The **2,4-dinitrophenylhydrazone** was prepared in the usual manner, washed with methanol and water, and dried over P_2O_5 at 55° for 6 hr. The crude material melted at 271–272°, and recrystallization from 2-propanol raised the melting point to 297°.

Anal. Calcd. for $C_{28}H_{20}N_4O_4$: C, 70.58; H, 4.23. Found: C, 70.34; H, 4.03.

Mixture melting points with the 2,4-DNP derivatives of the solid ketone prepared by method B, and from 2-lithium triptycene and acetonitrile (method C), respectively, showed no depression. The infrared spectra of the respective 2,4-DNP derivatives [3290 (NH), 2930 (s) (triptycene >CH), 1620 (s) (—C═N—) (s), 1595 and 1345 (s) (NO_2), 832 (s) (1,2,4-trisubstituted benzene), and 740 cm.$^{-1}$ (s) (*ortho*-disubstituted benzene)] were superimposable.

Likewise, the 4-nitrophenylhydrazone of the ketone was prepared and recrystallized from dilute ethanol; m.p. 269–270°. A mixture melting point with the 4-nitrophenylhydrazone from C was undepressed, and the infrared spectra of the two derivatives [3325 (w) (NH), 2930 (s) (triptycene >CH), 1610 (—C═N—), 1595 and 1335 (s) (NO_2), and 745 cm.$^{-1}$ (s) (*ortho*-disubstituted benzene)] were superimposable.

Anal. Calcd. for $C_{28}H_{21}N_3O_2$: C, 77.94; H, 4.91. Found: C, 78.11; H, 5.20.

B.—To 6.35 g. (0.025 mole) of triptycene in 60 ml. of carbon disulfide was added 6.67 g. (0.05 mole) of anhydrous $AlCl_3$. The mixture turned orange, then brown. With stirring, 2.55 ml. (0.025 mole) of acetic anhydride was added dropwise at a rate so as to maintain reflux (25 min.). After refluxing for 20 min. the mixture was worked up with ice–hydrochloric acid as under A and extracted into methylene chloride. The pale yellow solid was recrystallized from cyclohexane to yield 4 g. of solid, m.p. 172–183°. Thin layer chromatography (silica gel G, 8:2 methylcyclohexane–ethyl acetate, iodine vapor visualization) gave two spots, R_f 0.15 and 0.31 besides a faint spot at R_f 0.58 (triptycene). Column chromatography of 350 mg. over Florisil using methylcyclohexane–ethyl acetate (8:2) furnished two ketonic products. Both had infrared bands at 2935 (w) (>CH), 1675 (aryl conjugated ketone), and 745 cm.$^{-1}$ (*ortho*-disubstituted benzene). On standing at 4° for 1 week the material with R_f 0.31 crystallized, m.p. 201–202°; it showed no melting point depression with the ketone obtained by method A.

The oily substance (R_f 0.15) yielded an orange 2,4-DNP derivative, R_f 0.13, m.p. 298° (from isopropyl alcohol). A mixture melting point with the 2,4-DNP derivative (m.p. 297°) of the ketone from method A (R_f 0.31 in the same solvent systems) was depressed (m.p. 275–285°). The infrared spectra of the two 2,4-DNP derivatives were very similar, but the small amount of this oily ketone was not investigated further.

C.—To 0.35 g. (0.05 g.-atom) of lithium in 20 ml. of ether under a nitrogen atmosphere at −10° was added 2.45 ml. (0.025 mole) of *n*-butyl bromide in 75 ml. of ether. After stirring at −10° for 2 hr., 3.33 g. (0.01 mole) of 2-bromotriptycene[2] was added in one portion. The mixture was stirred further at 0° for 3 hr., 24 ml. of acetonitrile was added, and stirring was continued at 26° for 10 hr. Decomposition of the mixture with a saturated solution of NH_4Cl, extraction with ether, drying (Na_2SO_4), and removal of the ether furnished a solid which was recrystallized from dilute ethanol. A portion (1 g.) of 2-bromotriptycene crystallized first. The mother liquors on concentration gave 800 mg. (27%) of crude ketone; infrared bands at 1675 (C═O), 2930 (triptycene), and 740 and 625 cm.$^{-1}$ (aromatic). This material still contained some 2-bromotriptycene as shown by thin layer chromatography on silica gel G in methylcyclohexane–ethyl acetate (8:2). The bromo compound on visualization with iodine vapor showed up as a pink spot while the methyl ketone appeared as a yellow spot. Separation of the ketone was effected best as the 2,4-DNP derivative which crystallized from isopropyl alcohol and after drying over P_2O_5 for 6 hr. melted at 297°. A sample of this derivative did not depress the melting point of the corresponding derivative prepared by method A. The infrared spectra of the two derivatives were superimposable. Likewise, the *p*-nitrophenylhydrazone melted at 270–271° (from dilute ethanol); the mixture melting point with the corresponding derivative from method A was 270–271°. The two infrared spectra were superimposable.

1-Nitrotriptycene.—To a stirred refluxing mixture of 17.8 g. (0.075 mole) of 98% anthracene and 150 ml. of dry acetonitrile were added simultaneously over a 4-hr. period from separate dropping funnels 13.65 g. (0.075 mole) of 6-nitroanthranilic acid in 200 ml. of acetonitrile and 21 ml. of *n*-amyl nitrite in 75 ml. of acetonitrile. The mixture was refluxed for 1 hr. after completion of addition and then the solvent was distilled and replaced by 200 ml. of xylene. Maleic anhydride (12 g.) was added, and the mixture was refluxed for 45 min. It was cooled and diluted with 300 ml. of benzene. This mixture was extracted three times with 100 ml. of 10% NaOH, the benzene extract was dried ($NaSO_4$), and the solvent was removed. The remaining solid was chromatographed on alumina moistened with petroleum ether (b.p. 30–60°) and then diluted with 3000 ml. of petroleum ether followed by 2000 ml. of benzene. A white solid which crystallized from the petroleum ether eluate on standing was filtered off, washed with methanol, and dried; m.p. 221–221.5°, yield 1.27 g. (5.6%).

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38. Found: C, 80.05; H, 4.31.

The infrared spectrum contained bands at 2930 (w) (>C–H, characteristic of triptycene), 1530 and 1355 (s) (NO_2), and 735 cm.$^{-1}$ (*ortho*-disubstituted benzene).

2-Nitrotriptycene was prepared essentially as was the 1-nitro isomer, starting with 71.4 g. (0.4 mole) of anthracene, 35.1 g. (0.3 mole) of *n*-amyl nitrite, 36.4 g. (0.2 mole) of 4-nitroanthranilic acid, and 49 g. (0.5 mole) of maleic anhydride. Work-up by continuous extraction with methylene chloride, and purification by chromatography over alumina with benzene, yielded 8.4 g. (14%) of a yellow solid, m.p. 269–270°. A small amount of contaminating anthraquinone was removed by sublimation at 140° (0.075 mm.). Recrystallization from methanol gave the pure material, m.p. 270–271°, yield 3.9 g. (6.5%).

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38. Found: C, 80.27; H, 4.41.

The infrared spectrum showed bands at 2930 (w) (>CH), 1520 and 1340 (s) (NO_2), and 745 cm.$^{-1}$ (*ortho*-disubstituted benzene, strong); n.m.r. spectrum showed a mirror image quintet centered at δ 7.10 (unsubstituted ring protons), doublets at 8.12, and one centered at 7.88 with J_{ab} of 2 c.p.s. (in the region of *ortho* protons, apparently *meta* splitting), singlet at 7.52 (probably the proton *meta* to NO_2), doublet at 5.7 (split of 3 c.p.s., probably due to a chemical shift), ratio of protons 1:1:1:4:4:2.

Synthesis of 3-Quinuclidinol by the Cyclodehydration of (4-Piperidyl)-1,2-ethanediol

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Received December 22, 1964

The fact that 4-β-hydroxyethylpiperidine was cyclized to quinuclidine[2] on activated alumina prompted us to carry out this type of reaction on the model (4-piperidyl)-1,2-ethanediol in hope of obtaining a new synthetic route to an azabicyclic alcohol.

The reaction scheme that was followed is depicted on p. 1332. Thus, 4-vinylpyridine (I) was oxidized by cold aqueous permanganate to (4-pyridyl)-1,2-ethanediol (II).[3] The glycol was best isolated as its hydrochloride, which was hydrogenated to the corresponding piperidyl glycol (III) hydrochloride. About 20% of 4-β-hydroxyethylpiperidine was also formed as a hydrogenolysis by-product. The glycol hydrochloride

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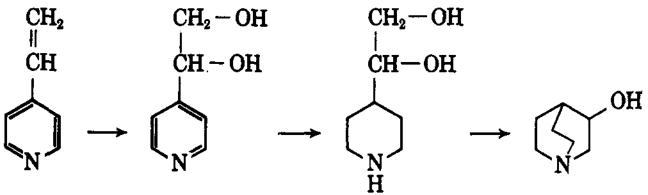
(1) (a) Edgewood Arsenal; (b) Temple University; (c) Deceased.

(2) S. Leonard and S. Elkin, *J. Org. Chem.*, **27**, 4635 (1962).

(3) This glycol has not been described previously, although it has been claimed [F. E. Cislak, U. S. Patent 2,743,277 (1956)] in unspecified yield from the reaction of the N-oxide of 4-(β-hydroxyethyl)pyridine with acetic anhydride. However, this reaction could not be performed successfully in the Chemical Research and Development Laboratories, nor in those of one of our contractors.



I II III IV

was converted to the free base III, which gave 3-quinuclidinol (IV) on treatment with activated alumina at 300°. Depending upon the conditions and catalyst used, varying amounts of an unknown alcohol, possibly 1-azabicyclo[2.2.1]heptyl-7-carbinol, plus several other low-boiling (presumably olefinic, not further investigated) products were also formed, as detected by gas–liquid chromatographic analysis.

Cyclodehydrations of amino alcohols, although apparently only infrequently reported,[4] have been carried out under a variety of conditions. Of the various catalysts (aluminum, barium, calcium, strontium, and magnesium oxides) examined in our study, alumina proved to be the most effective. Interestingly enough, however, of five commercial aluminas screened in this study, only the Woelm neutral or (better) basic grade produced a satisfactory yield of 3-quinuclidinol.

The simplicity and the results of our cyclodehydration study suggest that the method may be of synthetic utility as a general route to other azabicyclic alcohols. A related reductive cyclization of amino alcohols on Raney nickel has been used for the synthesis of azabicyclic fused ring systems.[5] This reaction, however, although formally a cyclodehydration, apparently proceeds by a mechanism that precludes the formation of bridged ring systems.[5,6]

Experimental

Infrared spectra were recorded in dilute carbon tetrachloride in 1- or 2-cm. quartz cells on a Perkin-Elmer Model 237B grating spectrophotometer. Neutralization equivalents were measured electrometrically, using a Beckman Model H-2 pH meter. Gas–liquid chromatographic (g.l.c.) retention times are given for a 10 ft. × 0.25 in. column of Carbowax 20 M (15%) on Gas-Chrom P (60/80) at 120 ml./min. (He) at the indicated column temperatures.

(4-Pyridyl)-1,2-ethanediol (II).—Potassium permanganate (52.6 g., 0.33 mole) in 1.5 l. of water was added dropwise, over a 2-hr. period, to 4-vinylpyridine (52.5 g., 0.5 mole) in 450 ml. of water. During the addition, the reaction mixture was stirred vigorously and cooled in an external bath to maintain a reaction temperature of 2–4°. After the addition, the mixture was allowed to stand overnight at ambient temperature. The manganese dioxide was filtered (glass-sintered funnel, F) and washed several times with hot water (50 ml. per wash). The washings and filtrate were combined and extracted with three 500-ml. portions of ether. On evaporation of the combined ether washings, 7 g. of vinylpyridine was recovered. The aqueous solution was acidified (pH 1) with concentrated hydrochloric acid and the resultant solution was evaporated to dryness under reduced pressure. Methanol (200 ml.) was added to the light yellow solid residue and a potassium hydroxide–methanol solution (13%) was added to the stirred suspension until pH 9 was obtained. The mixture was filtered and the potassium chloride filter cake was washed several times with acetone. The acetone washings were combined with the methanol filtrate and the solvents were removed under reduced pressure. The dark, viscous, oily residue was dissolved in warm acetone (600 ml.) and filtered from the residual potassium chloride. After removing the acetone on a steam bath, the pink residue was recrystallized several times by dissolving the product in hot acetone–benzene (1:1), decolorizing with charcoal, filtering, and concentrating the filtrate to approximately one-half of its original volume. The solution was seeded (see below) and allowed to cool slowly to ambient temperature, with occasional swirling. In this way, the pure product (II), 21.2 g. (35%, based on recovered starting material), m.p. 71–73° dec., was obtained.

Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; O, 23.00; neut. equiv., 139.2. Found: C, 60.3; H, 6.4; O, 22.8; neut. equiv., 140 (pK_a 4.90 at 0.015 ionic strength).

Its infrared spectrum (dilute solution) showed a single, unresolved, broad (3550–3675 cm.$^{-1}$ at its base), O–H stretching band with a maximum at 3625 cm.$^{-1}$.

In earlier work, attempts to distil the glycol led to extensive decomposition. However, a small quantity of the product distilled as an extremely viscous yellow oil, b.p. 142–145° ($<1\ \mu$). The distillate, which gave a correct analysis, crystallized on standing at ambient temperature to form a waxy solid. Recrystallization from ether–acetone (1:1) gave a product, m.p. 70–72°, which was used as the seed crystals mentioned above.

(4-Pyridyl)-1,2-ethanediol Hydrochloride.—The acidified (pH 1) aqueous solution obtained from the oxidation (as above) of 52 g. of 4-vinylpyridine was concentrated, under reduced pressure, to about 100 ml. The potassium chloride which precipitated was filtered and the filtrate was allowed to evaporate spontaneously to dryness. The solid residue (50 g.) that contained some potassium chloride was recrystallized from ethanol to give 47 g. (0.27 mole, 54%) of the hydrochloride of II, m.p. 126–130°. Recrystallization from isopropyl alcohol gave a product, m.p. 131–133°, neut. equiv. 179 (calcd. 175.6).

(4-Piperidyl)-1,2-ethanediol (III).—The pyridyl glycol (II) hydrochloride (18.3 g., 0.104 mole) in 15 ml. of 1 *N* hydrochloric acid and 30 ml. of ethanol was reduced in a Parr hydrogenator at 66 p.s.i.g. over platinum dioxide (0.5 g.) at ambient temperature. After 4 hr., hydrogen uptake had ceased. The fact that a 20% excess of hydrogen had been absorbed indicated that some hydrogenolysis (see below) had probably occurred. The mixture was filtered to remove the catalyst, then concentrated, under reduced pressure, on the steam bath. The viscous residue was dissolved in 100 ml. of boiling ethanol. On standing at room temperature there was obtained 12 g. (64%) of (4-piperidyl)-1,2-ethanediol hydrochloride (III HCl), m.p. 150–152°. An analytical sample, m.p. 155–156°, was obtained by recrystallization from isopropyl alcohol.

Anal. Calcd. for $C_7H_{16}ClNO_2$: C, 46.28; H, 8.88; O, 17.61; neut. equiv., 181.7. Found: C, 46.2; H, 8.8; O, 17.6; neut. equiv., 178 (pK_a 10.85 at 0.20 ionic strength).

The hydrogenolysis product was isolated from another run. Thus, the total crude product (II HCl) obtained as a solid residue from the oxidation of 52.5 g. of 4-vinylpyridine (as above) was hydrogenated in 90 ml. of ethanol over 1 g. of platinum dioxide. The catalyst was filtered; the filtrate was concentrated under reduced pressure and then treated with an excess of sodium methoxide in methanol. After filtering the sodium chloride, the solvent was removed and the residue was distilled at 0.050 mm. to give fraction 1, 4.7 g., b.p. 108°; fraction 2, 1.4 g., b.p. 108–125°; and fraction 3, 20.0 g., b.p. 125–130°, a viscous, colorless oil, $n^{25}\text{D}$ 1.5155. Fraction 3 was shown (g.l.c., 245°) to be essentially pure piperidyl glycol III (22.8 min.), contaminated by a few percent of 4-β-hydroxyethylpiperidine (4.4 min.).

The infrared spectrum of the piperidyl glycol (III) in dilute solution shows a doublet for the O–H stretching band: 3635 (free OH) and 3590 cm.$^{-1}$ (intramolecularly bonded -OH· · ·OH).

G.l.c. analysis indicated fractions 1 and 2 were essentially pure 4-β-hydroxyethylpiperidine, the infrared spectrum (film) of which was identical to that of an authentic sample.[7] The 4-β-hydroxyethylpiperidine could not be efficiently removed by redistillation of the glycol. Indeed, redistillation resulted in the formation of a few per cent of a new impurity, identified as 3-quinuclidinol (4.1 min., 245°) by g.l.c. analysis. The latter is apparently formed by thermal cyclodehydration of the glycol.

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[4] (a) Yu. K. Yur'ev, G. P. Mikhailovskii, and S. Z. Shapiro, *Zh. Obshch Khim.*, **19**, 2217 (1949); (b) L. J. Kitchen and C. B. Pollard, *J. Am. Chem. Soc.*, **69**, 854 (1947); (c) C. Glacet and T. M. Deram, *Compt. rend.*, **239**, 889 (1954); (d) T. Ishiguro, E. Kitamura, M. Matsumura, and H. Ogawa, *J. Pharm. Soc. Japan*, **75**, 1370 (1955); (e) A. S. Sadykov, M. Karimov, and Kh. A. Aslanov, *Zh. Obshch. Khim.*, **33**, 3414 (1963).

[5] M. G. Reinecke and L. R. Kray, *J. Org. Chem.*, **29**, 1736 (1964).

[6] L. T. Plante, W. G. Lloyd, C. E. Schilling, and L. B. Clapp, *ibid.*, **21**, 82 (1956).

[7] Kindly furnished by Reilly Tar and Chemical Corp.

The hydrogenolysis product[8] is best removed from the glycol, therefore, by recrystallization of the hydrochloride salt before liberation of the free base.

Fractions 1 and 2 were combined, treated (0.17 g.) with 2 ml. of methyl iodide in 4 ml. of isopropyl alcohol, warmed on the steam bath, then allowed to cool to room temperature. The solid thus obtained was recrystallized from isopropyl alcohol to give 1,1-dimethyl-4-(2-hydroxyethyl)piperidinium iodide, m.p. 169.5–170.5°.

Anal. Calcd. for $C_9H_{20}INO$: C, 37.90, H, 7.07. Found: C, 37.7; H, 6.9.

3-Quinuclidinol (IV).—A 13-mm.-diameter glass reactor tube was packed with 10 g. of Woelm basic alumina (Alupharm Chemicals, New Orleans, La.), then heated to 300° in a muffle furnace, and maintained at that temperature while a stream of nitrogen was passed through at a rate of about 30 ml./min. Then, the piperidyl glycol III, 4.8 g. (0.033 mole), in an open-end glass carrier tube (80 × 10 mm.), was inserted into the reactor tube just to the point where the latter entered the muffle furnace. The apparatus was inclined about 10° downward from the horizontal such that the glycol, when warmed to about 100° with a heating tape, slowly flowed down onto the alumina surface. Product formation was observed a few minutes later, and the reaction appeared to have been completed in less than 1 hr. The product, which had condensed as a viscous liquid in the cold portion of the exit tube, was dissolved in 23 ml. of methanol. Titration of a 1-ml. aliquot of this solution indicated a 43% yield (total base) was obtained. G.l.c. analysis (240°) indicated a composition of about 80% quinuclidinol (4.1 min.), about 15% of an unidentified alcohol (from infrared, possibly 1-azabicyclo[2.2.1]heptyl-7-carbinol) (3.7 min.), and a few per cent of a second unknown product (2.9 min.). (In other runs, minor amounts of several other lower boiling products were also observed.) The remaining 22 ml. of the methanol solution was mixed with about 30 ml. of benzene (to azeotrope the water) and the solvents were removed under reduced pressure. The residue was recycled through another hot column, which now contained 3 g. of Woelm neutral alumina at 190–200°. The first condensate (liquid) was collected in a short collector tube (10-mm. diameter), which had been inserted into the column at its point of exit from the furnace. This forerun was removed, and the product then condensed as a solid and was washed out with methanol. The methanol was evaporated, and heptane was added and evaporated to remove residual methanol. The solid that had precipitated was collected to give 1.34 g. (0.0105 mole, 32%) of 3-quinuclidinol, m.p. 205–210°. The product thus obtained from another run melted at 218–220° (lit.[9] m.p. 221–223°) after trituration with hot heptane, and gave an infrared spectrum (in potassium bromide) which was identical with that of authentic[9] 3-quinuclidinol.

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[8] Although not investigated, this side reaction possibly could be prevented by decreasing the proportion of the reduction catalyst and the acidity of the medium, or by changing to an acetic acid solution.

[9] L. H. Sternbach and S. Kaiser, *J. Am. Chem. Soc.*, **74**, 2215 (1952).

Organometallic Chemistry. IX. The Metalation of Benzocyclobutene with Sodium and Potassium Alkyls[1,2]

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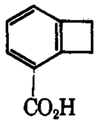
Received December 21, 1964

About five years ago, a reaction between butylpotassium and benzocyclobutene (1) was carried out as part of a projected study of the effect of strain on hydrocarbon acidity.[3] Although this study, which was also to include indane and tetralin, did not materialize, the initial observations with benzocyclobutene, incomplete as they are, seem to be of sufficient interest for publication in this form.

When a freshly prepared suspension of butylpotassium in pentane was stirred for 3.5 hr. with 1 equiv. of **1**, followed by treatment with an excess of Dry Ice, only a single acid was obtained in purified form, and this in low yield. An identical acid was later obtained in somewhat higher yield as the sole product (other than caproic acid) after carbonation of a mixture of amylsodium with 1 equiv. of **1** which had been allowed to react for 1 week. This acid had m.p. 188–191° (sublimes) and therefore was not the known α-carboxylic acid which was reported[4] to melt at 76.5°. That this acid was isomeric was evident from the microanalytical results as well as the neutral equivalent, and the conclusion was reached that this material was either the 3-carboxylic acid (**2**) or the 4-isomer (**3**). Consistent with this conclusion was the carbonyl absorption in the infrared at 1675 cm.$^{-1}$ (KBr) typical for an aromatic acid. Diazomethylation provided the methyl ester, m.p. 50.5–51° (ν_{max}^{KBr} 1727 cm.$^{-1}$), whose ultraviolet spectrum ruled out the possibility that it was a styrene derivative. In view of the fact that metalation of alkyl aromatic substrates usually occurs *meta* or *para* to the alkyl substituent,[5] structure **3** was considered more likely to be correct. This tentative assignment was made in spite of the presence in the infrared spectra of the acid and its methyl ester (**2a**) of strong bands (779 and 749 cm.$^{-1}$ in the acid, 776 and 729 cm.$^{-1}$ in the ester) attributed to out-of-plane bending vibrations of aromatic CH groups and associated with a 1,2,3-substitution pattern.[6] Reluctance to weigh this evidence heavily was conditioned by the lack of available infrared data on substances of this sort and by the observation that the spectra of methyl 2,3-dimethylbenzoate and 3,4-dimethylbenzoate were not so neatly classified as might have been anticipated. Thus, while the 2,3-isomer displayed a pair of strong bands (763 and 747 cm.$^{-1}$) consistent with the normal correlation,[6] the 3,4-isomer showed only a single strong band in this region (760 cm.$^{-1}$) and even this one occurred at lower frequency than expected.[6]



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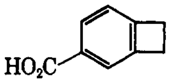

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An unambiguous structural assignment was eventually made after comparison of the n.m.r. spectrum of **2a** with those of the two isomeric dimethylbenzoate esters mentioned above. In the accompanying figure are shown tracings of the aromatic proton patterns observed in the spectra of these compounds, and it becomes clear on inspection that the acid resulting from

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[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support of this research.

[2] Paper VIII: R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3241 (1964).

[3] The potential synthetic utility of the reaction was, of course, not to be overlooked.

[4] M. P. Cava, R. L. Litle, and D. R. Napier, *J. Am. Chem. Soc.*, **80** 2257 (1958).

[5] R. A. Benkeser, D. J. Foster, D. M. Sauve, and J. F. Nobis, *Chem. Rev.*, **57**, 867 (1957).

[6] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 27.