reduction was followed as described above. The toluene phase of the reduction mixture was found to be composed of three components in the ratio of 3:1:2.7 as detected by vpc on a polyethylene glycol column (programmed from 100 to 230° at 8°/min temperature rise). Chromatography on Florisil gave in the petroleum ether fraction two components, whose vpc retention time corresponded to that of the first two peaks of the reduction mixture, compounds **11** and **12**. The infrared spectrum of this mixture showed only hydrocarbon peaks. The ultraviolet spectrum indicated the presence of an olefin showing λ_{max} at 267 nm.

After removal of the solvent, 2-methyl-2-phenylindan (**11**) was obtained as a colorless oil [3.3 g (15 mmol), 44.7%, calculation based on vpc ratio] and was distilled *in vacuo* (0.5 mm, 90°). Vpc retention time proved this compound to be the first peak.

Anal. Calcd for $C_{16}H_{16}$: C, 92.30; H, 7.69. Found: C, 92.28; H, 7.77.

Various methods were employed to effect the isolation of the second component, 2-methyl-3-phenylindene (**12**). Among these were fractional distillation as well as separation by vpc on an Apiezon L preparative column, all of which proved fruitless.

It was shown, however, by vapor phase chromatography that the olefin **12** obtained in this reduction mixture was not identical with 2-phenyl-3-methylindene (**13**) which was prepared independently, as shown by their different retention times. Thus, it is concluded that the olefin obtained in this reduction mixture is the other isomer, 2-methyl-3-phenylindene (**12**), as predicted by the proposed mechanism.[2]

The third component was obtained from the petroleum ether-benzene (1:1) eluate, and was identified as starting ketone 2-methyl-2-phenyl-1-indanone (**10**) [3.0 g (13 mmol), 40%, calculation based on vpc ratios].

Kinetic Studies in the Clemmensen Reduction of 2-Phenyl-1-indanone-*2*-d_1 (4) and 2-Phenyl-1-indanone (1).—The two reactions below were run under identical Clemmensen conditions.

To a solution of 0.5 g of mercuric chloride in 7.5 ml of D_2O (99.8% D) and 0.25 ml of DCl (38% in D_2O) there was added 5 g of granular zinc. After 15 min of stirring, the liquid was decanted and the amalgamated zinc was washed twice with D_2O. To this zinc amalgam there was added a solution of 2.5 g (11 mmol) of 2-phenyl-1-indanone-*2*-d_1 (**4**) in 20 ml of toluene, 3.5 ml of D_2O, and 22.5 ml of DCl.

The undeuterated ketone (**1**) was subjected to identical Clemmensen conditions at the same time.

Kinetic measurements were carried out by following the increase of the uv absorption of 2-phenylindene-**3**-d_1 (**6**) and 2-phenylindene (**4**), respectively, at 315 nm. Aliquots of 0.100 ml were taken from the reaction mixture at different times and diluted with methanol to obtain an optical density reading of 0.3–0.8; these readings were then converted to a common volume (50 ml).

The change of optical density (D) with time was measured. The first-order rate constants were calculated from the following equation.

$$K = \frac{1}{t}\ln\frac{D_\infty - D_0}{D_\infty - D}$$

$$K_H = 6.490 \times 10^{-2}\ \text{sec}^{-1};\ K_D = 4.146 \times 10^{-2}\ \text{sec}^{-1}$$

A graph of log $(D_\infty - D_0)/(D_\infty - D)$ *vs.* time (see Figure 1) gave a straight line, indicating that the reaction is first order under these conditions. From the slopes of the lines K_H and K_D were obtained. K_H/K_D was found to be 1.53. This represents the average of four runs.

Registry No.—**4**, 39253-52-6; **5**, 39253-53-7; **6**, 39253-54-8; **7**, 39253-55-9; **8**, 39253-56-0; **10**, 10474-32-5; **11**, 39253-58-2.

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Modified Birch Reductions. Lithium in *n*-Alkylamines

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p-Methoxyanisole, *p*-methylanisole, *p*-*tert*-butylanisole, *N,N*-dimethyl-*p*-toluidine, and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine were reduced using lithium–*n*-propylamine–*tert*-butyl alcohol reagent. The anisoles gave results equivalent to the Birch (liquid ammonia) reductions while the anilines gave mainly the tetrahydro derivatives. In the reduction of *p*-di-*tert*-butylbenzene and *p*-dicyclohexylbenzene using lithium–ethylamine–ethyl alcohol the principal respective products were 1,4-di-*tert*-butyl-1,4-cyclohexadiene and 1,4-dicyclohexyl-1,4-cyclohexadiene. This procedure may provide a general approach for preparing many cyclohexadiene derivatives in good yield and purity, which have not been accessible by any simple methods described hitherto. Upon reduction of 2,3-dimethylnaphthalene with lithium–ethylamine–ethyl alcohol the tetrahydro derivative 2,3-dimethyl-1,4,5,8-tetrahydronaphthalene was formed as the major product. The reduction of *p*-di-*tert*-butylbenzene with lithium–ethylamine provided an improved synthesis of 1,4-di-*tert*-butylcyclohexene, while reduction of *p*-diisopropylbenzene afforded 1,4-diisopropylcyclohexene; 1,4-dicyclohexylcyclohexene and 1,4-dimethylcyclohexene were also prepared using lithium–ethylamine.

The Birch reduction of aromatic compounds to the corresponding dihydro compounds by use of alkali metals and alcohols in liquid ammonia is a very useful synthetic procedure. In laboratories where Birch reductions are not frequently run, the use of an alkylamine, such as ethyl- or *n*-propylamine, as the solvent would be safer and more convenient than liquid ammonia. Benkeser[1] has previously reported that the reduction of ethylbenzene, cumene, *tert*-butylbenzene, and anisole using lithium–methylamine–alcohol combinations gave yields comparable with those of the Birch reductions. The purpose of this work was to investigate the synthetic scope and limitations of reductions of para-substituted aromatics with lithium–alkylamine–alcohol combinations and lithium–alkylamine combinations.

Reduction of Para-Substituted Anisoles.—The results obtained on reduction of *p*-methoxyanisole (**1**), *p*-methylanisole (**3**), and *p*-*tert*-butylanisole (**5**) to the corresponding 1-methoxy-4-substituted 1,4-cyclohexadienes using lithium–*n*-propylamine–*tert*-butyl alcohol are summarized in Table I. Preliminary experiments on the reduction of **1** indicated that the concentration of lithium and the presence of alcohol were the most

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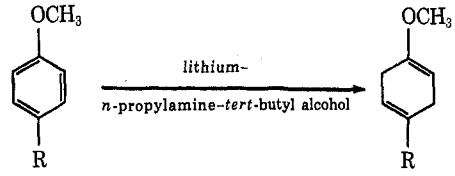
[1] R. A. Benkeser, *et al.*, *J. Org. Chem.*, **28**, 1094 (1963). For a comprehensive treatment of Birch reductions and metal–amine reductions, several reviews on both theoretical and synthetic aspects exist in the literature: R. L. Augustine, "Reduction: Techniques and Applications in Organic Synthesis," Marcel Dekker, New York, N. Y., 1968; A. J. Birch, *Quart. Rev.* (*London*), **4**, 69 (1950); A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958); H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, part 2, Wiley, New York, N. Y., 1963; R. G. Harvey, *Synthesis* **4**, 161 (1970); A. J. Birch and G. Subba Rao, *Advan. Org. Chem.*, **8**, 1 (1971); E. M. Kaiser, *Synthesis*, **8**, 391 (1972).

TABLE I

REDUCTION OF PARA-SUBSTITUTED ANISOLES



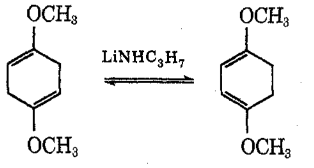
R	Anisole	Product	Yield, %	Birch redn yields, %
OCH_3	1	2	64	94[a]
CH_3	3	4	61[b]	33[c]
			64	70[d]
				80[e]
				45[f]
				80[g]
t-C_4H_9	5	6	49[h]	35[i]
				63[j]

[a] Reported in ref 3. [b] Ethyl alcohol used. [c] Isolated as 4-methyl-3-cyclohexen-1-one and 4-methyl-2-cyclohexen-1-one in ref 5. [d] Reported in ref 18. [e] Isolated as 4-methyl-3-cyclohexen-1-one by E. A. Braude, *et al.*, *J. Chem. Soc.*, 3228 (1958). [f] Isolated as 4-methyl-2-cyclohexen-1-one by W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968). [g] Isolated as the ethylene ketal of 4-methyl-3-cyclohexen-1-one by W. C. Agosta and W. L. Schreiber, *J. Amer. Chem. Soc.*, **93**, 3947 (1971). [h] Contaminated with 9% *p-tert*-butylphenol. [i] Reported by R. D. Stolow, *J. Org. Chem.*, **28**, 2862 (1963). [j] Reported in ref 19.

important variables. The amount of reduction was proportional to the amount of lithium used, and reductions without alcohol led to large quantities of 1,4-dimethoxy-1,3-cyclohexadiene (**7**, conjugated dihydro), rather than 1,4-dimethoxy-1,4-cyclohexadiene (**2**, unconjugated dihydro). The presence of **7** is attributed to the influence of the amide anion catalyzing the development of conjugation. Changes in the nature and/or concentration of the amine and of the alcohol, or some variation of the temperature, seemed to have little or no effect upon the course and extent of reductions.

The reduction of **5** presented some difficulties; a low boiling fraction was always present which was tentatively identified by nmr analysis as a mixture of isomeric *tert*-butylcyclohexenes. The product, 1-methoxy-4-*tert*-butyl-1,4-cyclohexadiene (**6**) was always contaminated with *p-tert*-butylphenol even after strong base washes. The hydrogenolysis of the methoxy moiety is quite common[2–4] and the demethylation of anisoles has been reported in both Birch (liquid ammonia) reductions[3,5] and lithium–amine reductions.[6]

The isomerization of **2** by refluxing for 1.5 hr with lithium *n*-propylamide gave a mixture containing 69% **7** and 31% **2**. Birch[7] reports that 1,4-cyclohexadienes are equilibrated with the 1,3-dienes to the extent of 75–80% by strong bases such as potassium amide in liquid ammonia and potassium *tert*-butoxide in DMSO. Refluxing for 7.5 hr with lithium *n*-propylamide gave a complex mixture of the compounds **1**, **2**, and **7**. Birch[3,4] previously reported that dihydroanisoles undergo dehydrogenation when subjected for longer periods of time to reaction conditions which can effect conjugation.



2 **7**

Reduction of *N*,*N*-Dimethylanilines.—*N*,*N*-Dimethyl-*p*-toluidine (**8**) was treated with lithium–*n*-propylamine–*tert*-butyl alcohol, and the crude product was hydrolyzed to give a low yield (21%) of ketonic product. On the basis of glc analysis this consisted of ~90% 4-methylcyclohexanone (**9**) and 10% 4-methyl-3-cyclohexenone (**10**). Another reduction of **8** was attempted using one half the lithium used previously. The reduction was incomplete as evidenced by the presence of **8**, identified by the nmr and ir spectra of the crude product. Hydrolysis of crude product gave a low yield (24%) of ketone[8] which contained 65% **9** and 35% **10** (Scheme I).

The reduction of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine with lithium–*n*-propylamine–*tert*-butyl alcohol was carried out using the diminished quantity of lithium. The aromatic amine was not completely reduced as evidenced by the ir spectrum of the crude product. This was hydrolyzed and converted to the dioxime of 1,4-cyclohexanedione in very low yield (1.7%).[9]

The Birch reductions of *N*,*N*-dimethylanilines using lithium and *tert*-butyl or *tert*-amyl alcohol are superior to lithium–amine–alcohol combinations, giving products which contain no more than 5% tetrahydro derivatives.[7] Stork[10] found, however, that the use of ethanol in the reductions of *N*,*N*-dimethylanilines gave higher proportions (34–47%) of tetrahydro products.

Krapcho and Bothner-By[11] previously reported that *p*-di-*tert*-butylbenzene (**11**) with lithium–ammonia–ethyl alcohol experienced no reduction reaction. The reduction of **11** with lithium–ethylamine–ethyl alcohol has now been realized; a product mixture containing 86% 1,4-di-*tert*-butyl-1,4-cyclohexadiene (**12**) and 14% 1,4-di-*tert*-butylcyclohexene (**15**) has been obtained in good yield. Purification gave **12** in 56% overall yield. This procedure may possibly provide a general approach for preparing cyclohexadiene derivatives in good yield and purity. Using lithium–*n*-propylamine–ethyl alcohol afforded a mixture containing 55% **11**, 43% **12**, and 2% **15**. Using the lithium–ethylamine–ethyl alcohol reagent, *p*-dicyclohexylbenzene (**13**) was reduced to 1,4-dicyclohexyl-1,4-cyclohexadiene (**14**) in 73% yield (Table II).

The Stolow and Ward[12] synthesis of **15** from **11**, using lithium in refluxing ethylenediamine has frequently

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(2) A. J. Birch, P. Hextall, and S. Sternhell, *Aust. J. Chem.*, **7**, 256 (1954).

(3) A. J. Birch, *J. Chem. Soc.*, 102 (1947).

(4) A. J. Birch and G. S. R. Subba Rao, *Aust. J. Chem.*, **23**, 1641 (1970).

(5) A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(6) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

(7) A. J. Birch, *et al.*, *J. Chem. Soc. C*, 637 (1971).

(8) Analysis of ketones does not take into account a tetrahydro product such as 4-dimethylamino-1-methylcyclohexene or the isomeric hexahydro products *cis*- and *trans*-1-dimethylamino-4-methylcyclohexane, because, being amines, they are removed during hydrolysis.

(9) In this reduction, starting material or tetrahydro or hexahydro products would be removed as salts during hydrolysis.

(10) G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4604 (1956).

(11) A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

(12) R. D. Stolow and R. A. Ward, *J. Org. Chem.*, **31**, 965 (1966).

SCHEME I

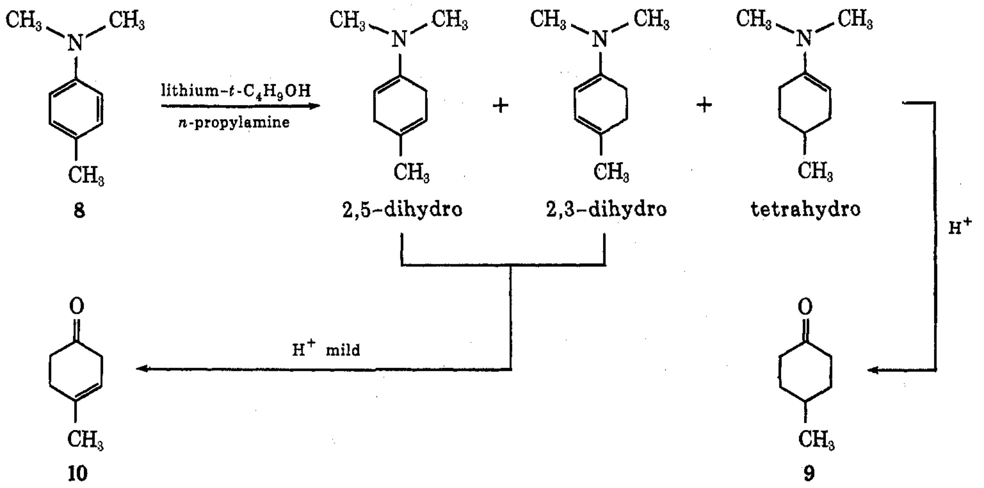
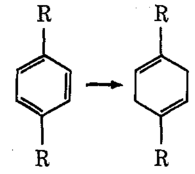


TABLE II

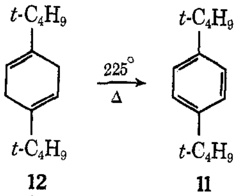
REDUCTION OF *p*-DIALKYLBENZENES



R	Alkylbenzene	Cyclohexadiene	Yield, %
Lithium–Ethylamine–Ethyl Alcohol Reagent			
tert-C_4H_9	11	12	56
c-C_6H_{11}	13	14	73[a]
Lithium–Ethylamine			
t-C_4H_9	11	15	74
c-C_6H_{11}	13	16	76
i-C_3H_7	17	18	92
CH_3	19	20	60

[a] Nmr showed 4% starting material.

been cited as an example of lithium–amine reductions. However, their total yield of contaminated **15** was 44%, and this material contained 12% starting compound. Lithium in ethylamine at 0° gave rise to pure **15** in 74% yield. This reduction of **11** to **15**, as in the previous preparation of **12**, appeared to afford high yields only with ethylamine. Reduction of **11** with lithium–*n*-propylamine gave a crude reaction mixture containing 16% **15** and 84% **11**.

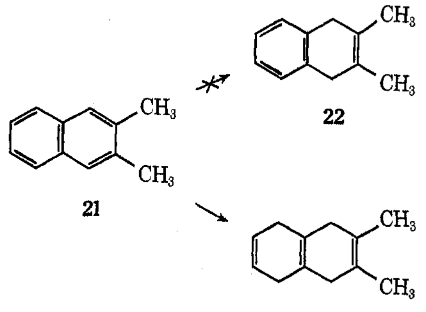


12 **11**

The difference between lithium in ethylamine and lithium in refluxing ethylenediamine is due to the fact that *N*-lithioethylenediamine ($LiNHCH_2CH_2NH_2$), a product of the reduction reaction, is a powerful dehydrogenating reagent capable of converting dihydrobenzenes to aromatics.[13] The intermediate **12** may be further reduced to **15** or be dehydrogenated to **11** with *N*-lithioethylenediamine in refluxing ethylenediamine.

Moreover, in an attempt to use glc for analysis, a sample containing **12** was subjected to an injection port temperature of 255° and was partially dehydrogenated to **11**.[14] The lithium–ethylamine reagent was also used with *p*-dicyclohexylbenzene (**13**), *p*-diisopropylbenzene (**17**), and *p*-xylene (**19**) to show the scope of this reaction.

Reduction of 2,3-Dimethylnaphthalene.—In an attempt to obtain **22**, 2,3-dimethylnaphthalene (**21**) was reduced using the lithium–ethylamine–ethyl alcohol reagent. Because of the greater reactivity of naphthalenes in reductions, a smaller excess of lithium was used compared with that used in the reduction of **11** to **12**. Analysis of the reaction product showed that reduction had gone beyond the dihydro state to the tetrahydro compound yielding a mixture of ~82% **23** and 18% **21**. Increasing the amount of lithium to a slight stoichimetric excess for reduction to the tetrahydro state gave pure **23** in 72% yield. This product was readily identified by the simplicity of its nmr spectra arising from its highly symmetrical structure.



21 **22** **23**

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[13] L. F. Fieser and M. Fieser, "Reagents of Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967.

[14] There have been studies in recent literature on pyrolysis of 1,4-cyclohexadiene to benzene. See references cited in R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie Academic Press, Germany, 1970.

Experimental Section[15]

General Procedure for Reduction Using Lithium–Amine–Alcohol.—A three-necked, oven-dried, 500-ml round-bottom flask equipped with thermometer, magnetic stirrer, and Dry Ice condenser was used for all reductions. The flask was cooled in an ice bath, and the aromatic substrate, the amine, and the first portion of alcohol were added. The alcohol and lithium were usually added in three portions. The alcohol was always added before the lithium and was always in slight excess. The lithium was cut into small pieces and washed with petroleum ether (bp 40–60°). The lithium was added when the flask cooled to 0° and was allowed to react completely before the next portion of alcohol and lithium was added. The total reaction time after the first lithium addition was usually 5–6 hr. The *n*-propylamine was then distilled off or the ethylamine evaporated using a steam bath. The flask was then cooled and 200 ml of ice–water and 300 ml ether were added. The aqueous layer was extracted with two 150-ml portions of ether. The combined ether layers were washed with two 100-ml portions of water and dried over magnesium sulfate. The ether solution was then rotary evaporated to the crude product.

Reductions Using Lithium–Ethylamine.—These used 146 ml (100 g) of ethylamine and the lithium was added in two portions. About 3 hr after the first lithium addition, the dark blue color faded. After an additional 3.5 hr, an excess of ethanol was added and the ethylamine allowed to evaporate.

1,4-Dimethoxy-1,4-cyclohexadiene (2).—A solution of 13.5 g (0.098 mol) of 1,4-dimethoxybenzene (1) (Aldrich) in 225 ml of *n*-propylamine was reduced by 39.8 g (0.537 mol) of *tert*-butyl alcohol and 3.60 g (0.523 g-atom, 40 cm) of lithium. Evaporation of the ether solution gave a dark red oil which solidified upon cooling. The crude solid was dissolved in 50 ml of petroleum ether (bp 40–60°) and this solution was passed through a short column of neutral alumina. The clear petroleum ether solution was evaporated on a steam bath to a clear liquid which solidified upon cooling. The white crystals were filtered and dried to give 8.8 g (64%) of pure **2**: mp 51–53° (lit.[3] mp 54°); nmr δ 2.73 (m, 4 H), 3.48 (s, 6 H), 4.47 (m, 2 H); ir (Nujol) 1675 (s), 1220 (s), 1180 (s), 1040 (s), 780 (s), 700 cm^{-1} (s); mol wt (mass spectrum) 140.

For further identification a suspension of 4.0 g (0.028 mol) of **2** and 25 ml of 10% HCl was heated on a steam bath for 1 hr. The reaction mixture was extracted with two 25-ml portions of CHCl$_3$ and the CHCl$_3$ was evaporated on a steam bath. A yellow oil was obtained which solidified upon cooling. Recrystallization from 10 ml of absolute EtOH gave 0.7 g (23%) of white 1,4-cyclohexanedione: mp 76–78° (lit.[3] mp 78°); nmr δ 2.62 (s); ir (Nujol) 1700 (s), 1130 (s), 960 (s), 700 cm^{-1} (s). Conversion of the dione to the dioxime[16] gave white crystals: mp 195–196° (lit.[17] mp 188°); ir (Nujol) 3300–3300 (s), 1650 cm^{-1} (s).

1-Methoxy-4-methyl-1,4-cyclohexadiene (4). A. *tert*-Butyl Alcohol.—Following the previously described procedure, 12.0 g (0.098 mol) of *p*-methylanisile (3) (Aldrich) was reduced. Distillation of the light yellow-brown crude material gave 7.8 g (64%) of clear, sweet-smelling **4**: bp 56–57° (9 mm) [lit.[4] bp 80° (20 mm)]; nmr δ 1.65 (s, 3 H), 2.63 (m, 4 H), 3.45 (s, 3 H), 4.48 (m, 1 H), 5.27 (m, 1 H); ir (neat) 1700 (m), 1675 (s), 1220 (s), 1180 (s), 780 (s), 700 cm^{-1} (s); mol wt (mass spectrum) 124. Nmr and ir data correlate with literature values.[4]

B. Ethyl Alcohol.—This reduction was carried out exactly as above using 24.0 g (0.537 mol) of ethyl alcohol instead of *tert*-butyl alcohol. Distillation gave 7.4 g (61%) of **4**, bp 56° (9 mm). Following the procedure of Birch,[18] **4** was converted to an authentic sample of 4-methyl-3-cyclohexenone (**10**) (crude ketone): nmr δ 1.77 (s, 3 H), 2.40 (s, 4 H), 2.75 (m, 2 H), 5.43 (m, 1 H); ir (neat) 1700 (vs), 1190 (s), 1050 (s), 770 cm^{-1} (s); vpc R_t 14.25 min on a 12 ft × 0.25 in. 10% silicone on Chromosorb W column at 85° with He flow rate of 78 ml/min and He pressure of 62 psi. Glc analysis showed the product to contain ∼5% 4-methylcyclohexanone (**9**). Retention time and peak enhancement were used to identify **9**.

1-Methoxy-4-*tert*-Butyl-1,4-cyclohexadiene (6).—A solution of 16.1 g (0.098 mol) of *p*-*tert*-butylanisole (5) was reduced using 3.1 g (0.457 g-atom) of lithium and 36.5 g (0.475 mol) of *tert*-butyl alcohol. Distillation gave two fractions. The first fraction, 1.7 g, bp 56–58° (8 mm), was shown by nmr analysis to contain a small amount of **6** with the isomeric *tert*-butylcyclohexenes as major product. The isomeric *tert*-butylcyclohexenes were tentatively identified by absorptions attributed to them in the nmr at δ 0.88 (s), 1.33–2.25 (br m), 5.45 (m), 5.68 (m). The second fraction consisted of 8.6 g (49%) of **6**: bp 92° (8 mm) [lit.[19] bp 43° (0.4 mm)]; nmr δ 1.05 (s, 9 H), 2.72 (m, 4 H), 3.48 (s, 3 H), 4.53 (m, 1 H), 5.43 (m, 1 H); ir (neat) 1675 (m), 1650 (m), 1220 (s), 1180 (s), 790 cm^{-1} (s); mol wt (mass spectrum) 166. Nmr analysis showed the presence of 9% *p*-*tert*-butylphenol. The *p*-*tert*-butylphenol was further identified in an orientation experiment where it was extracted from the distillation residue. The nmr and ir spectra of the crude extract matched perfectly with authentic spectra of *p*-*tert*-butylphenol. The crude phenol and an authentic sample of *p*-*tert*-butylphenol were converted into its benzoate: mp (crude extract) 81–82° (lit.[20] mp 82°); mp (authentic) 81.5–82.0°; mmp 81–82°. Ir spectra of the benzoates matched perfectly. In some runs, the conjugated diene, 1-methoxy-4-*tert*-butyl-1,3-cyclohexadiene, was observed and identified from its nmr: nmr δ 1.05 (s, 9 H), 2.17 (s, 4 H), 3.45 (s, 3 H), 4.78 (d, 1 H, J = 7 Hz), 5.40 (d, 1 H, J = 7 Hz).

Reduction of *N*,*N*-Dimethyl-*p*-toluidine (8). A.—A solution of 13.3 g (0.098 mol) of *N*,*N*-dimethyl-*p*-toluidine (8) (Eastman White Label) in 225 ml of *n*-propylamine was reduced with 39.8 g (0.537 mol) of *tert*-butyl alcohol and 3.60 g (0.523 g-atom, 40 cm) of lithium. Petroleum ether (bp 40–60°) was used for extraction. The crude reduction product was hydrolyzed by stirring with 100 ml of 1 *N* HCl. Distillation of the crude ketone gave three fractions, bp 73–75° (25 mm), totaling 3.3 g. To identify the ketone, a 2,4-dinitrophenylhydrazone (DNPH)[16] was made using 0.5 g of the middle fraction. The crude orange solid had mp 130–135° (unclear melt). (The literature reports the following values. DNPH of 4-methyl-3-cyclohexenone: orange,[18] mp 120–121°; orange,[21] mp 131–134°; orange,[7] mp 128–129°. DNPH of 4-methylcyclohexanone: orange,[21] mp 133–134°.) In the effort to differentiate between the saturated and unsaturated ketone by effecting acid-catalyzed conjugation of the DNPH, a small amount was heated with 1 drop of concentrated H$_2$SO$_4$ in EtOH for a few minutes. The orange product of this reaction had mp 128–130°. (The literature reports the following values. DNPH of 4-methyl-2-cyclohexenone: crimson,[18] mp 173–174°; crimson,[21] mp 172–175°.)

Glc analysis (Table III) of the distillation fractions of a 12 ft × 0.25 in. 10% silicone on Chromosorb W column at 85° showed the first fraction to contain 90% 4-methylcyclohexenone (**9**) and 10% 4-methyl-3-cyclohexenone (**10**), while the third fraction contained 87% **9** and 13% **10**. Identification was made by comparison of

TABLE III

GLC ANALYSIS (10% SILICONE ON CHROMOSORB W AT 85°)

Fraction	4-Methylcyclohexanone, %	4-Methyl-3-cyclohexenone, %
1	71	29
2	65	35
	62 (nmr)	38 (nmr)
3	63	37

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[15] Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer with polystyrene calibration at 1601 cm^{-1}. Absorption bands are reported in reciprocal centimeters and intensities are reported as vs (very strong), s (strong), m (medium), and w (weak). Nmr spectra was recorded on a Varian Model A-60 spectrometer in carbon tetrachloride with tetramethylsilane (TMS) as the internal standard. The chemical shifts are reported in parts per million (δ). Mass spectra were recorded on a CEC Model 21-110 B double focusing spectrometer. Vapor phase chromatography was performed on a F & M Model 200 chromatograph with thermal conductivity detector. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich. All boiling points and melting points are uncorrected. Melting points were determined on a Mel-Temp apparatus. The *n*-propylamine and ethylamine were Eastman Kodak White Label grade. The *n*-propylamine was purified by stirring over sodium for 1 or 2 days and then distilling from the mixture. The lithium was obtained from Foote Mineral Co. in the form of ribbon (0.089 g/cm) in petrolatum.

[16] R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964.

[17] Beilstein reports the melting point of the dioxime at 188°, but also reports that quick heating gives a melting point of 200° and slow heating a melting point of 192° with slight decomposition.

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retention times and peak enhancement with those of authentic ketones. An authentic sample of **9** was prepared according to literature:[22] bp 169–170° (lit.[22] bp 168–170°); nmr δ 0.95 (d, 3 H), 1.00–2.00 (br, 5 H), 2.10 (m, 4 H); ir (neat) 1710 cm^{-1} (vs); glc R_t 12.25 min on a 12 ft × 0.25 in. 10% silicone on Chromosorb W column at 85° with He flow rate of 78 ml/min and He pressure of 62 psi.

B.—Using 2.03 g (0.294 g-atom, 22.5 cm) of lithium and 22.9 g (0.309 mol) of *tert*-butyl alcohol, 13.3 g (0.098 mol) of **8** was reduced. The crude reduction product was hydrolyzed by stirring for 1 hr with 5.1 g (0.041 mol) of oxalic acid and in 40 ml of H_2O. Ir and nmr spectra of the crude ketone product showed the presence of **8**. Removal of **8** by acid washes and distillation gave three clear fractions: (1) 0.3 g, bp 75–76° (25 mm); (2) 1.7 g, bp 76–77° (25 mm); (3) 0.6 g, bp 65–70° (20 mm).

Reduction of *N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine.—A solution of 12.7 g (0.098 mol) of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine[23] in 200 ml of *n*-propylamine was reduced with 13.0 g (0.175 mol) of *tert*-butyl alcohol and 1.14 g (0.166 g-atom, 6.4 cm) of lithium. A dark red oil was obtained after petroleum ether extraction and evaporation. The ir spectrum indicated the presence of some starting material. Hydrolysis of the crude product with 50 ml of 10% HCl followed by $CHCl_3$ extraction gave 2.5 g of a dark red-black liquid which showed presence of carbonyl in the ir at 1700 cm^{-1}. Conversion of this material to its dioxime afforded a dark red-black gummy solid which could not be recrystallized. The filtrate from the dioxime preparation yielded, after sitting for 2 days, 0.5 g of dark brown crystals, mp 192–203°. The crystals were recrystallized from 95% EtOH to give 0.2 g of dioxime (1.7% from tetramethyl): mp 194–198° (lit[17] mp 188°); ir (Nujol) 3300–3000 (s), 1650 cm^{-1} (s) (the ir spectrum matches the spectrum of authentic 1,4-cyclohexanedione dioxime).

1,4-Di-*tert*-butyl-1,4-cyclohexadiene (**12**).—A solution of 12.4 g (0.066 mol) of *p*-di-*tert*-butylbenzene (**11**) in 146 ml (100 g) of anhydrous ethylamine was reduced with 16.4 g (0.356 mol) of EtOH and 2.12 g (0.308 g-atom, 23.3 cm) of lithium. The crude product was recrystallized from MeOH to give 10.1 g of white crystals: mp 53–56°; nmr analysis, 86% diolefin, 14% monoolefin. This material was recrystallized twice more from MeOH to give 7.1 g (56%) of white fluffy crystals of **12**: mp 61.5–62.5°; nmr δ 1.03 (s, 18 H), 2.67 (m, 4 H), 5.48 (m, 2 H) (no monoolefin present); ir (Nujol) 1310 (w), 1270 (w), 1040 (m), 950 (m), 800 cm^{-1} (m); mol wt (mass spectrum) 192.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.52; H, 12.38.

The *p*-di-*tert*-butylbenzene (**11**) was prepared according to the literature.[24] Two recrystallizations gave white crystals: mp 75–77° (lit.[24] mp 78°); nmr δ 1.32 (s, 18 H), 7.23 (s, 4 H); ir (Nujol) 1500 (w), 1250 (w), 1120 (w), 1010 (2), cm^{-1} 820 (s).

1,4-Dicyclohexyl-1,4-cyclohexadiene (**14**).—In a procedure analogous to the preparation of **12**, 12.0 g (0.050 mol) of *p*-dicyclohexylbenzene (**13**) in 146 ml (100 g) of anhydrous ethylamine was reduced by 1.6 g (0.231 g-atom) 17.5 cm) of lithium and 12.3 g (0.265 mol) of ethanol. The crude product was recrystallized from absolute ethyl alcohol to give 10.7 g of white solid, mp 88.5–90.5°. Nmr analysis indicated the composition of this material to be 79% **14** and 21% **13**. Four recrystallizations from ethyl alcohol gave 8.9 g (73%) of white flakes (nmr analysis showed 4% starting material): mp 91.0–92.5°, nmr δ 0.83–2.33 (br m, 22 H), 2.60 (m, 4 H), 5.38 (m, 2 H); ir (Nujol) 950 (m), 880 (w), 850 (w), 800 cm^{-1} (w); mol wt (mass spectrum) 244.

Anal. Calcd for $C_{18}H_{28}$: C, 88.46; H, 11.54. Found: C, 88.37; H, 11.62.

1,4-Di-*tert*-butylcyclohexene (**15**).—Reduction of 12.4 g (0.066 mol) of *p*-di-*tert*-butylbenzene (**11**) in 146 ml (100 g) of ethylamine required 2.70 g (0.392 g-atom, 30 cm) of lithium. Recrystallization from MeOH gave 9.4 g (74%): mp 54.0–55.0° (lit.[12] mp 54.0–54.5°); nmr δ 0.88 (s, 9 H), 1.02 (s, 9 H), 1.02–2.38 (br m, 7 H), 5.42 (m, 1 H); ir (Nujol) 1240 (w), 1030 (w), 830 (w), 805 cm^{-1} (w); mol wt (mass spectrum) 194; glc R_t 5.5 min on a 6 ft × 0.25 in. 10% Carbowax on Chromosorb W column at 175° with He flow rate of 78 ml/min and He pressure of 62 psi.

1,4-Dicyclohexylcyclohexene (**16**).—This compound was prepared in an analogous manner to the preparation of **15**. The only change in procedure was that the 16.0 g (0.066 mol) of *p*-dicyclohexylbenzene (**13**) was dissolved in 292 ml (200 g) of anhydrous ethylamine owing to lack of solubility. The crude product was recrystallized from an ethyl alcohol–methyl alcohol mixture to give 12.3 g (76%) of white crystals, mp 107–108°. Nmr analysis showed no starting material. An analytical sample was recrystallized from ethyl alcohol: mp 107° (lit.[25] mp 111–113°); nmr δ 0.78–2.33 (br, m, 29 H), 5.35 (m, 1 H); ir (Nujol) 900 (w), 890 cm^{-1} (w); mol wt (mass spectrum) 246.

Anal. Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.60; H, 12.55.

1,4-Diisopropylcyclohexene (**18**).—A solution of 15.9 g (0.098 mol) of *p*-diisopropylbenzene (**17**) (Aldrich) in 146 ml (100 g) ethylamine was reduced with 4.05 g (0.588 g-atom, 45 cm) of lithium. Distillation gave 14.9 g (92%) of clear **18**: bp 92° (20 mm); n^{24}D 1.4584; nmr δ 0.88 (d, 6 H), 0.97 (d, 6 H) (doublets are overlapping for isopropyl groups), 1.02–2.50 (br, m, 9 H), 5.31 (br, m, 1 H); ir (neat) 2900–2800 (vs), 1460 (s), 1380 (s), 1360 (s), 810 cm^{-1} (m); mol wt (mass spectrum) 166.

Anal. Calcd for $C_{12}H_{12}$: C, 86.66; H, 13.34. Found: C, 86.43; H, 13.46.

1,4-Dimethylcyclohexene (**20**).—The reduction of 13.3 g (0.125 mol) of *p*-xylene (**19**) (Eastman) in 146 ml (100 g) ethylamine required 5.2 g (0.755 g-atom, 57.6 cm) of lithium. Distillation gave 6.5 g (60%) of **20**: bp 112–113° (lit.[26] bp 124–126°); n^{24}D 1.4448 (lit.[26] (n^{24}D 1.4457); nmr δ 0.95 (d, 3 H) 1.03–250 (br m with strong s at 1.61, 10 H), 5.38 (br m, 1 H); ir (neat) 2900 (s), 1460 (s), 1380 (s), 1040 (m), 890 (m), 790 (m), 780 cm^{-1} (m).

Reduction of 2,3-Dimethylnaphthalene (**21**). **A.** A solution of 13.0 g (0.083 mol) of **21** in 146 ml (100 g) of ethylamine was reduced by 11.3 g (0.266 mol) ethyl alcohol and 1.79 g (0.261 g-atom, 20 cm) of lithium. Recrystallization from MeOH gave 9.6 g of white crystals: mp 64–70°; nmr analysis, 82% 2,3-dimethyl-1-4,5,8-tetrahydronaphthalene (**23**), 18% **21**.

B. Same as above except 17.1 g (0.370 mol) ethyl alcohol and 2.47 g (0.360 g-atom, 27.5 cm) of lithium were used. Recrystallization from ethyl alcohol gave 9.6 g (72%) of pure **23**: mp 67–69°; nmr δ 1.67 (s, 6 H), 2.43 (s, 4 H), 2.51 (s, 4 H), 5.70 (s, 2 H); ir (Nujol) 1380 (m), 1060 (w), 960 (w), 940 cm^{-1} (w); mol wt (mass spectrum) 160.

Anal. Calcd for $C_{12}H_{16}$: C, 89.92; H, 10.08. Found: C, 90.04; H, 10.03.

Dehydrogenation of 1,4-Di-*tert*-butyl-1,4-cyclohexadiene (**12**). **A.**—A solution of *N*-lithioethylenediamine was prepared under N_2 from 0.6 g (0.087 g-atom) of lithium and 35 ml of anhydrous ethylenediamine (distilled over sodium). A solution of 2.0 g (0.10 mol) of **12** in 65 ml of ethylenediamine was added and refluxed for 3 hr. Recrystallization of the crude product from MeOH gave 1.6 g (81%) of *p*-di-*tert*-butylbenzene (**11**): mp 75–77°; mmp 75–78° (no depression); nmr and ir spectrum matched those of authentic *p*-di-*tert*-butylbenzene.

B.—A sample of **12** which nmr analysis showed to contain 14% **15** was injected on the glc column with an injection port temperature of 255°. The chromatograph showed the product to contain 77% **12** (R_t 9.0 min), 13% **15** (R_t 5.5 min), and 10% **11** (R_t 10.5 min). Identity of the products was checked by peak enhancement and retention time. The glc was performed on a 6 ft × 0.25 in. 10% Carbowax on Chromosorb W column at 175° with He flow rate of 81 ml/min and He pressure of 62 psi.

Isomerization of 1,4-Dimethoxy-1,4-cyclohexadiene (**2**). **A.**—A solution of lithium *n*-propylamide was prepared by refluxing 0.36 g (0.052 g-atom) of lithium and 70 ml of *n*-propylamine for 4 days. A solution of 5.8 g (0.041 mol) of **2** in 40 ml of *n*-propylamine was added and refluxed for 1.5 hr under conditions which scrupulously excluded moisture and guaranteed an excess of base in solution throughout the isomerization. Nmr analysis of the crude product showed it to be 69% **7** [nmr 2.28 (s, 4 H), 3.48 (s, 6 H), 4.73 (s, 3 H)] and 31% **2**.

B.—Lithium *n*-propylamide was prepared from 0.73 g (0.105 g-atom) of lithium and 100 ml of *n*-propylamine by refluxing for 4 days. A solution of 12.3 g (0.088 mol) of **2** in 50 ml of *n*-propylamine was added and refluxed for 7.5 hr. Distillation gave two fractions: (1) 2.4 g, bp 31–58° (7 mm); (2) 5.6 g, bp

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78–74° (7 mm). Nmr analysis showed the first fraction to contain 76% anisole, 17% **7**, and 7% **2**, while the second fraction contained 51% **7**, 18% **2**, 11% **1**, and 10% anisole. Anisole was identified by comparison with the nmr spectrum of an authentic sample and by conversion into its sulfonamide derivative: mp (isolated) 109–110.5°; mp (authentic) 111.5–112° (lit.[20] mp 111°); mmp 111–112.5° (no depression); ir spectra of sulfonamides matched perfectly.

Registry No.—**1**, 150-78-7; **2**, 39000-58-3; **3**, 104-93-8; **4**, 20023-36-3; **5**, 5396-38-3; **6**, 22566-53-6; **7**, 39000-61-8; **8**, 99-97-8; **9**, 589-92-4; **10**, 5259-65-4; **11**, 1012-72-2; **12**, 39000-62-9; **13**, 1087-02-1; **14**, 39000-63-0; **15**, 5009-02-9; **16**, 39000-65-2; **17**, 100-18-5; **18**, 39000-66-3; **19**, 106-42-3; **20**, 2808-79-9; **21**, 581-40-8; **23**, 39000-67-4; 1-methoxy-4-*tert*-butyl-1,3-cyclohexadiene, 37720-49-3; lithium, 7439-93-2.

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Synthesis of *tert*-Carboxylic Acids from Olefins and Carbon Monoxide by Copper(I) Carbonyl Catalyst

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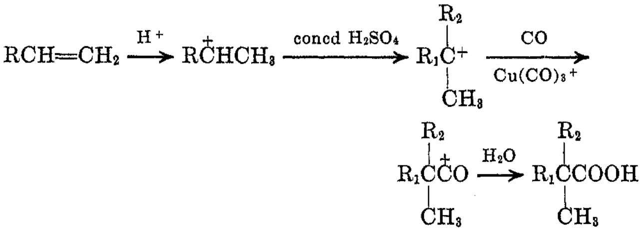
The new carbonylation reaction was proposed using Cu(I) carbonyl catalyst in concentrated H_2SO_4. In concentrated H_2SO_4 containing Cu(I) compound, olefins react with carbon monoxide at room temperature and atmospheric pressure to produce *tert*-carboxylic acids in high yields. Neither primary nor secondary carboxylic acids were found. The catalyst was prepared in concentrated H_2SO_4 from Cu(I) compounds and carbon monoxide. The amount of the Cu(I) compound sufficient for carrying out these carbonylation was as small as 0.2 mol/l. It is assumed that unstable Cu(I) tricarbonyl [$Cu(CO)_3^+$] is transiently formed in concentrated H_2SO_4. The yields of the *tert*-carboxylic acids are as follows: *tert*-C_7 acid, 72% from 1-hexene; *tert*-C_8 acid, 82% from 1-heptene; *tert*-C_9 acid, 94% from 1-octene; and *tert*-C_{11} acid, 97% from 1-decene. Reaction optimum temperature was 20–50° for the monoolefins. The yield and reaction rate decreased with the decrease of H_2SO_4 concentration. At the H_2SO_4 concentrations less than 80%, no carboxylic acids were obtained.

Much work has been published concerning the carbonylation of olefin with carbon monoxide. Reppe[1] and others[2] reported the reaction catalyzed by metal carbonyls, and mixtures of *n*-carboxylic acid and *sec*-carboxylic acid were obtained. This reaction proceeds at high temperature and high pressure. On the other hand, Koch[3] and others[4,5] obtained branched carboxylic acids by the carbonylation of olefins in strong acid such as H_2SO_4, HF, H_3PO_4, or $BF_3 \cdot H_2O$. However, metal catalysts were not used in Koch type reaction. All these reactions need high carbon monoxide pressures.

Recently we found that Cu(I) carbonyl was easily formed from Cu(I) compounds and carbon monoxide in concentrated H_2SO_4.[6] Cu(I) carbonyl has high catalytic activity in the carbonylation of alcohols to carboxylic acids at room temperature and atmospheric pressure.[7]

$$ROH \xrightarrow{H_2SO_4} R'^+ \xrightarrow[Cu(CO)_3^+]{CO} R'CO^+ \xrightarrow{H_2O} t\text{-}R'COOH$$

This paper describes the synthesis of *tert*-carboxylic acids, from olefins and carbon monoxide, catalyzed by Cu(I) carbonyl in concentrated H_2SO_4. From various types of olefins, *tert*-carboxylic acids are generally formed by the isomerization of the intermediate carbonium ion in concentrated H_2SO_4. The reactions using Cu(I) carbonyl catalyst provide new examples of the wide-ranging synthetic utility for carbonylation reactions.



$$RCH{=}CH_2 \xrightarrow{H^+} R\overset{+}{C}HCH_3 \xrightarrow{\text{concd } H_2SO_4} R_1\overset{R_2}{\underset{CH_3}{C^+}} \xrightarrow[Cu(CO)_3^+]{CO} R_1\overset{R_2}{\underset{CH_3}{\overset{+}{C}CO}} \xrightarrow{H_2O} R_1\overset{R_2}{\underset{CH_3}{C}}COOH$$

R_1 = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_7H_{15}
R_2 = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9

Results and Discussion

The results of *tert*-carboxylic acid synthesis catalyzed by Cu(I) carbonyl from olefin and carbon monoxide are shown in Table I. Various kinds of olefins (terminal or internal olefins) gave *tert*-carboxylic acids in concentrated H_2SO_4. This is due to the isomerization of the carbonium ion intermediate prior to the carbonylation. Primary or secondary carboxylic acids were not found.

Cuprous oxide and cuprous sulfate were used as the Cu(I) compounds. The effect of the amount of cuprous oxide is illustrated in Figure 1. Without cuprous oxide, the rate of reaction was very slow, and the yield of carboxylic acid was less than 10%. When cuprous oxide was added in concentrated H_2SO_4, the rate of reaction increased considerably. The reaction was almost complete in 1–2 hr, and *tert*-carboxylic acids were obtained in high yields. On the other hand, Cu(II) compounds do not exhibit any catalytic activity.

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