with two 50-ml portions of chloroform and the chloroform solutions were combined and washed once with water. Concentration of the chloroform to small volume resulted in the precipitation of a crystalline solid which was recrystallized from methylene chloride-ether to give 1,3-dihydroxypropan-2-one 1,3-dipalmitate (37 g, 84%) as small plates, mp 81-82°.

Anal. Calcd for $C_{35}H_{66}O_5$: C, 74.0; H, 11.7. Found: C, 73.6; H, 11.5.

1,2,3-Trihydroxypropane 1,3-Dipalmitate.—1,3-Dihydroxypropan-2-one 1,3-dipalmitate (10.0 g) was dissolved in a mixture of tetrahydrofuran (250 ml) and benzene (50 ml). Water (15 ml) was slowly added to this solution with stirring and the temperature of the mixture reduced to approximately 5° by external cooling in an ice bath; a milky-white suspension resulted. Sodium borohydride[10] (1.0 g) was added to this heterogeneous mixture; after a further 30 min, the reaction mixture was worked up as described above to give 1,2,3-trihydroxypropane 1,3-dipalmitate (10 g, 99%) as a waxy white solid, mp 67-68°, which was recrystallized from chloroform to give mp 72-73° (lit.[12] mp 72-74°). Thin layer chromatography showed no trace of the 1,2 isomer [tlc system hexane-ethyl acetate (6:1)].

Registry No.—1,3-Dihydroxypropan-2-one 1,3-dioleate, 24472-44-4; 1,3-dihydroxypropan-2-one 1,3-dipalmitate, 24472-45-5.

[12] See ref 9, Vol. 3, p 1267.

Cyclization at the Less Nucleophilic Center of a β-Diketone Dicarbanion through a Dicarbanion-Benzyne Intermediate[1]

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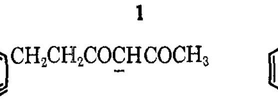
Bunnett and Skorcz[2] have shown that addition of 6-(*o*-chlorophenyl)-2,4-hexanedione (**1**) to excess potassium amide in liquid ammonia affords 1-acetyl-2-tetralone (**2**). A study of the possible intermediates in this cyclization promised to be of particular interest since, although monocarbanion-benzyne **3** appeared to be the intermediate that cyclizes, dicarbanion-benzyne **4** may be the intermediate that cyclizes to give **2**. If so, this would be the first example where the less nucleophilic 3-carbanionic center of a β-diketone dicarbanion reacts preferentially to the much more nucleophilic terminal 1-carbanionic center of such a β-diketone dicarbanion with an electrophilic group.[3]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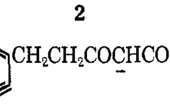
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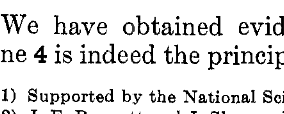
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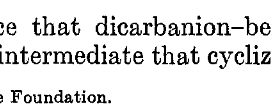
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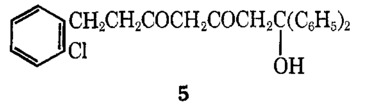
We have obtained evidence that dicarbanion-benzyne **4** is indeed the principal intermediate that cyclizes to give **2**, and that the monocarbanion and dicarbanion are formed at a faster rate than an appreciable amount of benzyne, the electrophilic center for cyclization to **2**. Thus, not only could chloro β-diketone **1** be recovered after conversion to its monocarbanion or dicarbanion salts by direct or inverse addition of 1 or 2 mol equiv of potassium amide in liquid ammonia, but the dicarbanion was also condensed at its terminal position with benzophenone to give carbinol-β-diketone **5**. This mode of intermolecular condensation is characteristic of such 1,3 dicarbanions.[3] The yield of **5** was 41%, which is approximately the same as that reported (42%) earlier for cyclic β-diketone **2**.[2]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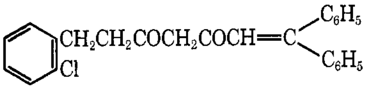
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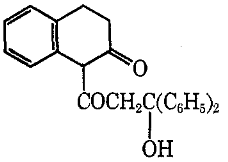
The structure of **5** was supported, not only by analysis and absorption spectra, but also by dehydration with acid to give β-diketo olefin **6** in 30% yield. The structure of **6** was also supported by analysis and absorption spectra.

The conversion of chloro β-diketone **1** to its monocarbanion was accompanied by slight coloration which was probably due to a trace amount of benzyne formation. The related β-diketone, 6-phenyl-2,4-hexanedione, which has no chlorine failed to produce coloration under similar conditions. In both cases the β-diketone was recovered quantitatively upon acidification.

The conversion of chloro β-diketone **1** to its dicarbanion was accompanied by distinct coloration, but only **1** was recovered after neutralization; none of **2** was found.

Cyclic β-diketone **2** was converted to its dipotassio salt and condensed with benzophenone to form carbinol-β-diketone **7** in 73% yield; on prolonged standing, **7** underwent dehydration to give the unsaturated β-diketone which was isolated as the pyrazole derivative.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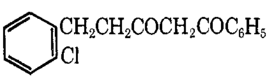
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In contrast to chloro β-diketone **1**, chloro β-diketone **8** failed to afford an isolable product when treated with 2 molar equiv of potassium amide in liquid ammonia followed by 1 molar equiv of benzyl chloride or benzophenone, and, when **8** was treated with excess potassium amide in liquid ammonia, a polymeric material was obtained. The isolation of polymeric material suggests that an intermolecular condensation may have taken precedence over an intramolecular cyclization.

The starting chloro β-diketones **1** and **8** were readily prepared from *o*-chlorobenzyl chloride and the dicarbanions of acetylacetone and benzoylacetone, respectively. Chloro β-diketone **1** can now be made in a

[1] Supported by the National Science Foundation.

[2] J. F. Bunnett and J. Skorcz, *J. Org. Chem.*, **27**, 3836 (1962).

[3] C. R. Hauser and T. M. Harris, *J. Amer. Chem. Soc.*, **80**, 6360 (1958); R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961); T. M. Harris and C. R. Hauser, *ibid.*, **29**, 1391 (1964).

single step which is more convenient than the three-step method formerly employed.[2]

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus in open tubes and are uncorrected. Analyses were performed by M-H-W Laboratories, Garden City, Mich., and by Janssen Pharmaceutica, Beerse, Belgium. Ir spectra were obtained with a Perkin-Elmer Model 137 or 237 spectrometer. Nmr spectra were obtained on a Varian A-60 nuclear magnetic resonance spectrometer, and shifts are reported in parts per million downfield (δ) from an internal tetramethylsilane (TMS) standard.

Preparation of 6-(*o*-Chlorophenyl)-2,4-hexanedione (1).—To a stirred slurry of 0.828 mol of $NaNH_2$[4] in 500 ml of anhydrous NH_3(l), cooled with a Dry Ice-acetone bath and blanketed with nitrogen, was added 43.5 g (0.435 mol) of acetylacetone in 50 ml of dry ether. The resulting mixture was stirred for 20 min, followed by the addition, during 7 min, of 58.2 g (0.362 mol) of *o*-chlorobenzyl chloride in 50 ml of dry ether. At the end of a 2-hr stirring period, the ammonia was evaporated as 250 ml of dry ether was added. Crushed ice (100 g) was then added, followed by 70 ml of concentrated HCl. The layers were separated, and the aqueous layer was extracted with three 100-ml portions of ether. The combined ether extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was distilled to give 59.2 g (73%) of 6-(*o*-chlorophenyl)-2,4-hexanedione (1): bp 143° (3 mm) [lit.[2] bp 120–123° (2 mm)]; ir (neat) 3096, 1667, 1610, 1449, 1318, 1279, 947, 925, 814, and 766 cm^{-1}; nmr (CCl_4) δ 1.90 (s, 3 H, CH_3–), 2.0–3.15 (m, 4 H, –CH_2CH_2–), 5.30 (s, 1 H, C_3 H_{enol}), and 6.75–7.3 (m, 4 H, Ar–H).

The melting point of the pyrazole of 1 prepared in the standard manner was 66–68° (ligroin) [(lit.[2] mp 67–68°)]. Compound 1 also gave a violet ferric chloride test.

Cyclization of 1 to Form 1-Acetyl-2-tetralone (2).—A solution of 0.263 mol of potassium amide in NH_3(l) was added, during 20 min, to a well-stirred solution of 11.23 g (0.05 mol) of 6-(*o*-chlorophenyl)-2,4-hexanedione (1) in 125 ml of dry ether. The mixture was stirred an additional 1 hr and then neutralized with 13.40 g (0.25 mol) of solid NH_4Cl. The ammonia was evaporated as 250 ml of dry ether was added; this was followed by addition of 250 ml of 3 *N* HCl. The layers were separated, and the aqueous layer was extracted with three 100-ml portions of ether. The combined ether layers were dried ($MgSO_4$), filtered, and concentrated; an oil remained. The oil was shown to contain β-diketone 2 by conversion to its copper chelate, mp 228–230° (methanol) (lit.[2] mp 229–230.5°), and its pyrazole (49%), mp 136–138° (ether–ligroin) (lit.[2] 137–138°).

In one case, crystallization of the oil was effected upon prolonged standing (6–9 months), while other procedures failed to induce crystallization. After three recrystallizations from ethanol, 1-acetyl-2-tetralone (2), mp 73–76°, resulted: ir ($CHCl_3$) 1540, 760, and 700 cm^{-1}. This represented a 67% yield of 2.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.54; H, 6.43. Found: C, 76.44; H, 6.39.

The compound gave a violet ferric chloride test, and a pyrazole of 2 which was prepared in the standard manner had mp 136–138° after one recrystallization from ether–ligroin (lit.[2] 137–138°).

Conversion of 1 to Its Monoanion.—To a stirred solution containing 0.0915 mol of KNH_2 in 200 ml of NH_3 (l) and cooled by a Dry Ice–acetone bath and blanketed by nitrogen was added 22.45 g (0.10 mol) of 6-(*o*-chlorophenyl)-2,4-hexanedione (1) in 75 ml of dry ether. Some red coloration was noted.[5] The cooling was discontinued, and the mixture was stirred an additional 20 min. The ammonia was evaporated as 250 ml of dry ether was added, and *ca.* 100 g of crushed ice was slowly added, followed by 30 ml of cold concentrated HCl. The layers were separated, and the aqueous layer was extracted with two 100-ml portions of ether; the combined ether layers were dried ($MgSO_4$). After filtration, the solvent was evaporated to give an essentially quantitative (>95%) recovery of starting material. Similar results were observed when the solution of base was added to a cooled (−78°) solution of 1 from an inverse addition flask, the difference being less coloration.

Conversion of 1 to Its Dianion.—The procedure for conversion of 1 to its dianion was the same as previously described for the conversion of 1 to its monoanion, except that the KNH_2 was prepared from twice the amount of potassium, 7.13 g (0.183 g-atom). Only starting material 1 was found in the final residue.

Condensation of Dianion of 1 with Benzophenone.—Potassium amide was prepared in a 250-ml inverse addition flask from 2.15 g (0.055 g-atom) of potassium in 125 ml of anhydrous NH_3(l). The base was then added to a well-stirred solution of 5.61 g (0.025 mol) of 6-(*o*-chlorophenyl)-2,4-hexanedione (1) in 25 ml of dry ether. Upon completion of the addition a red-brown color resulted, and after stirring for 20 min, 4.55 g (0.025 mol) of benzophenone dissolved in 20 ml of dry ether was added; the mixture was stirred for 3 hr. The mixture was then inversely neutralized by pouring the reaction mixture into a large flask containing an excess of NH_4Cl dissolved in 100 ml of anhydrous NH_3(l). The ammonia was replaced by an equal volume of dry ether, and 200 ml of a 10% HCl soln was added. After separation of the layers, the aqueous layer was further extracted with three 75-ml portions of ether and the combined ether extracts were dried ($MgSO_4$). After filtration and evaporation of the solvent, 20–30 ml of absolute ethanol was added, and upon shaking a solid crystallized. After recrystallization from absolute ethanol, 4.00 g (41%) of 7-(*o*-chlorophenyl)-1,1-diphenyl-3,5-heptanedione-1-ol (5), mp 92–94°, was obtained: ir ($CHCl_3$) 3400, 1600, 1160, 755, 700 cm^{-1}; nmr ($CDCl_3$) δ 2.48–3.13 (m, 4 H, –CH_2CH_2–), 3.22 (s, 2 H, –CH_2–), 5.38 (s, 1 H, C_4 H_{enol}), and 7.00–7.50 (m, 14 H, Ar–H).

Anal. Calcd for $C_{25}H_{23}ClO_3$: C, 73.79; H, 5.70; Cl, 8.71. Found: C, 73.85; H, 5.67; Cl, 8.53.

Dehydration of 5 to Give β-Diketone–Olefin 6.—To a 1.0-g (0.00246 mol) sample 5 was added 10 ml of acetic acid. The mixture was stirred and cooled in an ice bath, while 1.0 ml of concentrated H_2SO_4 was added dropwise. The ice bath was removed, and the mixture was allowed to warm to room temperature. After 30 min, complete solution was effected, and the mixture was poured into a stirred ice–water mixture. The paste which resulted was removed by filtration and allowed to stand overnight. The residue was taken up in absolute ethanol and filtered. Crystallization resulted after standing at 0° for several days. The crude product was recrystallized from ethanol to give 0.28 g (30%) of 7-(*o*-chlorophenyl)-1,1-diphenyl-1-heptene-3,5-dione (6): mp 72–73.5°; ir ($CHCl_3$) 3077, 2433, 1618–1563, and 930 cm^{-1}; nmr ($CHCl_3$) δ 2.30–2.99 (m, 4 H, –CH_2CH_2–), 5.25 (s, 1 H, C_4 H_{enol}), 6.38 (s, 1 H, C_2 H), and 7.09–7.50 (m, 14 H, Ar–H).

Anal. Calcd for $C_{25}H_{21}ClO_2$: C, 77.21; H, 5.44; Cl, 9.12. Found: C, 77.12; H, 5.44; Cl, 9.12.

Preparation of the Dianion of 1-Acetyl-2-tetralone (2) and Condensation with Benzophenone to Form 7.—A 0.0478-mol solution of $NaNH_2$ in 500 ml of anhydrous NH_3(l) was prepared in a 1-l, inverse addition flask. This slurry was added to a stirred solution of 4.10 g (0.0218 mol) of 1-acetyl-2-tetralone (2) in 50 ml of dry ether. After 20 min, 3.96 g (0.0218 mol) of benzophenone was added, and the mixture was stirred an additional 20 min. The mixture was then inversely neutralized as previously described for 5, and the ammonia was replaced by 250 ml of dry ether. This was followed by the addition of 250 ml of water; the layers were separated. The aqueous layer was extracted with two 50-ml portions of ether, the combined ether extracts were dried (Na_2SO_4), filtered, and concentrated, and the residue was distilled to give 7 as a red liquid (73%), bp 161–165° (12 mm).

Anal. Calcd for $C_{25}H_{22}O_3$: C, 81.05; H, 5.99. Found: C, 81.05; H, 5.92.

Carbinol–β-diketone 11 was found to undergo dehydration upon prolonged standing (1 year). An ir spectra of the resulting oil lacked hydroxyl absorption in the region 3300–3500 cm^{-1}, and, when the oil was treated with an ethanolic solution of hydrazine, the pyrazole of 7, mp 158–160° (methanol), was obtained in good yield.

Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.78. Found: C, 86.11; H, 5.84.

Preparation of 5-(*o*-Chlorophenyl)-1-phenyl-1,3-pentanedione (8).—5-(*o*-Chlorophenyl)-1-phenyl-1,3-pentanedione (8), bp 173° (0.07 mm), was prepared in 73% yield from reaction of 29.1 g (0.180 mol) of *o*-chlorobenzyl chloride with the dicarbanion of benzoylacetone prepared from reaction of 34.74 g (0.213 mol) of

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[4] C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. React.*, **8**, 122 (1954).

[5] In a control experiment, 0.10 mol of 6-phenyl-2,4-hexanedione was added to a solution containing 0.0915 mol of KNH_2 in NH_3 (l) and no coloration was observed. 6-Phenyl-2,4-hexanedione was recovered nearly quantitatively after neutralization.

benzoylacetone and 0.430 mol of $NaNH_2$ in NH_3 (l). This procedure is analogous to that described for chloro β-diketone **1**.

Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.22; Cl, 12.36. Found: C, 71.11; H, 5.33; Cl, 12.26.

The absorption spectra for **8** contained the following: ir 3106, 2950, 1618, 1055, 756, and 694 cm^{-1}; nmr δ 2.40–3.21 (m, 4 H, $-CH_2CH_2-$), 6.0 (s, 1 H, C_2 H_{enol}), and 6.9–7.8 (m, 9 H, Ar-H).

The pyrazole of **8** was prepared in the standard manner and was recrystallized from methanol, mp 99–101°.

Anal. Calcd for $C_{17}H_{15}ClN_2$: C, 72.17; H, 5.34; Cl, 12.53; N, 9.95. Found: C, 72.43; H, 5.45; Cl, 12.76; N, 9.86.

Registry No.—**2**, 24118-62-5; **5**, 24118-63-6; **6**, 24118-64-7; **7**, 24118-65-8; **8**, 24118-66-9; pyrazole of **7**, 24110-98-3; pyrazole of **8**, 24118-71-6.

Coupling of Carbanions. Formation of Succinic Acid Derivatives

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Alkali metal diphenylmethides have previously been shown to react with certain polyhalides by a displacement on halogen to give the dehalogenation product from the halide and a benzhydryl halide.[1] While the halogenated compound has been isolated from the reaction with carbon tetrachloride,[2] under the usual reaction conditions (addition of halide to anion) it reacts further with the anion to give tetraphenylethane (Scheme I).

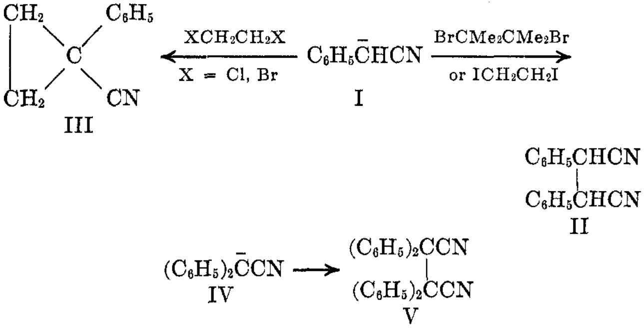
SCHEME I

$$(C_6H_5)_2CH_2 \xrightarrow{KNH_2} (C_6H_5)_2\bar{C}H \xrightarrow{X\text{-}C\text{-}C\text{-}X} (C_6H_5)_2CHX \xrightarrow{(C_6H_5)_2\bar{C}H} (C_6H_5)_2CHCH(C_6H_5)_2$$

Several such reactions to give halogen compounds from carbanions have been reported.[3] We now report the synthetic utility of this reaction in the coupling of anions from nitriles and esters to give succinic acid derivatives.

Phenylacetonitrile and Diphenylacetonitrile.—Potassio- and sodiophenylacetonitrile (I), prepared from the nitrile and potassium or sodium amide, was previously shown to undergo generally twofold alkylation with alkyl halides.[4] Thus reaction with ethylene chloride gives equal amounts of 1-phenylcyclopropanecarbonitrile (III) and phenylacetonitrile. It was previously shown that ethylene iodide and ethylene bromide react with potassium diphenylmethide by displacement on halogen to give the dimeric product (tetraphenylethane), while ethylene chloride undergoes twofold alkylation to give 1,1,4,4-tetraphenylbutane.[1] In agreement with this, ethylene iodide reacts with I to give the dimer, 2,3-diphenylsuccinonitrile (II), but ethylene bromide *does not* effect dimerization, and, like ethylene chloride, undergoes twofold alkylation (see Scheme II). In none of the cases studied did 2,3-dibromo-2,3-dimethylbutane, a ditertiary halide, undergo alkylation.

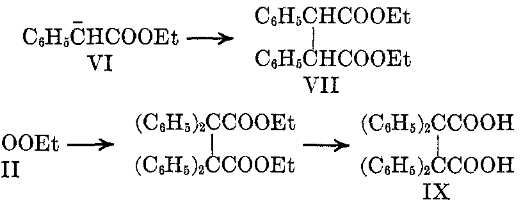
SCHEME II



The yields of II in the dimerization reactions were difficult to reproduce, apparently because this nitrile can undergo dehydrocyanation with potassium amide or other anion.[5] Such a dehydrocyanation is not possible with dimer V, which was obtained from potassiodiphenylacetonitrile (IV) in 85% yield even when the direct addition procedure was employed.

Ethyl Phenylacetate and Ethyl Diphenylacetate.—The potassium derivatives of these esters were readily prepared from the esters and ammoniacal potassium amide. The product from the latter ester, diethyl tetraphenylsuccinate, was not obtained crystalline and was identified by hydrolysis to the acid (see Scheme III). The yields of these reactions are summarized in Table I.

SCHEME III



$$\underset{\text{VI}}{C_6H_5\bar{C}HCOOEt} \longrightarrow \underset{\text{VII}}{\begin{array}{c} C_6H_5CHCOOEt \\ | \\ C_6H_5CHCOOEt \end{array}}$$

$$\underset{\text{VIII}}{(C_6H_5)_2\bar{C}COOEt} \longrightarrow \begin{array}{c} (C_6H_5)_2CCOOEt \\ | \\ (C_6H_5)_2CCOOEt \end{array} \longrightarrow \underset{\text{IX}}{\begin{array}{c} (C_6H_5)_2CCOOH \\ | \\ (C_6H_5)_2CCOOH \end{array}}$$

TABLE I

DIMERIZATION OF ANIONS OF ESTERS AND NITRILES

Anion (mol)	Halide (mol)	Product (yield, %)
I (0.05)	$BrCMe_2CMe_2Br$ (0.025)	II (16, *meso;* 37, *dl*) CN^- (22)
I (0.05)	$BrCMe_2CMe_2Br$ (0.025)[a]	II (6, *meso;* 63, *dl*)
I (0.1)	$BrCH_2CH_2Br$ (0.05)	Phenylacetonitrile (92) III (91)
I (0.05)	ICH_2CH_2I (0.025)	II (33)
I (0.1)	Cl_3CCCl_3 (0.05)	II (5, *meso;* 45, *dl*)
IV (0.05)	$BrCMe_2CMe_2Br$ (0.025)	V (85)
VI (0.08)	$BrCMe_2CMe_2Br$ (0.04)	VII (36)
VI (0.1)	Cl_3CCCl_3 (0.05)	VII (54, *meso;* 24, *dl*)
VIII (0.05)	$BrCMe_2CMe_2Br$ (0.025)	IX (54)

[a] The inverse addition procedure was employed.

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(1) W. G. Kofron and C. R. Hauser, *J. Amer. Chem. Soc.*, **90**, 4126 (1968).

(2) W. G. Kofron and C. R. Hauser, *J. Org. Chem.*, **28**, 577 (1963).

(3) F. H. Rash, S. Boatman, and C. R. Hauser, *J. Org. Chem.*, **32**, 372 (1967); R. L. Gay, T. F. Crimmins, and C. R. Hauser, *Chem. Ind.* (London), 1635 (1966).

(4) C. R. Hauser and W. R. Brasen, *J. Amer. Chem. Soc.*, **78**, 494 (1956).

(5) For related dehydrocyanations, see C. R. Hauser and W. R. Brasen, *ibid.*, **78**, 82 (1956).