Lithium Aluminum Hydride Reduction of 1-Methyl-*trans*-4-*t*-butylcyclohexene Oxide (1).—Complete reduction of epoxide 1 was obtained using the same conditions employed for epoxide 2. Analysis of the product by g.c. (Polyglycol E-4000) showed three peaks **9** (32%), **10** (60%), and **11** (8%) which were eluted in that order. The retention time of peak **9** corresponded to that of an authentic sample, and the infrared spectra were identical. The retention times of **10** and **11** were the same as those of these components produced in the reduction of ketone **6**. No detectable amounts of **8** and **12** were observed.

Oxidation of the Reduction Product of Epoxide 1.—To a solution of 101 mg. (0.59 mmole) of the crude reduction product from epoxide 1 in 0.4 ml. of ether was added with stirring 0.21 ml. of a solution prepared from 5 g. of sodium dichromate dihydrate, 3.75 ml. of sulfuric acid, and 21.25 ml. of water.[13] The mixture was cooled at 20° during the addition and was maintained at 25° for 1 hr. After work-up, there was obtained 0.095 g. of a yellow oil which partially solidified on standing. G.c. analysis (Polyglycol E-4000 at 149°) showed the following: two unknown components in trace amounts with retention times of 13.1 and 17.1 min.; 61% of ketone **6** (no trace of **7** was detected on g.c. analysis with TCEP) with retention time of 22.3 min.; 30% of **9** (26.8 min.); 5.3% of alcohol **10** (29.4 min.); and 2.6% of alcohol **11** (34.6 min.). It may be calculated that alcohol **10** is oxidized approximately 2.2 times as fast as **11** under these conditions, lending further support to the assignment.

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[13] *Cf.* H. C. Brown and C. P. Gary, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

The Aromatization of a Substituted Cyclohexanol by the Action of Sulfuric Acid[1]

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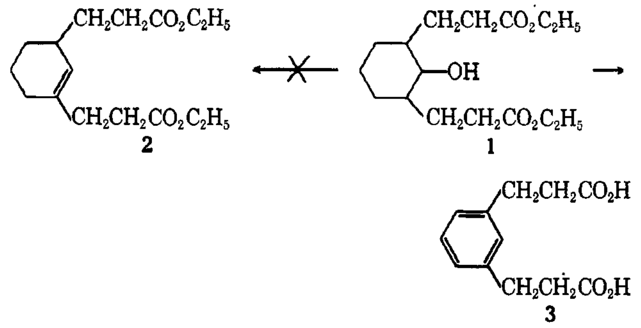
Received April 20, 1965

During the course of other investigations it was desired to dehydrate diethyl 2-hydroxy-1,3-cyclohexanedi-β-propionate, mixed isomers **1**, to the corresponding olefin **2**, the latter compound being a potentially attractive reactant for the preparation of *cis*-1,3-cyclohexanedipropionic acid.[3]

When **1** was treated with the common dehydrating agents such as phosphorus oxychloride–pyridine, phosphoric acid, *p*-toluenesulfonic acid, or phosphorus pentoxide, complex mixtures were obtained from which could be isolated reactant **1** and a δ-lactone fraction (b.p. 170–171° at 0.5 mm.) but none of the desired olefin **2**.[4]

In an attempt to avoid ester hydrolysis and to promote dehydration, a 50% sulfuric acid–acetic acid mixture was employed. Heating **1** in such a mixture ultimately resulted in isolating a maximum yield of 30% of a diacid, m.p. 149–150°. Similarly, the δ-lactone fraction also gave the same diacid but in lower yield. This acid was identified as benzene-1,3-dipropionic acid (**3**), a compound previously reported in the early literature by Kipping.[5] Comparison of the melting points of the acid **3** and its dimethyl ester, m.p. 52–53°, with those reported,[5] as well as elemental analyses and infrared, ultraviolet, and n.m.r. spectra confirm the structure of **3**. In addition, during the reaction period, copious amounts of sulfur dioxide were evolved, indicating the reduction of the sulfuric acid.[6]



There are several examples in the literature where sulfuric acid acts as an aromatizing–oxidizing agent. None were found, however, which proceeded *via* dehydration and subsequent aromatization. For example, Doering and Beringer[8] reported the aromatization of cyclohexenone and cyclohexanone derivatives to phenols by the action of sulfuric acid; the reaction was shown to proceed *via* intermediate sulfonic acid derivatives. Similarly, Noyce[9] reported the formation of *p*-methylacetophenone by the action of concentrated sulfuric acid on camphenilone. In these cases, however, the oxygen function is not lost during aromatization.

More analogous to the system reported here is the formation of 1,3-cyclohexadiene by reaction of cyclohexanol with potassium hydrogen sulfate.[10] When **1**, however, was treated similarly, elimination did not occur.[6]

No doubt this interesting reaction involves dehydration followed by sulfonation and subsequent elimination of the elements of sulfurous acid, leading ultimately to aromatization. Whether the reaction proceeds *via* the intermediate formation of a δ-lactone or α,β-unsaturated ester, as suggested by formation of some unsaturated ester, or *via* direct sulfonation of an olefin such as **2** cannot be determined at this time.

A brief examination of the reaction of other cyclohexanol systems[11] under a variety of sulfuric acid concentrations and reaction times gave varying amounts of tarry materials, but no distillable aromatic products or products extractable into ether. Whether aromatic materials are present in the tarry residues was not readily determined. In this respect, it is of interest that **3** could be isolated in reasonable yield, while the other alcohols employed failed to give any isolable simple aromatic compounds.

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[1] Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

[2] To whom inquiries should be sent: Central Research Department, Monsanto Company, St. Louis, Mo. 63166.

[3] (a) T. L. Westman, R. Paredes, and W. S. Brey, *J. Org. Chem.*, **28**, 3512 (1963); (b) T. L. Westman and A. E. Kober, *ibid.*, **29**, 2448 (1964).

[4] With phosphorus pentoxide, the crude reaction product had infrared and ultraviolet spectra which indicated the presence of α,β-unsaturated ester. No pure components could be isolated, however.

[5] F. S. Kipping, *J. Chem. Soc.*, 53 (1888).

[6] Similarly, treating the diester **1** with thionyl chloride–pyridine gave the acid **3** in very low yield along with the formation of elemental sulfur during distillation of the product. Heating the diester **1** with potassium hydrogen sulfate[7] gave a product from which only reactant or lactone could be isolated (*vide infra*).

[7] L. Ruzicka and H. Goedhart, *Helv. Chim. Acta*, **14**, 1165 (1931).

[8] W. v. E. Doering and F. M. Beringer, *J. Am. Chem. Soc.*, **71**, 2221 (1949).

[9] D. S. Noyce, *ibid.*, **72**, 924 (1950).

[10] H. Hock and F. Depke, *Chem. Ber.*, **84**, 349 (1951).

[11] The compounds investigated included 2,6-dimethylcyclohexanol (*cis* and *trans* isomers), 2,6-di-*t*-butylcyclohexanol, 2-ethyl- and -methylcyclohexanol, ethyl cyclohexanol-2-acetate, and ethyl cyclohexanol-2-propionate (all mixed isomers).

Experimental Section[12]

Diethyl 2-Hydroxy-1,3-cyclohexanedi-β-propionate (1).—In 200-ml. of absolute ethanol was dissolved 30 g. (0.1 mole) of diethyl 2,6-cyclohexanonedipropionate[3a] and the solution was cooled in an ice bath, with magnetic stirring. Over a period of 20 min. 2.1 g. (0.055 mole) of sodium borohydride was added in portions. After stirring the mixture an additional 2 hr. at room temperature, the mixture was poured into 400 ml. of ice–water and the resultant cloudy solution was extracted twice with 200-ml. portions of chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate, the chloroform was removed *in vacuo*, and the residue was distilled to give 24 g. (81%) of 1, b.p. 183–185 (0.25 mm.), $n^{20}D$ 1.4950.

As noted previously,[3] satisfactory elemental analyses or solid derivatives are difficultly prepared for these systems. The product 1 had an infrared spectrum consistent with a hydroxy ester, with infrared bands at 3300 and 1740 cm.$^{-1}$. This material may, however, contain some δ-lactone as a contaminant.

Reaction of 1 with Sulfuric Acid–Acetic Acid. Benzene-1,3-dipropionic Acid (3).—In a mixture of 70 ml. of glacial acetic acid and 70 ml. of concentrated sulfuric acid was dissolved 87.0 g. (0.29 mole) of 1. The mixture was refluxed for 7 hr. during which time sulfur dioxide was evolved (hood!), and tarry material was observed to form. After this time the mixture was poured into *ca.* 300 ml. of ice–water and the whole was extracted with two 150-ml. portions of ether. The combined ethereal extracts were filtered through a glass-wool plug (to remove difficultly separable tarry residues) and dried over anhydrous sodium sulfate, and the ether was removed *in vacuo*. The oily residue was esterified by treatment with ethanol-sulfuric acid[3b] and distilled to give a main fraction, 24 g., b.p. 150–155° (0.5 mm.), and a smaller second fraction, 4.3 g., b.p. 170° (0.5 mm.); the latter fraction was shown to contain δ-lactone as evidenced by a strong band in the infrared at 1740 cm.$^{-1}$.[13] The first fraction, whose infrared, ultraviolet, and n.m.r. spectra were consistent with a *meta*-substituted benzene derivative, was hydrolyzed with ethanolic potassium hydroxide, acidified, and isolated in the usual manner to give 15.5 g. (30%, based on 1) of benzene-1,3-dipropionic acid (3) after two recrystallizations from water, m.p. 149–150° (lit.[5] m.p. 146–147°).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; neut. equiv., 111. Found: C, 64.76; H, 6.10; neut. equiv., 110.

Dimethyl Benzene-1,3-dipropionate.—Treatment of a small sample of 3 in ether with an ethereal solution of excess diazomethane followed by removal of solvent and recrystallization from methanol–water gave the dimethyl ester of 3, m.p. 52–53° (lit.[5] m.p. 51°).

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[12] All melting points are corrected; boiling points are uncorrected Distillations were performed on a Nester and Faust spinning-band column (32 theoretical plates).

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 186.

Synthesis and Reactions of 1-Aminobicyclo[n.1.0]alkanes

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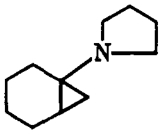
Received July 20, 1965

In the course of our studies[1-4] on the reactions of olefins with methylene halides and zinc–copper couple, we found that the reagent reacted with selected cyclic enamines to yield 1-aminobicyclo[*n*.1.0]alkanes **1–3**.[5] For this reaction, the preferred method involves adding the enamine to a preformed solution[3] of the reagent prepared from methylene chloroiodide and zinc–copper couple. The availability of these amines and the current interest in cyclopropene chemistry[6] prompted an investigation of elimination reactions which might result in the formation of fused-ring cyclopropenes.[7] We now report evidence for the formation of bicyclo[3.1.0]hexene-$\Delta^{1,5}$ (**4**) in the reaction of 1-bicyclo[3.1.0]hexyltrimethylammonium bromide (**5**) with methyl- or phenyllithium. The principal product in these reactions is 1-methyl- (**6**) or 1-phenylbicyclo[3.1.0] hexane (**7**), respectively. A possible precursor for **6** and **7** would be **4** formed by either or both of two eliminative routes (a and b). Based on the known reactivity of methyl groups in quaternary systems,[8] route b is preferred. In the reaction sequence involving phenyllithium, a second product, 1-benzylbicyclo[3.1.0]hexane, was obtained. This is considered to arise from toluene, and subsequently benzyllithium, which is formed in this side reaction.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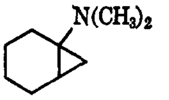

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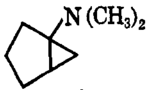

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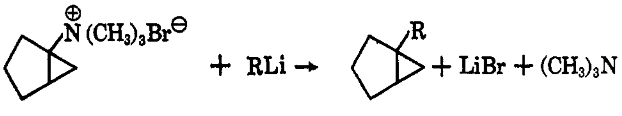
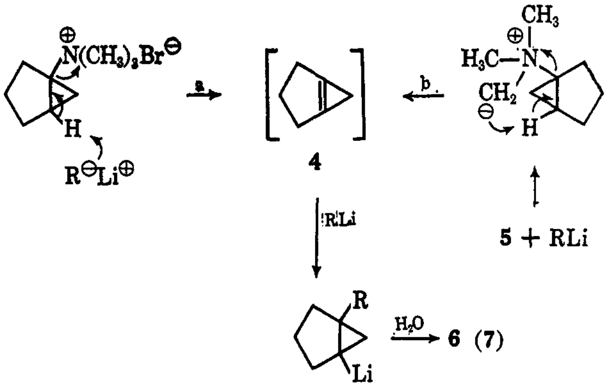


5

6, R=CH$_3$

7, R=Ph



$$5 + PhLi \longrightarrow PhCH_3 + LiBr + 3$$

Although alkyllithium reagents do not usually add to olefinic linkages, there is precedent for the reaction.[9] The alternative to the intermediacy of **4** would involve direct displacement of trimethylamine from **5**. Although the formation of toluene and **3** appears to involve a displacement reaction, the reaction occurs on a primary carbon, *i.e.*, a methyl group. In order to

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[1] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958).

[2] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[3] E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

[4] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[5] We are indebted to Dr. B. C. McKusick for suggesting this possibility.

[6] The subject was recently reviewed by F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

[7] Two examples have been reported by G. L. Closs and R. Boll, *J. Am. Chem. Soc.*, **85**, 3904 (1963).

[8] G. Wittig and M. H. Wetterling, *Ann.*, **557**, 193 (1947).

[9] G. Wittig and J. Otten, *Tetrahedron Letters*, 601 (1963).