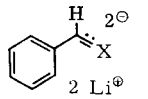
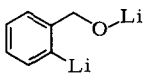
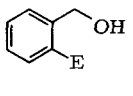


(1), X = S, O

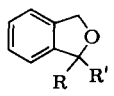


(2)

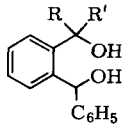
The new reagent (2) reacts with electrophiles to form the products (3) and (4a) compiled in Table 1. The diols (3d)—(3g) obtained with carbonyl compounds cyclize on treatment with hydrochloric acid/ether[5] to give the dihydroisobenzofurans (4b)—(4e) (Table 1, bottom).



(3)



(4)



(5)

The physical data of the known compounds [(3a), (3c), (3f), (3g), (4a), (4d), (4e)] are in agreement with literature data. Elemental analysis and IR and NMR spectra confirm the structures given. Double metalation of α,α-dideuteriobenzyl alcohol proves that (2) is not formed *via* (1), X = O.

Table 1. Products of types (3), (4), and (5) obtained from benzyl alcohols and alkyl halides or carbonyl compounds. The yields of (3a)—(3g) and (5a)—(5d) are based on the electrophile. The air bath temperatures recorded on bulb-to-bulb distillation (Büchi GKR 50) are given as boiling points.

Reactants		Products	Yield [%]	M.p. [°C] or B.p. [°C/torr]
(2) +	Methyl iodide	(3a), E = CH_3	30	115/20
(2) +	Butyl iodide	(3b), E = n-C_4H_9	Trace	
(2) +	Butyl bromide	(3b), E = n-C_4H_9	21	
(2) +	Butyl chloride	(3b), E = n-C_4H_9	55	72/0.1
(2) +	Iodine	(3c), E = I	58	91—93
(2) +	Cyclohexanone	(3d), E = $C(OH)(CH_2)_5$	71	55—57
(2) +	4-*t*-Butyl-cyclohexanone	(3e), E = $C(OH)(CH_2)_2CH(CH_2)_2$ with $C(CH_3)_3$	68	122—126
(2) +	Benzaldehyde	(3f), E = $CH(OH)C_6H_5$	95	76
(2) +	Formaldehyde	(3g), E = CH_2OH	70	63–65
(2) +	Carbon dioxide	(4a), R/R′ = O	50	72—74
(3d)		(4b), R/R′ = $(CH_2)_5$	95	145/10
(3e)		(4c), R/R′ = $(CH_2)_2CH(CH_2)_2$ with $C(CH_3)_3$	92	70–75/3 × 10^{-2}
(3f)		(4d), R = C_6H_5, R′ = H	85	35
(3g)		(4e), R = R′ = H	88	192/760
(6a) +	Benzaldehyde	(5a), R = H, R′ = CH_3	88	156—159
(6b) +	Benzaldehyde	(5b), R = H, R′ = C_2H_5	82	131—135
(6c) +	Benzaldehyde	(5c), R = H, R′ = C_4H_9	92	118—119
(6d) +	Benzaldehyde	(5d), R = R′ = CH_3	86	oil

Other α-phenylalkanols react in the same way as benzyl alcohol. Thus we obtained the benzhydrols (5a), (5b), (5c) (mixture of diastereomers), and (5d) on treatment of the *ortho*-lithiated derivatives (6a)—(6d) (Table 1) of 1-phenylethanol, -1-propanol, -1-pentanol, and 2-phenyl-2-propanol, respectively, with benzaldehyde.

General procedure

A solution of *n*-butyllithium (20 mmol, *ca.* 1.5 M in hexane) is added in two portions, one half over a period of 10 min and the second all at once, to a vigorously stirred mixture of benzyl alcohol (10 mmol), light petroleum (b.p. 30—40 °C; 20 ml), and tetramethylethylenediamine (TMEDA) (20 mmol) at room temperature under an inert atmosphere. After heating under reflux for 11 h the mixture is cooled to −78 °C and the electrophile (7 mmol) is added. The temperature is allowed to rise to room temperature, the mixture is poured into dilute sulfuric acid, and the product worked up as usual with ether.

Received: April 12, 1978 [Z 986 IE]
German version: Angew. Chem. 90, 553 (1978)

CAS Registry numbers:
(2), 55274-02-7; (3a), 89-95-2; (3b), 66810-79-5; (3c), 5159-41-1; (3d), 58931-26-3; (3e), 66810-78-4; (3f), 1586-01-2; (3g), 612-14-6; (4a), 87-41-2; (4b), 171-80-2; (4c), 66810-77-3; (4d), 7111-66-2; (4e), 496-14-0; (5a), 66810-76-2; (5b), 66810-75-1; (5c), 66810-74-0; (5d), 13616-48-3; (6a), 66810-73-9; (6b), 66810-72-8; (6c), 66810-71-7; (6d), 66810-70-6

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Simple Method for the Esterification of Carboxylic Acids[1]

By *Bernhard Neises* and *Wolfgang Steglich*[*]

In spite of its successful use in the synthesis of some sugar and amino acid derivatives[3b] the dicyclohexylcarbodiimide (DCC)[2, 3a] method has not been generally adopted as a method for the preparation of carboxylates and thiolates,

[*] Prof. Dr. W. Steglich, B. Neises
Institut für Organische Chemie und Biochemie der Universität
Gerhard-Domagk-Strasse 1, D-5300 Bonn (Germany)

chiefly because of the variable yields, which are satisfactory only in the case of phenols and thiophenols[4], and the tendency for undesirable *N*-acylureas to be formed. The favorable catalytic action of pyridine in such reactions[3] suggested that the 10^4-fold more effective acylation catalyst 4-dimethylaminopyridine (DMAP) might prove to be a useful agent in our present studies on the esterification of carboxylic acids[1, 5].

Indeed, we have found that addition of 3—10 mol % DMAP accelerates the DCC-activated esterification of carboxylic acids with alcohols or thiols to such an extent that formation of side products is suppressed and even sterically demanding esters *(1)* are formed in good yields at room temperature (see Table 1).

$$RCO_2H + R'XH \xrightarrow[DMAP]{C_6H_{11}N{=}C{=}NC_6H_{11}} RCOXR'$$

(1), X = O, S

Table 1. Esters and thioesters *(1)*.

	Compound	Yield [%] [a]
(1a)	Methyl 1-phenylcyclohexane-1-carboxylate	87
(1b)	Methyl cinnamate	98
(1c)	Methyl 4-methoxybenzoate	61
(1d)	Methyl 2,6-dihydroxybenzoate	96.5
(1e)	Methyl 2,4,6-trimethylbenzoate	74
(1f)	Methyl 1,6-dihydroxy-8-methoxy-3-methylanthraquinone-2-carboxylate (methyl dermoluteinate)	55
(1g)	Di-*tert*-butyl malonate	85.5, 29.5 [b]
(1h)	*tert*-Butyl hydrocinnamate	68
(1i)	*tert*-Butyl pentaacetyl-D-gluconate	82.5
(1j)	*tert*-Butyl 2,5-cyclohexadiene-1-carboxylate	84, 34 [b]
(1k)	*tert*-Butyl cinnamate	68
(1l)	*tert*-Butyl benzoate	40
(1m)	*tert*-Butyl 2,6-dihydroxybenzoate	54
(1n)	*tert*-Butyl 3,5-dinitrobenzoate	84
(1o)	Di-*tert*-butyl *rac*-4,4',6,6'-tetrachlorodiphenate	91.5
(1p)	Glycerol tristearate	87.5
(1q)	*S*-Ethyl propanethioate	85
(1r)	*S*-Ethyl 16-hydroxyhexadecanethioate	92
(1s)	*S*-Ethyl 2,5-cyclohexadiene-1-carbothioate	90
(1t)	*S*-*tert*-Butyl cyclohexanecarbothioate	91

[a] The yields refer to pure products and are not optimized. All esters gave correct elemental analyses and spectroscopic data consistent with their constitution. B.p. [and m.p.] of the new compounds: *(1i)* oil; *(1j)* 80 °C/0.5 torr (Kugelrohr); *(1m)* 135/0.5 (KR); *(1o)* [82—84 °C]; *(1r)* [57]; *(1s)* 60/0.2 (KR).
[b] Without DMAP addition.

Thus, the sensitive 2,5-cyclohexadiene-1-carboxylic acid is transformed into the *tert*-butyl ester *(1j)* and into the *S*-ethylthioester *(1s)* quite smoothly, while the method generally recommended for its esterification, namely the boron trifluoride-etherate method, can be used only for the preparation of esters of primary and secondary alcohols[6]. The *tert*-butyl esters of 3,5-dinitrobenzoic acid *(1n)* and glycerol tristearate *(1p)* can also be prepared by this method, in contrast to the non-catalyzed reaction in which *N*-acylureas are formed[7]. 2,4,6-Trimethylbenzoic acid, which can be regarded as inert under normal esterification conditions, reacts with methanol/DCC/DMAP to give the methyl ester *(1e)* in 74 % yield.

Also thioesters *(1)*[8] can be conveniently prepared by the DMAP-catalyzed DCC method, and the yields are considerably higher than those obtained in the non-catalyzed reaction[9]. As example it is shown that synthesis of the thioester *(1r)* of 16-hydroxyhexadecanoic acid is possible without protection of the hydroxy groups. In contrast to some of the other methods, the DCC/DMAP method has the advantage that the free thiols can be used.

The possibility of synthesizing *tert*-butyl esters reaches a limit with more bulky, *i. e.* sterically hindered carboxylic acids. Thus, in the case of adamantanecarboxylic acid, 1-phenylcyclohexane-1-carboxylic acid and 2,4,6-trimethylbenzoic acid the symmetrical anhydrides were isolated instead of the *tert*-butyl esters. The unreactive 4-methoxybenzoic acid also gives only the anhydride, together with some *N*-acylurea, whose formation has been established only in this reaction so far. In the esterification of *Z*-amino acids with *tert*-butyl alcohol or 2-methyl-2-propanethiol under standard conditions some racemization was observed, but this can be largely avoided at lower temperatures and with shorter reaction times.

Procedure

To a stirred solution of 10 mmol carboxylic acid in 10 ml anhydrous CH_2Cl_2 (in the case of sparingly soluble acids, in DMF) is added 30—110 mg DMAP and 20—40 mmol alcohol or thiol (10 mmol with alcohols or thiols which are not easily removable without significant loss; 3.4 mmol with glycerol). DCC is added to the reaction mixture at 0 °C, which is then stirred for 5 min at 0 °C and 3 h at 20 °C. Precipitated urea is then filtered off and the filtrate evaporated down *in vacuo*. The residue is taken up in CH_2Cl_2 and, if necessary, filtered free of any further precipitated urea. The CH_2Cl_2 solution is washed twice with 0.5 N HCl and with saturated $NaHCO_3$ solution, and then dried over $MgSO_4$. The solvent is removed by evaporation and the ester isolated by distillation or recrystallization. Crystalline products can be obtained in pure form by filtration on a short silica gel column (eluent CH_2Cl_2 or $CHCl_3$.

Received: April 24, 1978 [Z 989 IE]
German version: Angew. Chem. *90*, 556 (1978)

CAS Registry numbers:
(1a), 17380-78-8; *(1b)*, 103-26-4; *(1c)*, 121-98-2; *(1d)*, 2150-45-0; *(1e)*, 2282-84-0; *(1f)*, 27152-37-0; *(1g)*, 541-16-2; *(1h)*, 16537-10-3; *(1i)*, 66921-97-9; *(1j)*, 61812-52-0; *(1k)*, 14990-09-1; *(1l)*, 774-65-2; *(1m)*, 66921-96-8; *(1n)*, 5342-97-2; *(1o)*, 66921-95-7; *(1p)*, 555-43-1; *(1q)*, 2432-42-0; *(1r)*, 66921-94-6; *(1s)*, 66921-93-5; *(1t)*, 54829-37-7; 1-phenylcyclohexane-1-carboxylic acid, 1135-67-7; cinnamic acid, 621-82-9; 4-methoxybenzoic acid, 100-09-4; 2,6-dihydroxybenzoic acid, 303-07-1; 2,4,6-trimethylbenzoic acid, 480-63-7; 1,6-dihydroxy-8-methoxy-3-methylanthraquinone-2-carboxylic acid, 26071-13-6; malonic acid, 141-82-2; hydrocinnamic acid, 501-52-0; pentaacetyl-D-gluconic acid, 17430-71-6; 2,5-cyclohexadiene-1-carboxylic acid, 4794-04-1; benzoic acid, 65-85-0; 3,5-dinitrobenzoic acid, 99-34-3; *rac*-4,4',6,6'-tetrachlorodiphenic acid, 53663-22-2; stearic acid, 57-11-4; propionic acid, 79-09-4; 16-hydroxyhexadecanoic acid, 506-13-8; cyclohexanecarboxylic acid, 98-89-5; methanol, 67-56-1; *tert*-butanol, 75-65-0; glycerol, 56-81-5; ethanethiol, 75-08-1; *tert*-butanethiol, 75-66-1

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Photochemical Reductive *trans*-Elimination from *trans*-Diazidotetracyanoplatinate(IV)[**]

By *Arnd Vogler, Alfred Kern*, and *Jürgen Hüttermann*[*]

Oxidative additions and reductive eliminations number among the most important reactions of transition metal complexes and are of special utility in the chemistry of organometallic compounds. Reductive *cis*-eliminations have also been observed as light-induced processes[1]. Thus, irradiation of $[IrClH_2(PPh_3)_3]$ leads to *cis*-elimination of H_2 and formation of $[IrCl(PPh_3)_3]$ in a single step; the elimination of H_2 is concerted, no hydrogen atoms are formed in the photoprocess[1b]. Photochemical reductive *trans*-eliminations have so far not been reported. We have now been able to demonstrate such a reaction with $[Pt^{IV}(CN)_4(N_3)_2]^{2-}$, which on irradiation is quantitatively converted into $[Pt^{II}(CN)_4]^{2-}$.

Of particular interest to us was whether this two-electron reduction of Pt^{IV} proceeded *via* a Pt^{III} intermediate, since it is generally assumed that both thermal[2a] as well as photochemical[2b] conversions of Pt^{IV} into Pt^{II} complexes involve two successive one-electron reductions. Should a Pt^{III} intermediate not be formed, then there are two mechanistic possibilities: While the cleavage of the two ligands in *cis*-elimination obviously does not involve formation of ligand radicals in the initial reaction step[1b] this could be possible on steric grounds in the case of *trans*-eliminations.

We conclude from our investigations that two N_3 radicals are formed in the initial step of photochemical reductive *trans*-elimination from *trans*-$[Pt(CN)_4(N_3)_2]^{2-}$ by simultaneous two-electron reduction without formation of a Pt^{III} intermediate:

$$[Pt^{IV}(CN)_4(N_3)_2]^{2-} \rightarrow [Pt^{II}(CN)_4]^{2-} + 2N_3^{\cdot}$$

Reaction of $K_2[Pt(CN)_4Br_2]$[3] with a large excess of KN_3 in water (reaction time 2 d) afforded the compound $K_2[Pt(CN)_4(N_3)_2]$, which was isolated in analytically pure form after recrystallization from acetone. The *trans* structure (D_{4h}) of the anion follows from the appearance of an IR band[3] (2181 cm^{-1}) in the region of the CN stretching vibrations. The electron absorption spectrum shows only one intense maximum ($\lambda = 302$ nm, $\varepsilon = 18300$) in the longwave region which is assigned to a ($N_3 \rightarrow Pt$)CT transition.

Irradiation of the CT band of the salt dissolved in water led to rapid evolution of nitrogen according to

$$[Pt(CN)_4(N_3)_2]^{2-} \rightarrow [Pt(CN)_4]^{2-} + 3N_2$$

The spectral changes observed during the photolysis (Fig. 1) show that no other products are formed, since the final spectrum was identical with that of $[Pt(CN)_4]^{2-}$[4] after prolonged irradiation; nor was any free azide detectable[5]. On complete absorption of light by the starting complex, the photochemical formation of $[Pt(CN)_4]^{2-}$ followed a zero order reaction. At excitation wavelengths of 300, 333, and 366 nm the quantum yield for the formation of $[Pt(CN)_4]^{2-}$ in water was $\Phi = 0.34 \pm 0.02$; in acetonitrile and ethanol it increased to $\Phi = 0.58$ and 0.61 ± 0.02, respectively. Unlike in aqueous solution, photolysis in ethanol leads also to formation of N_3^- as well as evolution of N_2.

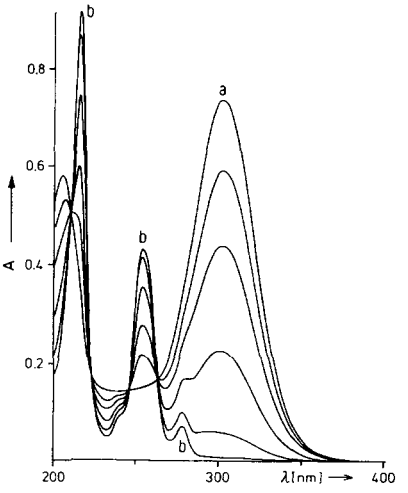

Fig. 1. Change in absorption spectrum during the photochemical transformation of *trans*-$[Pt(CN)_4(N_3)_2]^{2-}$, (a) in $Pt(CN)_4^{2-}$, (b) in aqueous solution (4×10^{-5} mol/l, 1 cm cuvette); excitation light: $\lambda = 300$ nm.

For identification of the primary products the photolysis of $[Pt(CN)_4(N_3)_2]^{2-}$ was carried out in ethanol glasses at 77 K and the irradiated samples investigated ESR spectroscopically. The observed signals could be assigned to N atoms[6] and CH_3CHOH radicals[7]. Pt^{III} signals[8] were not observed, even at 20 K.

N_3 radicals are extremely unstable. They dissociate very rapidly even at low temperatures into molecular nitrogen and N atoms[6b,c], which can be detected ESR spectroscopically. Finally, in the aqueous solution at room temperatures only N_2 is formed as stable end-product besides $[Pt(CN)_4]^{2-}$. In the presence of suitable reducing agents N_3 radicals can be reduced to azide[9]. The formation of CH_3CHOH radicals, which also were identified at low temperatures, and of free azide in the room temperature photolysis of $[Pt(CN)_4(N_3)_2]^{2-}$ in ethanol can be explained only in terms of a competing reaction of the N_3 radicals: besides dissociating, the N_3 radicals can obviously also be reduced by the solvent CH_3CH_2OH.

Received: December 17, 1976 [Z 987 IE]
revised: April 13, 1978
German version: Angew. Chem. *90*, 554 (1978)

CAS Registry numbers:
(1) (R = CH_3), 41308-25-2; *(1)* (R = C_6H_5), 41308-28-5; *(1)* (R = $CH(CH_3)_2$), 40854-38-4; *(1)* (R = $CH_2C_6H_5$), 66523-69-1; *(1)* (R = $CH(CH_3)C_6H_5$), 41308-29-6; *(2)* (R = CH_3), 66523-70-4; *(2)* (R = C_6H_5), 66523-71-5; *(2)* (R = $CH(CH_3)_2$, 66552-47-4; *(2)* (R = $CH_2C_6H_5$), 66523-72-6; *(2)* (R = $CH(CH_3)C_6H_5$), 66552-50-9; *(3)* (R = CH_3), 66523-76-0; *(3)* (R = C_6H_5), 66523-78-2; *(3)* (R = $CH(CH_3)_2$), 66523-80-6; *(3)* (R = $CH_2C_6H_5$), 66523-81-7; *(3)* (R = $CH(CH_3)C_6H_5$), 66523-83-9; $LiCH_3$, 917-54-4

[*] Prof. Dr. A. Vogler, Dipl.-Chem. A. Kern
Institut für Chemie der Universität
D-8400 Regensburg 2 (Germany)
Prof. Dr. J. Hüttermann
Institut für Biophysik und Physikalische Biochemie der Universität Regensburg (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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