This reaction was conducted exactly as described for the *meso*-diacid. The neutral product, 275.5 mg., crystallized upon removal of solvent. The infrared spectrum (CCl_4) of this substance was identical with that of the crude neutral product from electrolysis of the *meso*-diacid. Quantitative ultraviolet analysis (95% ethanol) showed 40.4% *trans*-stilbene with no accompanying *cis* isomer. An ultraviolet difference spectrum obtained with *trans*-stilbene of appropriate concentration in the solvent cell gave a spectrum of λ_{max} 240 m μ (A 2.07), 253 m μ (shoulder) (A 1.79). Chromatography of the crude neutral material on alumina (activity grade 2) afforded 149.0 mg. (63% by weight) of impure *trans*-stilbene as a white crystalline solid from 70% petroleum ether–benzene eluant, whose infrared spectrum was virtually identical with *trans*-stilbene. Recrystallization of this material from 95% ethanol gave pure *trans*-stilbene, identical with an authentic sample in m.p. and mixed m.p.

Attempted Isomerization of 2,3-Diphenylsuccinic Acids.—Small samples of *meso*- and *d,l*-2,3-diphenylsuccinic acids were separately dissolved in 90% pyridine–water containing triethylamine. All reagents were employed in quantities proportionate to those used in the preceding experiments. The solutions were maintained at 105° for 10 hours. The solvents were removed by distillation in vacuum, and the residual solids were thoroughly triturated with cold *N* hydrochloric acid, washed with water, and dried in high vacuum. In neither case could isomerization be detected by infrared analysis. Recovery of starting materials was confirmed by m.p. and mixed m.p.

Attempted Isomerization of *cis*-Stilbene.—A sample of *cis*-stilbene (360 mg., 2.0 mmoles) in 70 ml. of 90% pyridine–water and 1.20 ml. (8.0 mmoles) of triethylamine was heated at reflux

(18) Melting points are uncorrected. Analyses were by A. Bernhardt, Mulheim, Ruhr, and Dr. S. M. Nagy, M. I. T. Vapor phase chromatographic work was performed with an F and M model 300 instrument. Infrared data were obtained using Perkin-Elmer model 21 and Infracord spectrometers.

(19) S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 745 (1940); prepared from *meso*-2,3-diphenylsuccinonitrile (J. A. McCrae and R. A. B. Bannard, *Org. Syntheses*, **32**, 63 (1952)) which was in turn prepared from α -phenylcinnamonitrile (S. Wawzonek and Edwin M. Smolin, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 715).

(20) The melting point of this compound has been variously reported between 219° and 265°. The observed value is strongly dependent on heating rate.

(21) R. Shriner, R. C. Fuson and D. Y. Curtin, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y.

(22) Obtained by conversion of *meso*-diacid to the *d,l*-anhydride at 290°, followed by mild base hydrolysis, acidification and recrystallization from aqueous ethanol (m.p. 156–160°).

(12a) It has been suggested that the formation of carbonium ions from lead(IV) salts proceeds *via* acyloxonium cations RCOO^+ (ref. 3d). Although this possibility cannot now be excluded, it would not seem to be in good accord with the sensitivity of the rates of oxidative decarboxylation to the nature of R (e.g., as a primary, secondary or tertiary radical).

(13) Cf. G. Büchi, R. E. Erickson and N. Wakabayashi, *J. Am. Chem. Soc.*, **83**, 927 (1961); G. Büchi and J. Marvel, personal communication.

(14) A. Valenta, A. H. Grey, S. Papadopoulos and C. Podessa, *Tetrahedron Letters*, **20**, 25 (1960).

(15) M. Vilkas, *Bull. soc. chim. France*, 1350 (1960).

(16) L. L. McCoy and A. Zagalo, *J. Org. Chem.*, **25**, 824 (1960).

(17) Cf. J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

for 10 hours. The solvent was removed on a steam-bath in vacuum and the residual colorless oil was dried in high vacuum (328 mg.). The infrared spectrum of this oil showed no trace of *trans*-stilbene. Quantitative ultraviolet analysis (95% ethanol) showed that the oil contained less than 2.2% *trans*-stilbene, and was 84.8% pure in *cis*-stilbene.

Oxidative Decarboxylation of *d,l*-2,3-Diphenylsuccinic Acid by Lead Tetraacetate.—A suspension of 405.4 mg. (1.5 mmoles) of *d,l*-2,3-diphenylsuccinic acid in 0.18 mg. (177 mg., 2.2 mmoles) of pyridine and 3.0 ml. of dry benzene was cooled under nitrogen and treated with 700 mg. (1.9 mmoles) of lead tetraacetate (*cf.* ref. 8). The mixture was refluxed under nitrogen for 200 minutes during which time a white precipitate formed. The reaction mixture was cooled and filtered, and the solid was washed with *ca.* 10 ml. of benzene. The combined filtrate and washings were extracted successively with 20-ml. portions of water, *N* sodium hydroxide, water, *N* hydrochloric acid and water. After drying over magnesium sulfate the benzene solution gave upon evaporation 179.9 mg. of pale yellow solid, m.p. 105–113°. Quantitative ultraviolet spectroscopy showed that this material contained 63.0% *trans*-stilbene uncontaminated by *cis* isomer. Gradient elution chromatography using petroleum ether and benzene on activity grade 2 alumina gave a 66% recovery of white crystalline solid, m.p. 122.0–122.5°, identical in infrared with *trans*-stilbene, and undepressed in mixed melting point. This represents a 44% yield.

Oxidative Decarboxylation of *meso*-2,3-Diphenylsuccinic Acid by Lead Tetraacetate.—This reaction was carried out using identical amounts of reagents and conditions as described for the *d,l*-diacid. A solid neutral fraction (167.7 mg.) was obtained in like manner, which was 65.7% *trans*-stilbene containing no *cis*-stilbene, by quantitative ultraviolet analysis. Chromatography on alumina of activity grade 2 afforded 76% of *trans*-stilbene, identified by infrared, m.p. and mixed m.p. A small amount (2.5% by weight) of a carbonyl-containing compound was obtained from the chromatogram in pet. ether-benzene (infrared absorption at 5.75 μ) and was not further investigated. The over-all yield of *trans*-stilbene was 41%.

Attempted Isomerization of *cis*-Stilbene.—A solution of 270 mg. (1.5 mmoles) of *cis*-stilbene, 0.18 ml. (177 mg., 2.2 mmoles) of pyridine and 700 mg. (1.9 mmoles) of lead tetraacetate in 3.0 ml. of dry benzene was refluxed under nitrogen for 200 minutes. By a procedure identical with that used for the preceding reactions there was obtained 252.2 mg. of a colorless oil, the ultraviolet spectrum of which showed it to be *cis*-stilbene containing less than 3% *trans* isomer. A petroleum ether solution of this oil was filtered through alumina to give 64% recovery of *cis*-stilbene, identical in infrared with an authentic sample.

Oxidative Decarboxylation of α,β -Triphenyl- β -hydroxypropionic Acid²³ by Lead Tetraacetate.—The title compound (636 mg., 2.0 mmoles, m.p. 203–204.5°) and pyridine (0.25 ml., 0.25 g., 3.0 mmoles) in 8 ml. of dry benzene was treated with 1.52 g. (4.0 mmoles) of lead tetraacetate. The resulting solution was refluxed under nitrogen for 360 minutes. The reaction mixture was filtered through a column of 27 g. of alumina (activity grade 2) under benzene. Elution of the column with benzene afforded 386.7 mg. of white crystalline solid, m.p. 114–123° after one crystallization from 95% ethanol, raised to 132–135° by a second crystallization from aqueous ethanol (lit.²⁴ m.p. 136–137° for benzhydryl phenyl ketone). The infrared spectrum showed carbonyl absorption at 5.90 μ . A green color was observed when a sample of the ketone was warmed with concentrated sulfuric acid.²⁵ Elution of the chromatogram with ether gave 94.3 mg. of white crystalline solid, m.p. 220–220.5° after recrystallization from methylene chloride-ether (lit.²⁵ m.p. 218–219° for 1,1,2-triphenylethylene glycol-2-monoacetate). Crude yield of 71% of ketone and 14.2% of monoacetate was verified by a duplicate experiment. When the experiment was conducted in dry acetonitrile as solvent instead of benzene, there was obtained a 76% crude yield of ketone, m.p. 106–111°, and a 7.9% crude yield of monoacetate, m.p. 195–206°. Crystallization of the ketone from methylene chloride-ether gave material of m.p. 218–219°.

Typical Procedure. (\pm)-*exo*-Norborene-2-carboxylic Acid.—To a solution of (\pm)-*exo*-norborene-2-carboxylic acid²⁶ (2.884 g., 20.0 mmoles) in 40 ml. of anhydrous benzene and 2.37 g. (30.0 mmoles) of dry pyridine under nitrogen was added 7.59 g. (40.0 mmoles) of lead tetraacetate. The mixture was stirred and heated under gentle reflux for 400 minutes. The cooled mixture was poured onto 50 g. of Merck alumina (activity grade 2) in a 2.5 \times 6.5 cm. column, prepared in ether and washed thoroughly with 110 ml. of ether. The total eluant (150 ml.) was extracted with 3 \times 30 ml. of *N* sodium hydroxide, 2 \times 10 ml. of saturated salt solution, 3 \times 30 ml. of *N* hydrochloric acid,

and 2 \times 10 ml. of saturated salt solution. The organic layer was dried over Drierite, filtered and distilled slowly through a 24" Vigreux column until the head temperature reached 50°. A small sample was removed and analyzed by vapor phase chromatography (4 ft. Carbowax 20 M, 75°; retention time: 3 minutes 5 seconds). The remainder of the benzene was removed from the bulk of the reaction mixture and the residual yellow oil fractionated in a Holtzmann column. The fraction boiling at 137–140° (100 mm.) (0.991 g., 31.8%, n_D^{20} 1.4605) was collected, and was identical in infrared spectrum to authentic *exo*-norborenyl acetate. Vapor phase chromatography of the distillate showed a single peak (pentane solution, 4 ft. Carbowax 20 M, 75°; retention time: 3 minutes, 5 seconds; authentic *exo*-norborenyl acetate retention time: 2 minutes 55 seconds). Addition of one drop of bromine to the distilled benzene produced a permanent faint brown coloration. The residue from acetate distillation (0.222 g.) crystallized from 40% methanol-water to give a white solid, m.p. 125.9–126.8°, which sublimed readily at 56–65° (bath, 30 μ) to give 0.115 g. of white crystalline material, m.p. 126.2–127.0°, which is probably *exo*-norborenyl *exo*-norborenyl-2-carboxylate.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.93; H, 9.33.

Analysis of the above norborenyl acetate for contamination by the *endo* isomer was carried out by conversion with lithium aluminum hydride to norborneol and vapor phase chromatography on a 12-ft. column of 20% Ucon 50 HB 280 \times on Celite 545 at 160°. The reaction product was found to consist of >99% *exo* isomer; no *endo* isomer was detected.

Repetition of the above experiment without addition of pyridine to the reaction mixture gave substantially identical results, although the reaction rate was somewhat slower. Bubbling oxygen through the reaction mixture was without effect on the reaction product and yield.

Reaction of (\pm)-*endo*-Norborene-2-carboxylic Acid with Lead Tetraacetate.—Using the above procedure there was obtained a mixture of 97 \pm 1% *exo*- and 3 \pm 1% *endo*-norborenyl acetates, n_D^{20} 1.4610 in yields of 24–35% in a number of runs. In addition the residue from distillation of *exo*-acetate was sublimed at 75° (bath, 50 μ), crystallized from 40% methanol-water and resublimed at 85° (bath, 50 μ) to give 0.1055 g. of white crystalline solid, m.p. 123.5–124.0°, which is probably *exo*-norborenyl *endo*-norborenyl-2-carboxylate. The infrared spectrum (CCl_4) of this compound was distinctly different from the isomer mentioned above at several wave lengths.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.94; H, 9.41.

Experiments with Optically Active Norborene-2-carboxylic Acids.—Partially resolved acid was obtained by the procedure described previously. Runs with benzene solvent were carried out as described above and those in acetonitrile differed only in that the acetonitrile was removed by careful distillation before work-up. Experiments on the isolation of unreacted acid before completion of the oxidative decarboxylation showed that the starting *exo*- and *endo*-acids were unchanged under the reaction conditions. Results are summarized in Table I.

TABLE I

OXIDATIVE DECARBOXYLATION OF OPTICALLY ACTIVE NORBORNANE-2-CARBOXYLIC ACIDS BY $Pb(OAc)_2$ -PYRIDINE

	Acid, ^c [α] _D ²⁰	Acetate yield, %	α ²⁰ acetate ^d	% net retention
<i>exo</i> ,	-8.72 \pm 0.01°	28 ^a	-1.68 \pm 0.03°	42.5
<i>exo</i> ,	-4.52 \pm 0.29°	29 ^a	-0.683 \pm .02°	33.5
<i>endo</i> ,	-14.2 \pm 0.2°	35 ^b	-2.47 \pm .08°	42.2
<i>endo</i> ,	+8.63 \pm 0.4°	49 ^a	+1.14 \pm .01°	32.0

^a Acetonitrile solvent. ^b Benzene solvent. ^c Rotations measured in 95% ethanol, *c* 2.2 to 2.8, 1 dm. tube. ^d Rotation of neat acetate. ^e Rotations for optically pure *exo*- and *endo*-acids in 95% ethanol were taken as 27.8° and 30.6°, respectively.

Lead Tetraacetate Oxidation of 1-Hydroxycyclohexyl- α -methylacetic Acid.—The title compound² (3.444 g., 20 mmoles) was oxidized in the usual way. The reaction mixture was filtered through 35 g. of Merck aluminum oxide (act. gr. 2), the column washed with 120 ml. of ether and the combined elements washed with 3 \times 30 ml. of 2 *N* hydrochloric acid, 2 \times 20 ml. of 2 *N* sodium hydroxide and 4 \times 15 ml. of saturated salt solution. After the solution was dried over Drierite and concentrated on a Nester and Faust 18" 24-plate spinning band column, A 1/10 aliquot was treated to prepare a 2,4-dinitrophenylhydrazone

(27) C. H. DePuy and P. R. Storey, *Tetrahedron Letters*, 6, 20 (1959).

(28) *Cf.* J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, 81, 4088 (1959), for assignment of $\alpha_D \pm 12.3^\circ$ (neat) as maximum rotation of *exo*-norborenyl acetate.

(23) Phillip J. Hamrick and Charles R. Hauser, *J. Am. Chem. Soc.*, 82, 1957 (1960).

(24) H. Biltz, *Ber.*, 26, 1957 (1893).

(25) P. Chieffi, *Gazz. chim. ital.*, 40, II, 331 (1910).

(26) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, 81, 4083 (1959).

(DNP) in the usual manner.²¹ The bulk of the material was distilled from the same column, and two fractions were collected: (1) 0.347 g., b.p. 120–159.5°; and (2) 0.498 g., b.p. 159.5–160.0°. Fraction 2 showed only a weak carbonyl absorption at 5.83 μ , and formed a 2,4-DNP²¹ melting at 138.5–139.5° after crystallization from methanol, undepressed on mixed melting with authentic methyl cyclohexyl ketone (m.p. 140°). Column chromatography of the solid 2,4-DNP from the crude reaction mixture on alumina (act. gr. 2) gave three bands which were eluted with benzene (bands 1 and 2) and 1:4 ether–benzene (band 3), respectively. Evaporation and recrystallization from methanol gave

solids which were identified by melting points and mixed melting points as: band 1, methyl cyclohexyl ketone 2,4-DNP, m.p. 138.5–139.5°; band 3, cyclohexanone 2,4-DNP, m.p. 151–156° (reported²¹ m.p. 160°). Vapor phase chromatography of the crude reaction mixture on 4-ft. Silicone DC 200 at 151° and 4-ft. dinonyl phthalate at 140° showed four major components, present in approximately equal amounts, but no α -methylcycloheptanone could be detected. The absence of carbonyl absorption in the distilled product and the isolation of a derivative of methyl cyclohexyl ketone after acid treatment indicates the primary reaction product is the epoxide IV.

[CONTRIBUTION FROM THE CONVERSE LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

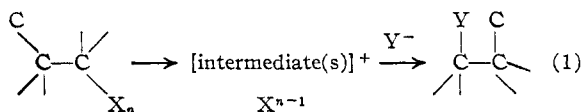
On the Norbornyl Cation Problem

BY E. J. COREY, J. CASANOVA, JR.,^{1a} P. A. VATAKENCHERRY^{1b} AND ROLAND WINTER

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Evidence is presented that deamination of *exo*- and *endo*-norbornylamines in acetic acid produces an unsymmetrical, essentially classical carbonium ion, but that the cation from solvolysis of *exo*-norbornyl arenesulfonates is essentially symmetrical.

The determination of structure and chemical properties of the various species which intervene in cationic rearrangements of carbon is central to the detailed understanding of such processes. The present formulations of these reactions, *e.g.* (1), usually include a



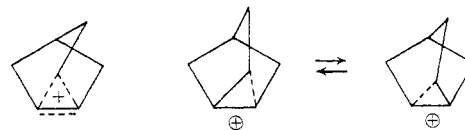
consideration of whether rearrangement occurs *simultaneously* with ionization to give a bridged "non-classical"

action, $\overset{\cdot\cdot}{\text{C}}-\overset{\cdot\cdot}{\text{C}}$ (anchimerically assisted ionization), or *after* ionization to a classical "carbonium ion." In either case there remains a question of whether the structure in which the migrating group forms a bridge across to the carbon atoms is a relatively stable intermediate which leads to product(s) directly by reaction with nucleophile or a transient on the way to a new (rearranged) classical carbonium ion. The intermediacy of such a bridged ion ought to assume increasing chemical significance as the ion becomes more stable than the alternative classical ions and as the energy barrier between these ions is diminished.

The behavior of a system in terms of these considerations might be expected to depend not only on the arrangement of carbon in the molecule but also on the nature of the process for cation generation and the interactions with neighboring solvent and solute molecules. Although it is already clear that the variable of the leaving group X is not trivial in the mechanistic scheme of things, the greater part of present knowledge on intermediates in carbonium ion rearrangements and on related matters, such as interaction of these intermediates with other ions and with solvent, is derived from the study of halide or sulfonate ester solvolysis. The use of other non-solvolytic reactions, *e.g.*, amine deamination, to distinguish between intermediate carbonium ion structures is rather less common for a number of reasons including in the case of amine deamination the inapplicability of kinetic analysis to the steps of interest and the irregularities which have been encountered in attempts to correlate product distribution with that from corresponding sulfonate ester or halide solvolysis in various systems.² It now appears

that in the case of deamination the enormous speed of decomposition of the diazonium ion is at least in part responsible for the apparent discrepancies.³ This, in turn, suggests that the amine reaction, an obviously practical method of carbonium ion generation, may complement the solvolysis approach in the development of a more general understanding of interconverting classical and non-classical cations. Indeed, as will be apparent from what follows, it seems inappropriate to generalize on the basis of solvolysis results *alone*, however quantitative, since the problems of cationic rearrangements of carbon are intrinsically multidimensional as a result of the number and significance of the independent variables. A clear understanding of cation behavior may, in fact, require the study of a spectrum of processes for ion *generation* as well as the variation of carbon structure, stereochemistry and reaction medium.

The present paper deals with some experiments on amine deamination and solvolysis in the 2-norbornyl series which were performed to extend existing knowledge in this remarkably instructive system.⁴ Winstein and Trifan have argued convincingly that the considerably greater solvolytic reactivity of *exo*-norbornyl arenesulfonate as compared to the *endo* isomer and the formation of racemic *exo*-acetate from acetolysis of optically active *exo*-sulfonate show that carbon-carbon σ -delocalization accompanies and assists ionization of the *exo* isomer. In addition, they consider that the symmetrical bridged ion is probably both the product of ionization and the direct precursor of *exo*-acetate, but they point out that an alternative formulation, a system of two equilibrated unsymmetrical non-classical ions, is not excluded. In the case of the solvolysis



of the *endo*-norbornyl arenesulfonate the mechanistic evidence is far less clear; it is not yet known, for example, whether *endo* \rightarrow *exo* sulfonate rearrangement

(2) Cf. H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 93–101, 123–136.

(3) See, for example, the review by J. H. Ridd, *Quart. Revs.*, **15**, 418 (1961), which summarizes recent studies on "conformational control" of rearrangement in deamination reactions of acyclic systems and refs. 10 and 12 given below.

(4) See S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).

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