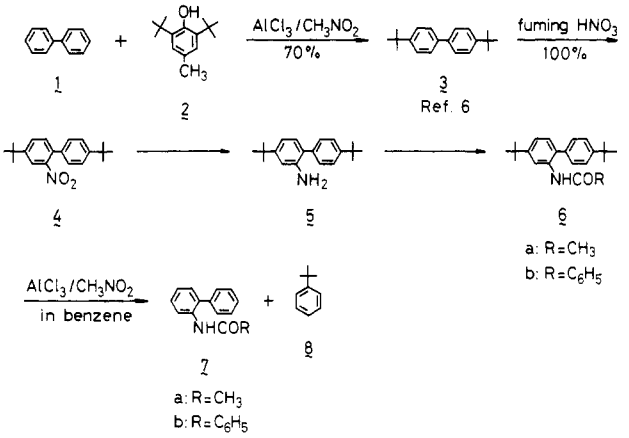
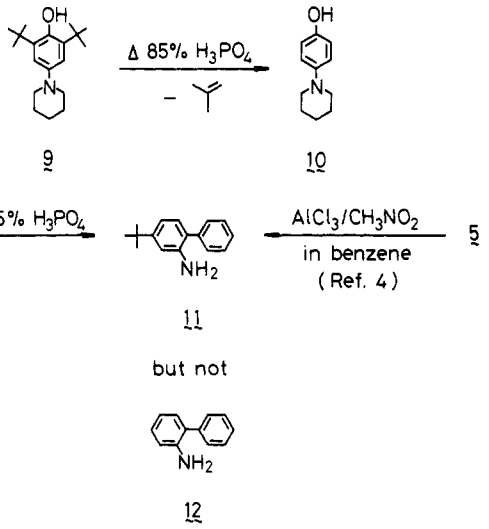
Scheme I



Scheme II



deed, *N*-acetyl-*o*-toluidine (**18**) and *N*-acetyl-2,6-dimethylaniline (**24**) were prepared from toluene (**13**) and *m*-xylene (**19**), respectively (see Scheme III).

Experimental Section

Transalkylation of 6a in Benzene. After a mixture of 200 mg (0.6 mmol) of **6a**, 300 mg (2 mmol) of aluminum chloride, and 6 mL of benzene is stirred at room temperature for 3 h, it is quenched with water and extracted with ether. The ether solution is washed with water, dried with sodium sulfate, and evaporated in vacuo to leave the residue, which was recrystallized from hexane to give 102 mg (79%) of **7a**: mp 123–124 °C; lit.[7] mp 120 °C.

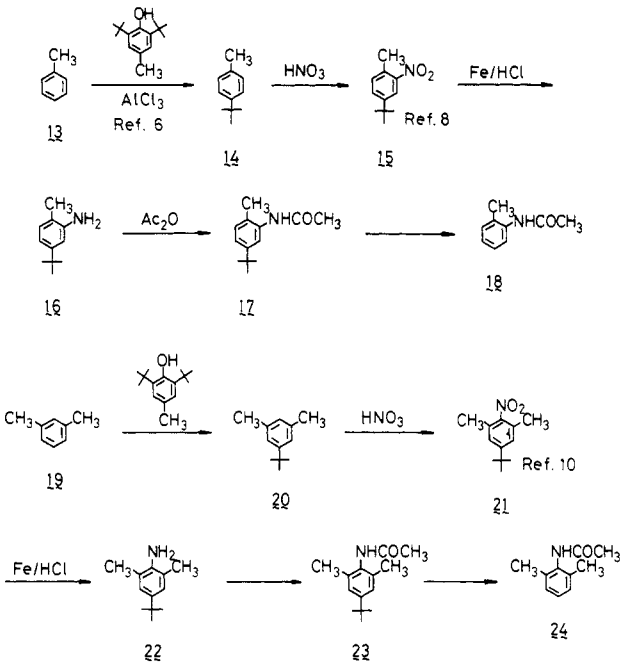
Transalkylation of 6b in Benzene. A mixture of 500 mg of **6b**, 550 mg (3.6 mmol) of aluminum chloride, and 15 mL of benzene is treated and worked up as described above to give 222 mg (63%) of **7b**: colorless needles, mp 88–89 °C (hexane). Anal. Calcd for $C_{19}H_{16}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.50; H, 5.60; N, 5.43.

Treatment of 5 with Refluxing 85% Phosphoric Acid. After a mixture of 200 mg of **5** and 6 mL of phosphoric acid is heated at 220 °C for 24 h, it is poured into a large amount of water, made basic to litmus with 10% sodium hydroxide, and extracted with ether. The ether solution is washed with water, dried with sodium sulfate, and evaporated in vacuo to leave the residue, which is chromatographed on silica gel with benzene as an eluent to give 120 mg (100%) of **11**: colorless needles (ethanol–water), mp 80–82 °C; lit.[4] mp 110–112 °C.

Transalkylation of 17 in Benzene. A mixture of 2.05 g (10 mmol) of **17**, 5.28 g (40 mmol) of aluminum chloride, and 100 mL of benzene is treated and worked up as described above to give 800 mg (54%) of **18**: colorless needles (hexane–benzene, 2:1); mp 109–110 °C, lit.[9] mp 110 °C.

(7) Sako, S. *Bull. Chem. Soc. Jpn.* **1934**, *6*, 54.
(8) Carpenter, M. S.; Easter, W. M.; Wood, T. F. *J. Org. Chem.* **1951**, *16*, 586.

Scheme III



Transalkylation of 23 in Benzene. A mixture of 2.19 g (10 mmol) of **23**, 5.28 g (40 mmol) of aluminum chloride, and 100 mL of benzene is treated and worked up as described above to give 1.33 g (82%) of **24**: colorless needles, mp 176–177 °C (hexane–benzene, 1:1), lit.[11] mp 177 °C.

Compounds **6a**, **6b**, **17**, and **23** were prepared in the usual manner.

6a: colorless needles, mp 136–138 °C (hexane). Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.60; H, 9.15; N, 4.21.

6b: colorless prisms, mp 146 °C. Anal. Calcd for $C_{27}H_{31}NO$: C, 84.11; H, 8.11; N, 3.63. Found: C, 84.31; H, 8.06; N, 3.63.

17: colorless needles, mp 97–98 °C (hexane). Anal. Calcd for $C_{18}H_{19}NO$: C, 76.05; H, 9.32; N, 6.82. Found: C, 76.05; H, 9.69; N, 6.95.

23: colorless needles, mp 156–157 °C (hexane–benzene, 5:1). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65, N, 6.39. Found: C, 77.10; H, 9.81; N, 6.59.

Registry No. **2**, 128-37-0; **5**, 70728-92-6; **6a**, 85336-15-8; **6b**, 85336-16-9; **7a**, 2113-47-5; **7b**, 7404-97-9; **8**, 98-06-6; **11**, 70729-04-3; **13**, 108-88-3; **14**, 98-51-1; **15**, 62559-08-4; **16**, 85336-17-0; **17**, 85336-18-1; **18**, 6830-82-6; **19**, 108-38-3; **20**, 98-19-1; **21**, 6279-89-6; **22**, 42014-60-8; **23**, 85336-19-2; **24**, 2198-53-0; benzene, 71-43-2.

(9) Kaufmann, A. *Ber.* **1909**, *42*, 3481.
(10) Carpenter, M. S.; Easter, W. M. *J. Org. Chem.* **1954**, *19*, 77.
(11) Busch, M. *Ber.* **1899**, *32*, 1008.

Reaction of Acrylonitrile with Benzophenone via the Derived Vinyl Carbanion

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Vinyl carbanion intermediates are formed in acid–base-type reactions of activated olefins of the type Y—

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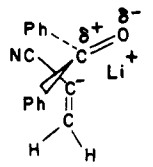
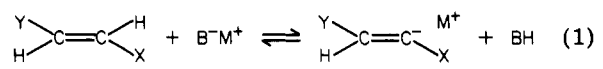


Figure 1.

C=CH — X, X being an electronegative substituent[1-4] (eq 1). The recent use of vinyl carbanions derived from β-

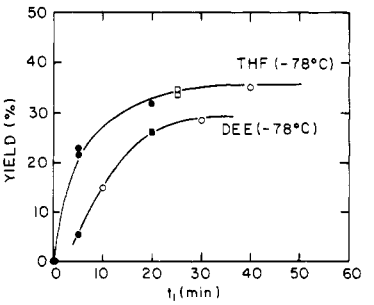


substituted acrylic acid derivatives and other 1,2-disubstituted ethylenes (X, Y: COOEt, $\overline{NCH_2CH_2CH_2CH_2}$;[5] COOEt, OMe;[4] COOEt, C_6H_5;[6] $CONEt_2$, $\overline{NCH_2CH_2CH_2CH_2}$;[7] CN, C_6H_5;[8] COC_6H_5, $\overline{NCH_2CH_2CH_2CH_2}$[4]) as nucleophiles is of great interest, since it offers a new synthetic route to the attachment of a substituted olefinic moiety to an electrophile, in one step. Except for one preliminary report,[6] a similar application of vinyl carbanions derived from nonsubstituted acrylic acid derivatives (CH_2=CHX) has not yet been reported. This might be due to the facile involvement of these activated olefins in other base-catalyzed reactions (Michael addition reactions and anionic polymerization) which depress the vinyl carbanion formation pathway.

The reaction of acrylonitrile (AN) and benzophenone in the presence of lithium diisopropylamide (LDA) was investigated in the present work, as a model reaction of vinyl carbanions derived from CH_2=CHX with the purpose of finding out the factors and experimental conditions affecting and leading to formation of these intermediates and their subsequent reaction with electrophiles.

Results and Discussion

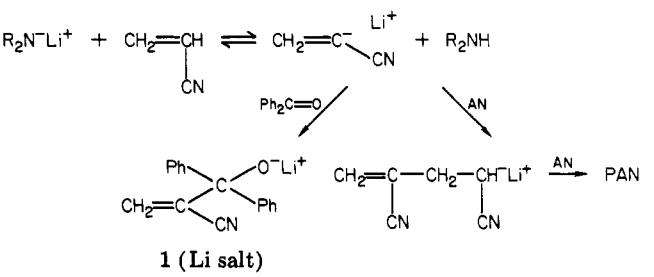
A solution of AN and benzophenone was added dropwise into a cooled solution of LDA in THF or in diethyl ether (DEE). The products recovered from the reaction mixture were 2-cyano-3-hydroxy-3,3-diphenylprop-1-ene (1) and polyacrylonitrile (PAN). The results are summerized in Table I. Yields of 1 as high as 35% were obtained in THF and in DEE, while PAN was formed almost exclusively in dimethoxyethane (DME), in DMF, or in DEE containing an effective solvating agent, hexamethylphosphortriamide (HMPT). It was thus obvious that the formation of 1 was dependent on the ion-pairing characteristics of the AN-lithium salt, CH_2=C^-—(CN)Li^+ (AN^- Li^+). An equilibrium mixture of contact (AN^-,Li^+) and solvent-separated (AN^- //Li^+) ion pairs should exist in DEE and THF.[9] In analogy to other carbanion lithium salts, the equilibrium concentrations of the AN^- //Li^+ ion pairs and the extent of ion-pair separation in these ion pairs increases with respect to the solvent used in the order DEE < THF < DME < DMF.[10]



Plot of Yield of A"-C(OH)Ph_2 vs t_1

Figure 2. Plot of the yield of 1 vs. t_1 t_2 values in the range of 0–40 min have the following assignments: ○, t_2 = 0 min; ●, t_2 = 20 min; □, t_2 = 35 min; ■, t_2 = 40 min. Effect of the rate of addition of the AN/Ph_2C=O solution on the yield of 1 (experimental conditions as for Table I).

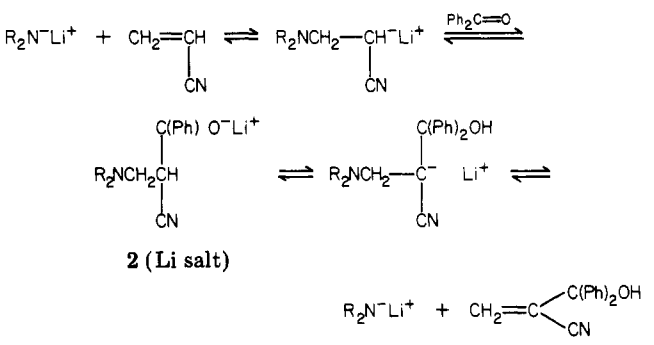
Scheme I[a]



1 (Li salt)

[a] R = *i*-Pr.

Scheme II



2 (Li salt)

Compound 1 was preferentially formed in the relatively poorly solvating mediums DEE and THF (in which ion pairs are of close proximity[9]) and not in DME and DMF, in which free ions predominate.[9] Formation of 1 under such conditions might be due to the possible existance of some kind of an AN^- Li^+·Ph_2C=O complex (schematically shown in Figure 1) in DEE and in THF only. In line with this, addition of HMPT to the DEE–AN–Ph_2C=O reaction mixture resulted in a very low yield of 1 (Table I, entry 15) presumably by converting AN^-,Li^+ ion pairs into HMPT-solvated highly separated ion pairs, which were incapable of coordinating with benzophenone.

Effect of Temperature. An increase of the yield of 1 on decreasing temperature was observed in THF and in DEE (compare entries 3 and 12, Table I). This was expected because the fraction of the nucleophilically more reactive solvent-separated ion pairs C^-//Li^+ (as compared to contact ion-pairs C^-,Li^+) and the degree of their ion-pair

(1) (a) Walborsky, H. M.; Turner, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 2273. (b) Arnett, J. F.; Walborsky, H. M. *J. Org. Chem.* **1972**, *37*, 3678.
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(7) Schmidt, R. R.; Talbiersky, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 171.
(8) (a) Schmidt, R. R.; Speer, H. *Synthesis* **1979**, 797. (b) Feit, B. A.; Melamed, U.; Schmidt, R. R.; Speer, H. *Tetrahedron* **1981**, *37*, 2143.
(9) Smid, J. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1971; Vol. I, Chapter 3.
(10) Chang, L.; Smid, J. *J. Am. Chem. Soc.* **1967**, *89*, 4547.

Table I. Effect of Solvent and Temperature on the Yield of 1 in the AN-LDA-Benzophenone Reaction System[a]

entry	solvent	temp, °C	$t_1 + t_2$,[b] min	yield of 1, g (%)
1	THF	0	15 + 20	0.090 (9.6)
2	THF	0	15 + 20	0.085 (9.0)
3	THF	0	28 + 20	0.105 (11.2)
4	DEE	0	15 + 20	0.150 (16.0)
5	DEE	0	15 + 20	0.140 (14.9)
6	DEE	0	25 + 20	0.180 (19.1)
7	THF	−78	1 + 0	c
8	THF	−78	5 + 0	0.220 (23.4)
9[e]	THF	−78	5 + 0	0.130 (13.8)
10[f]	THF	−78	5 + 0	0.260 (27.7)
11	THF	−78	25 + 35	0.315 (33.5)
12	THF	−78	25 + 35	0.326 (34.6)
13	DEE	−78	20 + 40	0.250 (26.6)
14	DEE	−78	20 + 40	0.270 (28.7)
15	DEE + HMPT[d]	−78	20 + 40	0.060 (6.4)
16	DME	−78	20 + 20	0.015 (1.6)
17	DME	−78	20 + 20	0.015 (1.6)
18	DME	−78	40 + 20	0.020 (2.1)
19	DMF	0	5 + 0	c
20	DMF	0	5 + 0.5	c

[a] [AN] = 4.0 mmol, [LDA] = 7.5 mmol, and [Ph_2C=O] = 6.0 mmol. [b] t_1 = time of addition of the AN/Ph_2C=O mixture; t_2 = reaction time after t_1. [c] PAN was the only product obtained. [d] [HMPT] = 4.0 mmol. [e] [LDA] = 4.0 mmol. [f] [LDA] = 12.0 mmol.

separation increased in etheral solvents on decreasing temperature.[11,12]

Effect of the Rate of Addition of Reactants. The rate of addition of the mixture of AN and benzophenone into the cooled LDA solution was found to be a critical factor. Addition in one portion or at high rates resulted in polymerization only. The yield of 1 increased up to a certain limit on decreasing the rate of addition and then became constant (Figure 2). It is obvious that relatively high concentrations of AN are in favor of polymerization on account of formation of 1 (Scheme I). It seems that at high rates of addition, most of the added AN is not being converted to the derived vinyl carbanion $AN^- Li^+$ but competes effectively with the benzophenone for the vinyl carbanion. The results clearly indicated that the yield of 1 was dependent on t_1 and very little on t_2 (Figure 2). The yield of 1 increased on increasing the ratio of [LDA]/[AN] (compare entries 8 and 9, Table I).

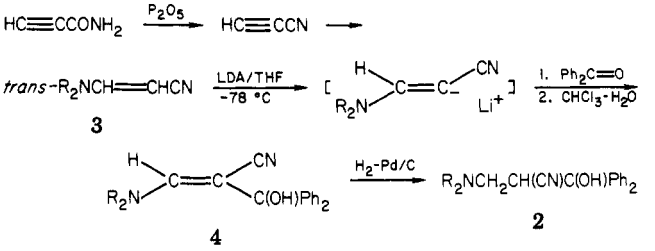
Although the addition product $R_2NCH_2CH_2CN$ was not detected at all, it could still be argued that the acrylonitrile derivative 1 was not formed via the vinyl carbanion intermediate but rather by an alternative addition–elimination mechanism such as in Scheme II. The addition product 2-cyano-3-(diisopropylamino)-1,1-diphenylpropan-1-ol (2) was synthesized and was reacted with LDA under the same experimental conditions in which 1 was formed. No elimination occurred, and 2 was recovered almost quantitatively. The addition–elimination mechanism for the formation of 1 (Scheme II) could thus be ruled out.

The synthetic sequence used to prepare the addition product 2 is summarized in Scheme III.

Experimental Section

Materials. Acrylonitrile and DMF were purified and dried as previously described.[13] THF was directly distilled from a

Scheme III



THF–sodium naphthalene solution into the reaction flask. DEE and DME were kept in a flask over sodium and directly distilled from it into the reaction flask. LDA was prepared by addition of the amine to an equimolar solution of butyllithium in *n*-hexane. All experimental manipulations and the reaction flask were as previously described.[6]

Reaction of Acrylonitrile with Benzophenone in the Presence of LDA. A solution of acrylonitrile (212 mg, 4.0 mmol) and benzophenone (1.09 g, 6.0 mmol) dissolved in THF (10 mL) was added dropwise during 35 min (t_1) into a cooled solution (−78 °C) of LDA (7.5 mmol) in THF (40 mL) containing 5 mL of hexane. The reaction mixture was further stirred for 25 min (t_2) at −78 °C, whereafter water and chloroform were added to it. The organic layer was separated from nonsoluble material (polyacrlonitrile), and the oil residue recovered from it was chromatographed on a silica gel column with a petroleum ether (bp 40–60 °C)–chloroform mixture (3:1) as the eluent to yield white crystals of 2-cyano-3-hydroxy-3,3-diphenylprop-1-ene: 325 mg (34.5%); mp 112 °C (from chloroform–petroleum ether); ^1H NMR ($CDCl_3$) δ 2.75 (s, 1 H, disappeared in presence of D_2O), 5.70 (s, 1 H), 6.00 (s, 1 H), 7.15–7.40 (m, 10 H); IR ($CHCl_3$) 3545, (OH), 2220 (C≡N), 1600 cm^{-1} (CH_2=C(CN)); MS, *m/e* 235 (for $C_{16}H_{13}NO$). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.71; H, 5.53; N, 5.95. Found: C, 81.63; H, 5.53; N, 5.95.

Synthesis of 2-Cyano-3-(diisopropylamino)-1,1-diphenylpropan-1-ol (2). (a) (*E*)-1-Cyano-2-(diisopropylamino)ethene (3). Propiolamide (3.00 g, 43.5 mmol) and phosphorus pentoxide (9 g) were heated together under nitrogen to yield cyanoacetylene: 1.90 g (85%); bp 35–36 °C. A solution of diisopropylamine (5.64 g, 56.0 mmol) in dry THF (5 mL) was added dropwise during 10 min into a solution of the cyanoacetylene obtained (1.90 g, 37.0 mmol) cooled in an ice bath. The reaction mixture, which became very dark, was further stirred for 2 h at room temperature. The crude oily residue, obtained after evaporation of the solvent, was crystallized from petroleum ether to give white crystals of 3: 3.4 g (60%); mp 102–104 °C; ^1H NMR ($CDCl_3$) δ 1.20 (d, 12 H, *J* = 8 Hz), 3.52 (heptet, 2 H, *J* = 8 Hz), 3.78 (d, 1 H, *J* = 15 Hz), 6.88 (d, 1 H, *J* = 15 Hz); MS, *m/e* 152 (for $C_9H_{16}N_2$).

(b) (*Z*)-2-Cyano-3-(diisopropylamino)-1,1-diphenyl-2-propen-1-ol (4). A solution of 3 (0.38 g, 2.5 mmol) and benzophenone (0.55 g, 3.0 mmol) in THF (10 mL) was added dropwise during 15 min into a solution of LDA (7.5 mmol) in THF (40 mL) at −78 °C. The reaction mixture was further stirred for 40 min, and water and chloroform were added. The crude residue recovered was crystallized (from petroleum ether–ethyl acetate) to yield the product 4: 0.38 g (45%); mp 152–154 °C; ^1H NMR ($CDCl_3$) δ 0.80 (d, 12 H, *J* = 8 Hz), 3.25 (br s, 1 H, disappeared on adding D_2O), 3.70 (heptet, 2 H, *J* = 8 Hz), 6.70 (s, 1 H), 7.00–7.55 (m, 10 H); MS, *m/e* 334 (for $C_{22}H_{26}N_2O$).

(c) 2-Cyano-3-(diisopropylamino)-1,1-diphenylpropan-1-ol (2). A solution of 4 (0.38 g, 13.0 mmol) in ethyl alcohol (20 mL) was hydrogenated for 24 h over a Pd/C (5%) catalyst. The crude product was chromatographed on a silica gel column using a petroleum ether–ethyl acetate mixture (6:1) as eluent to yield the product 2: 0.23 g (60%); mp 165–167 °C (from petroleum ether–chloroform); ^1H NMR ($CDCl_3$) δ 1.10 (d, 12 H, *J* = 8 Hz), 3.10 (br s, 1 H, disappeared on adding D_2O), 3.70–4.40 (m, 5 H), 7.10–7.50 (m, 10 H); MS, *m/e* 336 (for $C_{22}H_{28}N_2O$).

Reaction of 2 with LDA. A solution of 2 (0.168 g, 0.5 mmol) in THF (10 mL) was added dropwise during 15 min into a solution

(11) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307; **1965**, *87*, 669.
(12) Bhattacharyya, D. N.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 624.
(13) Feit, B. A.; Bigon, Z. *J. Org. Chem.* **1969**, *34*, 3942.

of LDA (2.50 mmol) in THF (40 mL) at −78 °C. The reaction mixture was further stirred for 60 min, and water and chloroform were then added. The crude reaction mixture contained compound **2** only as was evident from its TLC, ^{1}H NMR, and mass spectra.

Registry No. **2**, 85135-73-5; **3**, 85135-74-6; **4**, 85135-75-7; 2-cyano-3-hydroxy-3,3-diphenylprop-1-ene, 85135-76-8; acrylonitrile, 107-13-1; benzophenone, 119-61-9; propiolamide, 7341-96-0; cyanoacetylene, 1070-71-9; diisopropylamine, 108-18-9; LDA, 4111-54-0; THF, 109-99-9; DEE, 60-29-7; HMPT, 680-31-9; PME, 110-71-4; DMF, 68-12-2.

Oxidative Decarboxylation and Decarbonylation of 3,3-Dialkyl-2-oxo Carboxylic Acids and Esters

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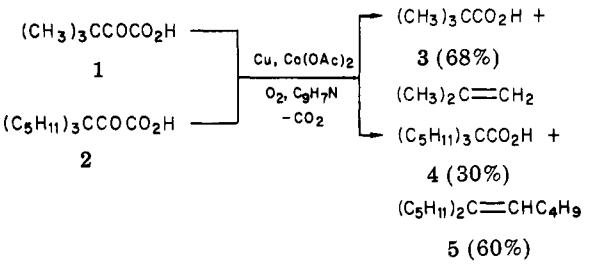
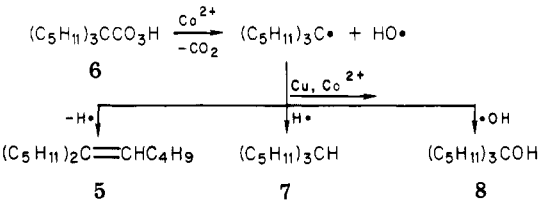
Trialkylacetic acid derivatives have been reported to have muscle-relaxing properties,[1] and many procedures are available for the preparation of the related acids.[2] Alkylation of α-metalated α-branched acids affords good yields (65–75%) of the trisubstituted acids; however, steric factors may limit the size of the three alkyl groups. The availability of 2-oxo acids and esters [$R_1R_2R_3CCOCO_2H$-(R)] in which R_1, R_2, and R_3 are unlike and may have greater than ten carbons suggested that oxidative decarboxylation or decarbonylation of such molecules might offer a procedure for preparing more highly substituted trialkylacetic acids.[3]

Oxidative decarboxylations of the 2-oxo acids **1** and **2** were studied. In the presence of Cu powder, Co(OAc)$_2$·4H$_2$O, O$_2$, and quinoline, the former was converted to pivalic acid (**3**) in reasonable yields while **2** gave a mixture of tripentylacetic acid (**4**) and 6-pentyl-5-undecene (**5**).



When **1** was heated alone with $CuCO_3$·$Cu(OH)_2$ at 130–140 °C, no reaction occurred. In the presence of Cu powder and quinoline, though, **1** was decarboxylated in 77% yield to pivalaldehyde. The addition of oxygen to this system led to 38% of **3**, which was increased to 48% by the introduction of Co(OAc)$_2$·4H$_2$O. The evolution of CO_2 varied from 90 to >100%, and qualitative evidence suggested that isobutylene also was formed.

Decarboxylation of **2** did not occur in the presence of Cu powder or a mixture of Cu and Co(OAc)$_2$·4H$_2$O; however, the introduction of O_2 to the latter system caused a rapid evolution of CO_2. Wieland noticed a similar reaction between pyruvic acid and peroxy disulfate in the presence of palladium.[4] The need for oxygen in the oxidative-decarboxylation reaction suggested the presence of free radicals to account for the formation of the olefin **5**, via loss of carbon dioxide from **4**. However, the latter was found to be stable to the oxidative-decarboxylation conditions. Another possible intermediate in this reaction might have been the peroxy acid **6**, which could have



produced **5**, **7**, and **8**. The autoxidation of aldehydes to peroxy acids is well-known and often is catalyzed by metals such as Co^{2+} or Mn^{2+}.[5] Also, the decomposition of peroxy acids, which is catalyzed by metal salts,[6] has produced alcohols, alkanes, alkenes, and other products.[7]

Although the alkane **7** and alcohol **8** were not observed when **2** underwent oxidative decarboxylation in the presence of Cu and Co^{2+}, olefin **5** and alcohol **8** resulted when **2** was caused to react with O_2 in quinoline solution to which only Co(OAc)$_2$ had been added. The ratio of **5** to **8** changed from 1:2 at 25 °C to 1:7 at 100 °C. Pasky has reported that the decarboxylation of **3** in the presence of Co(OAc)$_2$ and O_2 gave, among other products, *tert*-butyl alcohol.[8]

Oxidation of **2** with Cu as the only catalyst afforded **5** plus an unidentified compound. It is conceivable that the presence of Cu in the oxidative decarboxylation inhibited the formation of **8** or caused its rapid dehydration to **5**.

Trimethylpyruvic acid (**1**) was decarboxylated readily to pivalaldehyde by heating with copper powder in quinoline solution. Oxidative decarboxylation with Cu, Co(OAc)$_2$, O_2, and quinoline gave pivalic acid in 68% yield.

Attempts to decarbonylate ethyl 3,3-dipentyl-2-oxooctanoate (**9**) catalytically using powdered glass and Fe,

$$\underset{\mathbf{9}}{(C_5H_{11})_3CCOCO_2C_2H_5} \xrightarrow[160\ °C]{KOH,\ TEG} \underset{\mathbf{10}}{(C_5H_{11})_3CCH(OH)CO_2H}\ (94\%)$$

Pd–BaSO$_4$, or [$(C_6H_5)_3P]_3$RhCl were unsuccessful. The ester **9** was unreactive toward chromic acid, but was converted by alkaline KMnO$_4$ to the keto acid **2**. Alkali at 160 °C in triethylene glycol reduced **9** in 94% yield to the hydroxy acid **10** after acidification. Strong-base reductions of nonenolizable ketones have been carried out previously, as in the preparation of benzhydrol from benzophenone.[9] Two other 2-oxo esters ($R_1R_2R_3CCOCO_2C_2H_5$), where $R_1 = R_2 = R_3 = C_6H_{13}$ and $R_1 = C_4H_9$, $R_2 = C_5H_{11}$, and $R_3 = C_6H_{13}$, were reduced similarly in high yields. The hydroxy acid **10** was treated with periodic acid and was cleaved to

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