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.), $n^{20}\text{D}$ 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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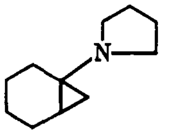
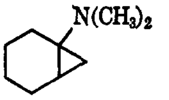
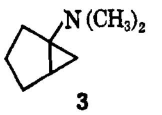
In the course of our studies[1-4] on the reactions of olefins with methylene halides and zinc–copper couple, we found that the reagent reacted with selected cyclic enamines to yield 1-aminobicyclo[*n*.1.0]alkanes **1–3**.[5] For this reaction, the preferred method involves adding the enamine to a preformed 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.



1



2



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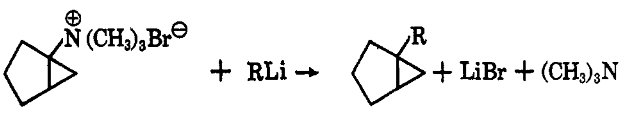
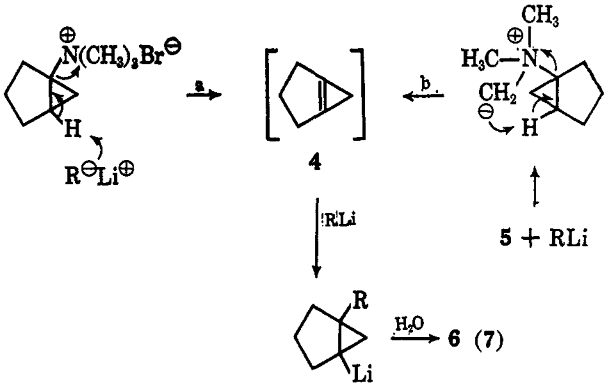


5 **6**, R = CH₃
7, R = Ph



$$5 + \text{PhLi} \longrightarrow \text{PhCH}_3 + \text{LiBr} + 3$$

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).

obtain 6 or 7 by this route, a displacement on tertiary carbon at a highly hindered site would be involved, and this process seems unlikely.

Experimental Section[10]

1-Pyrrolidinobicyclo[4.1.0]heptane (1).—Into a 200-ml. flask was charged zinc–copper couple[11] (13.46 g., 0.2 g.-atom), diethyl ether (62 ml.), and methylene iodide (53.6 g., 0.2 mole). A crystal of iodine was added, and the mixture was heated at reflux for 1 hr., whereupon the rate of gas evolution equalled 17 cc./min. The flask was chilled in ice–water under a positive nitrogen pressure and then filtered through a dry, sintered disk. One-half of this filtrate was charged into a 100-ml. flask and pyrrolodino-1-cyclohexene (14.7 g., 0.097 mole) (Aldrich) was added. An immediate reaction occurred, resulting in a gelatinous precipitate. The mixture was heated at reflux for 2 hr., cooled, and treated with two portions of hot ammonium chloride solution. The two-phase system was separated, and the aqueous phase was extracted with two 100-ml. portions of ether and then made alkaline with NaOH. The alkaline solution was extracted with two 100-ml. portions of ether, this extract was dried over magnesium sulfate and filtered, and the ether was evaporated. The residue was combined with the product from an identical reaction and distilled through a semimicro spinning-band column to give 2.57 g. (8%) of product, b.p. 70–74.5° (4 mm.). Purification by gas chromatography afforded pure product having $n^{25}\mathrm{D}$ 1.4876.

Anal. Calcd. for $C_{11}H_{19}N$: C, 80.00; H, 11.50; N, 8.50. Found: C, 79.67; H, 11.85; N, 8.68.

1-Dimethylaminobicyclo[4.1.0]heptane (2).—In a 500-ml. flask was charged chloroiodomethane (53 g., 0.3 mole), zinc–copper couple (20.2 g., 0.3 g.-atom), and ether (63 ml.). The mixture was heated at reflux with stirring for 1 hr. and 20 min. The flask was chilled in an ice–water bath, and dimethylamino-1-cyclohexene[12] (18.75 g., 0.15 mole) was added with stirring. A two-phase system resulted. Tetrahydrofuran (THF) (35 ml.) was added slowly to aid solution, and the mixture was stirred at reflux for 24 hr. The slurry was cooled in an ice bath, and aqueous ammonium chloride (100 ml.) was added slowly. The ether phase was discarded, and the aqueous phase was filtered, extracted twice with 50 ml. of ether, and then made alkaline with a solution of 40 g. of NaOH in 150 ml. of water. The alkaline solution was extracted with three 100-ml. portions of ether. This ether phase was dried over $MgSO_4$ and filtered, and the ether was distilled through a spinning-band column. Distillation of the residue afforded 1.7 g. (8.15%) of product, b.p. 76.5–77° (36 mm.). A sample purified *via* its picrate salt had $n^{25}\mathrm{D}$ 1.4596.

Anal. Calcd. for $C_9H_{17}N$: C, 77.70; H, 12.22; N, 10.08. Found: C, 77.74; H, 12.55; N, 9.97.

1-Dimethylaminobicyclo[3.1.0]hexane (3).—In the manner described for the preparation of 1-dimethylaminobicyclo[4.1.0]heptane, a reaction between zinc–copper couple (33 g., 0.49 g.-atom), chloroiodomethane (86.5 g., 0.49 mole), and dimethylamino-1-cyclopentene[12] (27.8 g., 0.25 mole) in diethyl ether (200 ml.) was carried out. Fractionation of the product through a semimicro spinning-band column gave 11.19 g. (35.8%) of product which had b.p. 78–81° (100 mm.), $n^{25}\mathrm{D}$ 1.4487–1.4495.

Anal. Calcd. for $C_8H_{15}N$: C, 76.80; H, 12.00; N, 11.20. Found: C, 76.70; H, 12.27; N, 11.04.

1-Bicyclo[3.1.0]hexyltrimethylammonium Bromide (5).—To a cold (−20°) solution of methyl bromide (9.5 g., 0.1 mole) in nitromethane (30 ml.) was added dropwise with stirring 1-dimethylaminobicyclo[3.1.0]hexane (4.91 g., 0.039 mole). The mixture was stirred at −20° for 2 hr. and then allowed to warm to 25° for 40 hr. Ether (250 ml.) was added, and the crystals were collected on a filter and dried under nitrogen to leave 8.0 g. (89%) of 5. A sample recrystallized from acetonitrile was obtained as white needles, m.p. 252° dec.

Anal. Calcd. for $C_9H_{18}BrN$: Br, 36.30. Found: Br, 36.25.

Reaction of 5 with Methyllithium.—To a stirred slurry of 1-bicyclo[3.1.0]hexyltrimethylammonium bromide (4.27 g., 0.019 mole) in ether (20 ml.) cooled to 0° was added a 2 *N* solution of methyllithium in ether (10 ml., 0.02 mole). The mixture was allowed to warm to 25° and to stir for 5 days. Water (25 ml.) was added, and the ether phase was separated. The aqueous phase was extracted with ether (25 ml.), the combined ether phase was dried over anhydrous magnesium sulfate and filtered, and the ether was removed by fractionation. The residue was flash distilled under vacuum to give 0.5 g. (30%)[13] of hydrocarbon product. Gas chromatography (g.c.) (triscyanoethylated glycerol) revealed one major and two very minor products. The major product was purified by g.c. and shown to be 1-methylbicyclo[3.1.0]hexane (6) by comparison of its n.m.r., infrared, and mass spectra.

1-Methylbicyclo[3.1.0]hexane (6).—This hydrocarbon was prepared in 61% yield from Zn–Cu couple (13 g., 0.2 g.-atom), methylene iodide (50 g., 0.19 mole), and 1-methylcyclopentene (8.2 g., 0.1 mole) in ether (60 ml.) according to the general procedure of Simmons and Smith[1–4]: b.p. 90°, $n^{25}\mathrm{D}$ 1.4310.

Anal. Calcd. for C_7H_{12}: C, 87.50; H, 12.50. Found: C, 87.54; H, 12.60.

Reaction of 5 with Phenyllithium.—To a stirred slurry of 1-bicyclo[3.1.0]hexyltrimethylammonium bromide (39.6 g., 0.18 mole) in ether (250 ml.) at 0° was added over 30 min. 1.84 *N* phenyllithium in benzene–ether (250 ml., 0.46 mole). The mixture was stirred at 0° for 3 hr. and then at 25° for 15 hr. The resulting red solution was treated with methanol (10 ml.) and water (250 ml.) whereupon the color disappeared. The organic phase was separated and extracted twice with water (250 ml.). After drying over anhydrous magnesium sulfate, the organic phase was distilled to give 2.16 g. of 1-dimethylaminobicyclo[3.1.0]hexane and 15.08 g. of hydrocarbon product, b.p. 45–55° (0.5 mm.). G.c. (15% squalane on Chromosorb W) revealed three components with areas of 78, 10, and 12%).

The major component was shown to be 1-phenylbicyclo[3.1.0]hexane by comparison of its infrared and proton n.m.r. spectra with those of a synthetic sample.

The second two components were collected together and then separated by chromatography on silica gel using pentane as solvent. The first component eluted is considered to be 1-benzylbicyclo[3.1.0]hexane. Thus, the proton n.m.r. spectrum has resonances at τ 9.6–9.75 (2H) (cyclopropyl methylene group), 7.28 (2H) (benzylic methylene group), 8.0–9.1 (7H) (broad multiplet), and 2.94 (5H) (aromatic protons). The mass spectrum reveals a parent peak at *m/e* 172 with large *m/e* at 91 (benzyl$^+$) and 81 (bicyclo[3.1.0]hexyl$^+$ or more probably cyclohexenyl$^+$).

The third component was identified as biphenyl, present in the phenyllithium used.

1-Phenylbicyclo[3.1.0]hexane (7).—This hydrocarbon was prepared from Zn–Cu couple (27.3 g., 0.435 g.-atom), methylene iodide (83.8 g., 0.315 mole), and 1-phenylcyclopentene (28.8 g., 0.182 mole) in ether (115 ml.) according to the general procedure of Simmons and Smith.[1–4] Flash distillation under vacuum gave 21.7 g. of product consisting of 66% of 7 and 34% of starting olefin. The product, 7, was separated by g.c. and had b.p. 236° (micro), $n^{25}\mathrm{D}$ 1.5458.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.15; H, 8.85. Found: C, 91.29; H, 8.96.

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[10] Melting and boiling points are uncorrected.

[11] R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

[12] E. P. Blanchard, Jr., *ibid.*, **28**, 1397 (1963).

[13] It should be noted that the cyclopropene mechanism requires 2 moles of alkyllithium reagent. This yield would then actually be 60% based on alkyllithium reagent.

Perfluoroalkanesulfonate Esters as Alkylating Agents

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The recent paper of Burdon and McLoughlin[1] concerning trifluoromethanesulfonate esters prompts us to report our results concerning these esters. Alkyl

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[1] J. Burdon and V. C. R. McLoughlin, *Tetrahedron*, [1] **21**, 1 (1965).