by 20-ft aluminum column packed with 20% Apiezon L on Chromosorb W. Helium was used as the carrier gas. The infrared absorption spectrum of the gaseous product shows bands in μ at 3.2 (>CH—), 3.4 and 3.45 (>CH_2), 6.1 (>C=C<), and 6.9 (>CH_2) with two broad and complex bands centered at 10.2 and 11.2. The nmr spectrum shows a triplet due to vinyl protons at τ 4.36 and a triplet due to methylene protons at 7.26 with J = 1 Hz. The mass spectrum gives a strong parent ion peak at m/e 80. An authentic sample of 1,4-cyclohexadiene gives the same values as above.

Preparation of 3,3,6,6-d_4-Cyclohexa-1,4-diene (I).—1,1,4,4-d_4-Buta-1,3-diene (0.10 mol) and *trans*-β-chloroacrylic acid (0.11 mol) were reacted, and the product was worked up in the same manner as with the unlabeled material, except that the product was not recrystallized from hexane. 3,3,6,6-d_4-2-Chlorohex-4-ene-1-carboxylic acid (11.7 g, 0.071 mol) was neutralized with 7.1 g of $KHCO_3$ dissolved in 50 ml of water. The water was removed under reduced pressure, and the dried salt along with 11 g of NaI was added to 100 ml of vacuum-distilled hexamethylphosphoramide. The system was evacuated through a Dry Ice–acetone trap to 0.5-mm pressure and heated to 50° for 4 hr. One trap-to-trap distillation under vacuum of the volatile material gave 3.8 g (45% based on butadiene) of I of about 98% purity as shown by vpc and nmr analysis. There was about 0.1% d_2-benzene (presumably 1,4-d_2-benzene), and the remainder of the impurities were higher boiling materials. Final purification was effected with preparative vpc using the column and the conditions used for the purification of unlabeled I in the previous experiment. The infrared absorption spectrum of I (gas phase) shows bands in μ at 3.25 (>CH—), 4.62 and 4.76 (>CD_2), 6.1 (>C=C<), and a poorly resolved triplet centered at 9.3 (>CD_2), with two broad bands centered at 10.4 and 11.3. There is no detectable methylene (>CH_2) absorption at 3.4 or 6.9 μ as there is in the unlabeled compound. The nmr spectrum shows a singlet at τ 4.36 due to the vinyl protons and at 7.25, the methylene proton region, there is a peak of about 1% the area of the vinyl proton peak.[7] Hence there is no detectable exchange of hydrogen at the 3,3,6,6-positions during the synthesis. The mass spectrum shows a molecular ion peak, which is the base peak, at m/e 84.

Registry No.—I, 17791-27-4; 2-chlorocyclohex-4-ene-1-carboxylic acid, 17791-28-5; 1,4-cyclohexadiene, 628-41-1.

[7] The manufacturer (ref 3) claimed at least 98% isotopic purity, and a check by nmr indicated that the 1,1,4,4 positions of the labeled butadiene had about 1% ^1H.

The Selective Oxidation of Large-Ring Organoboranes with Chromic Acid. The Synthesis of Macrocyclic Musk Compounds

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Contribution No. 408 from The Goodyear Tire and Rubber Company, Research Division, Akron, Ohio 44316

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The C_{16} musk compound, 8-cyclohexadecen-1-one (**5**),[1] was obtained in very low yield (*ca.* 5%) by pyrolytic cyclization of the yttrium salt of the corresponding C_{17} diacid.[2] The saturated ketone, cyclohexadecanone (**9**), was obtained in a slightly higher yield (*ca.* 16%) by cyclization (twofold condensation) of the dichloride of azelaic acid, followed by reduction of one of the carbonyl groups.[3] Both ketones were recently[4] formed by an acyloïn cyclization of aleuritic acid in about 5% yield. The odors of both ketones were reported as musklike.

The disadvantages of ring-closure methods to give unsaturated ketones have been realized for some time. Recently, the synthesis of a large-ring, unsaturated compound has been demonstrated by the olefin metathesis reaction[5] of cyclo olefins, which suggests the present approach, in which a large ring is used as the starting material. The macrocyclization of cyclooctene provides a mixture of large-ring compounds.[6] Under suitable conditions[7] the reaction can be directed to appreciable (*ca.* 20%) amounts of the dimer, 1,9-cyclohexadecadiene (**1**), which occurs as a mixture of the *cis,cis* (35%), *cis,trans* (53%), and *trans,trans* (12%) isomers.

The conversion of the large-ring diene by hydroboration into the C_{16} musk compound seemed especially attractive, if a reasonable amount of monohydroboration would occur. The addition of 1 equiv of diborane ($^1/_6B_2H_6$) was expected to give approximately 50% mono- and 25% dihydroborated compounds if the reaction went to completion. The cyclic diene (**1**) was treated with diborane (Scheme I) generated *in situ* by the addition of boron trifluoride etherate to sodium borohydride in diglyme.[8] The distribution of alkylboranes varied with the proportions of diborane. The unsaturated intermediate **2**, may be formed by addition of boron to either end of the double bond. The dihydroborated intermediates, **3** and **4**, may form in equal amounts if not affected by conformational preferences. The possibly of boron-bridged intermediates (from **3** and **4**) is presently under investigation.

Oxidation of organoboranes to the corresponding ketones with aqueous chromic acid added to ethyl ether has been reported.[9,10] This type of chromic acid oxidation, which is known to be selective for secondary alcohols in the presence of carbon–carbon double bonds[11] was found in this work to be selective as well for the alkylborane group in the presence of a carbon–carbon double bond, as is shown by the desired unsaturated ketone **5** (Scheme I). Oxidation also gives the diketones **8** and **10**, from the dihydroborated compounds, but in much lower yield (Table I) than initially predicted for addition of 1 equiv of diborane to the diene. This may be attributed to the insolubility of the dialkylborane which precipitates and resists further alkylation.

Gas chromatographic and ir analyses of recovered starting materials showed that when the diene was treated with 2 or 3 equiv of diborane the *cis,cis* isomer had always reacted to a greater extent than the *trans*,-

[1] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. II, part A, Elsevier Publishing Co., New York, N. Y., 1953, p 277.

[2] L. Ruzicka, M. Stoll, W. Scherrer, H. Schinz, and C. F. Seidel, *Helv. Chim. Acta*, **15**, 1459 (1932); L. Ruzicka, M. Stoll, and H. Schinz, *ibid.*, **9**, 249 (1926).

[3] A. T. Blomquist, J. Prager, and J. Wolinsky, *J. Amer. Chem. Soc.*, **77**, 1804 (1955); A. T. Blomquist and J. Wolinsky, *ibid.*, **77**, 5423 (1955).

[4] H. H. Mathur and S. C. Bhattacharyya, *Tetrahedron*, **21**, 1537 (1955).

[5] K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. F. Ward, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. L54; Advances in Chemistry Series, in press.

[6] N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci.*, **5**, 2209 (1967).

[7] N. Calderon and E. A. Ofstead, unpublished data.

[8] H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, **80**, 1552 (1958).

[9] H. C. Brown and C. P. Garg, *ibid.*, **83**, 2951 (1961).

[10] H. C. Brown and C. P. Garg, *ibid.*, **83**, 2952 (1961).

[11] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *ibid.*, 2402 (1951).

Scheme I

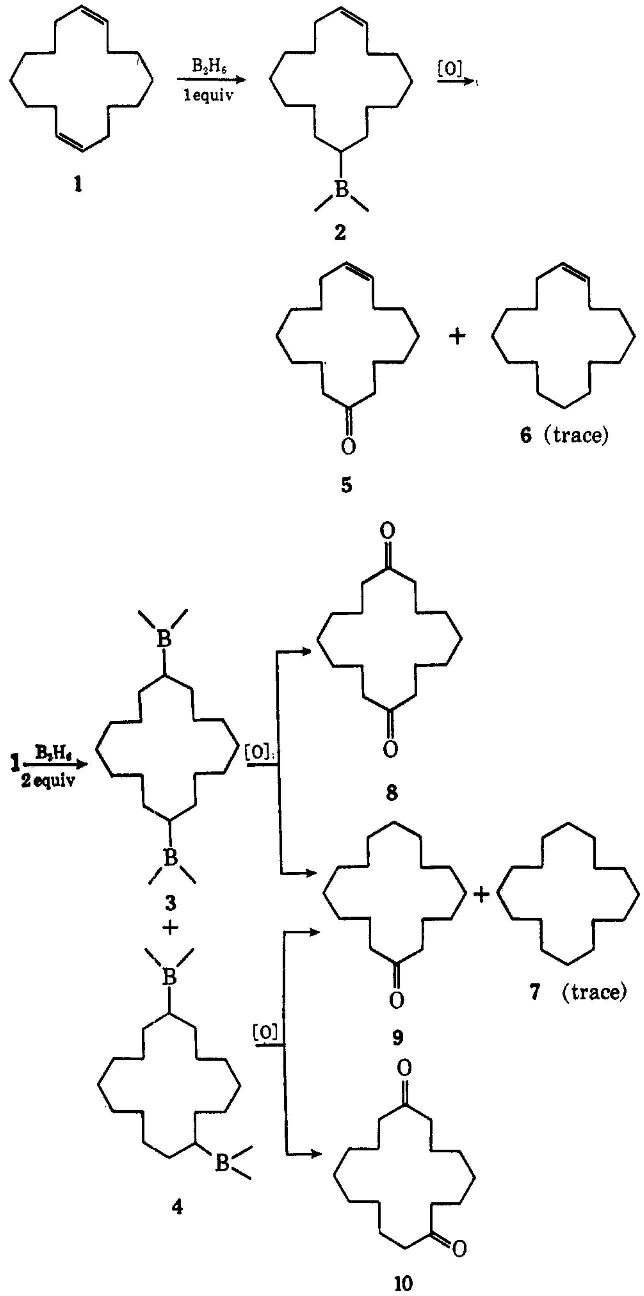


Table I

Product Distribution from Varied Amounts of Diborane[a]

Diborane diene, equiv	% 5	% 9	% (8 and 10)[b]
1	44	1	4
2	26	19	44
3	20	26	45

[a] Yields are based on glpc analysis utilizing an internal standard. [b] The diketones were shown by glpc analysis to be in equal amounts.

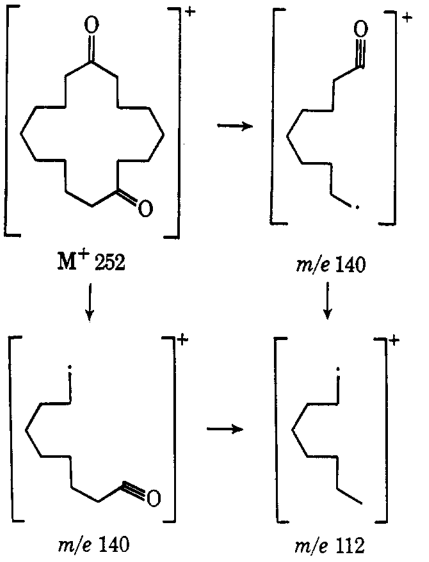
trans or *cis,trans*. However, of the six products obtained, the two that possess carbon–carbon double bonds are the cyclic alkene (**6**) and the unsaturated ketone (**5**), which are predominantly the *trans* isomers as shown by ir analysis.

The diketones possess a very mild odor similar to camphor instead of musk. The saturated monoketone has a musky odor almost identical with that of the unsaturated compound.

The presence of the saturated ketone **9** was unexpected; however, its formation is easily explained since the oxidation is carried out in the presence of mineral acid.[12] Reduction of carbon–carbon double bonds *via* hydroboration has been reported in good yield using organic acids, and in fair yield with mineral acids.[12] Protonation of one position of the dihydroborated intermediate, with oxidation at the other, would afford this saturated ketone. Traces of the saturated hydrocarbon **7** presumably arise by protonation of both hydroborated positions, while the trace of alkene **6** may arise from the monohydroborated intermediate.

The isomeric diketones have a nominal molecular weight of 252. Gas chromatographic analysis showed the presence of the two isomers with this mass, and their fragmentation patterns on the mass spectrometer can be used to distinguish between them. The proposed fragmentation pattern of the 1,8 diketone is shown in Scheme II. The fragmentation peak at *m/e* 140 is not readily accessible from the symmetrical diketone as it would require cleavage β to the keto group, which does not normally occur.[13] The presence of a metastable ion at *m/e* 77.4 ($140^2/252 = 77.7$) is in agreement with this pattern. A peak at *m/e* 112 which is believed to be a secondary fragment from the *m/e* 140, as well as from the *m/e* 252, was also present. The symmetrical diketone has a base peak at *m/e* 126, which indicates symmetrical α cleavage at both carbonyls.[13,14]

Scheme II



The change in over-all yield (Table I) in going from 2 to 3 equiv of diborane per mole of diene is negligible. The over-all yield, however, jumps about 40% when

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[12] J. R. Johnson, H. R. Synder, and M. C. Van Campen, Jr., *J. Amer. Chem. Soc.*, **60**, 115 (1938).

[13] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden–Day, Inc., San Francisco, Calif., 1964, p 17.

[14] F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press, Inc., New York, N. Y., 1963, pp 471–473; K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 153–157.

going from 1 to 2 equiv of diborane per mole of diene. It is apparent that when an excess of diene is available the major product after oxidation is the desired unsaturated ketone **5**.

Experimental Section

Diglyme and boron trifluoride etherate were purified according to procedures previously described.[15] The sodium borohydride (minimum 98% pure) was used as supplied by the Fisher Scientific Co.

The melting points were determined on a Fisher–Johns apparatus and are uncorrected. Elemental analyses were performed by the Analytical Section, Goodyear Tire and Rubber Co., Research Division. Infrared spectra, obtained on a Perkin-Elmer Model 137 spectrometer, are reported for liquids as films; as solids were melted on NaCl plates. The nmr spectrum was obtained on a Varian A-60 spectrometer and the mass spectra on an AEI MS-9 spectrometer. Glpc analyses were performed on a F & M instrument (Model 500), equipped with a 12 ft × 0.25 in. (o.d.) copper column containing 10% silicone rubber (SE-30) on Diatoport W. A column containing Carbowax 20M (10%) on Column Pak was used for preparative glpc.

Hydroboration.—A flask was fitted with a reflux condenser sealed with a calcium sulfate drying tube (indicator Drierite), a nitrogen inlet tube, and a dropping funnel containing 9.2 g (65 mmol) of boron trifluoride in 50 ml of diglyme. The flask contained 44.2 g (200 mmol) of 1,9-cyclohexadecadiene and 1.89 g (50 mmol) of sodium borohydride in 400 ml of diglyme. The BF_3 solution was added with stirring at a rate to maintain the temperature at 25–45° (1 hr). The reaction mixture was stirred after addition for 2 hr at room temperature.

Oxidation.—Ethyl ether (800 ml) was added for mild oxidation conditions and ease of separation. A solution of 26.6 g (266 mmol) of chromium trioxide and 39.2 g (400 mmol) of sulfuric acid in 100 ml of water (*ca.* 8 *N*) was added with stirring over a 1-hr period to maintain the temperature at 25–35°. The green chromic sulfate began to form upon addition of the oxidant. Refluxing was maintained for 3 hr after addition. Water (500 ml) was added, and the ether layer was separated. The aqueous layer was extracted twice with 200-ml portions of ether, and the extracts were combined. Excess oxidant in the ether portion was destroyed with solid sodium bisulfite, and the organic layer was then washed with a sodium carbonate solution. The organic material was dried over calcium chloride, and the solvents were removed, ethyl ether at 25 mm and diglyme by washing with water after removal of ether. The weight of the crude material was 43.0 g. The hydrocarbons were separated from the ketones by eluting them with petroleum ether (bp 37–46°) from a 1.5 × 36 in. column packed with activated alumina. The monoketones, **5** and **9**, were eluted with ethyl ether and were separated from each other by preparative glpc. The diketones, **8** and **10**, were eluted with methanol and further separated by glpc.

8-Cyclohexadecen-1-one (**5**).—A sample was prepared for analysis by vacuum distillation at 1 mm (bp 180°): mp 18–19° (lit.[2] mp 17–22°); ν_{max} 2990, 2910, 1710 (C=O), 1469, 1375, and 974 (*trans*—CH=CH—) cm^{-1}; *m/e* 236; nmr (CCl_4) δ 5.32 (broad triplet, olefinic), 2.37 (triplet, α-keto H), 1.32 (strong singlet, internal methylene H). The semicarbazone from aqueous methanol had mp 183–184° (lit.[3] mp 180–181°).

1,9-Cyclohexadecadione (**8**).—A sample was prepared for analysis by recrystallization from petroleum ether melted at 78–79° (lit.[2] mp 80–82°): ν max 2990, 2910, 1715 (C=O), 1470, 1375, 1121, 1025, and 717 cm^{-1}; *m/e* 252. The disemicarbazone from aqueous methanol had mp 228–229° (lit.[2] mp 225–227°).

Cyclohexadecanone (**9**).—A sample recrystallized twice from petroleum ether for analysis melted at 57–59° (lit.[2] mp 59.5–60.2°): ν max 2990, 2910, 1707 (C=O), 1480, and 730 cm^{-1}; *m/e* 238.

1,8-Cyclohexadecadione (**10**) was recrystallized twice from petroleum ether before analysis: mp 75–77°; ir identical with that of **8**; *m/e* 252.

Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.1; H, 11.1. Found: C, 75.9; H, 11.1.

Cyclohexadecene (**6**) was separated by preparative glpc for spectral analysis: *m/e* 222; ν max 3010, 2990, 2910, 1450, 1470, 975 (strong), and 720 cm^{-1}.

Cyclohexadecane (**7**) was separated by preparative glpc for spectral analysis: *m/e* 224; ν max 2990, 2910, 1460, 1470, and 1385 cm^{-1}.

Registry No.—Chromic acid, 7738-94-5; **6**, 6568-44-1; **7**, 295-65-8; **10**, 17853-46-2.

Acknowledgment.—The author wishes to acknowledge Dr. Nissim Calderon and Dr. Eilert A. Ofstead, for providing the 1,9-cyclohexadecadiene and suggesting its potential use as a musk precursor.

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Formation of 1,1-Dimethyl-3,3-diphenylindan from the Triphenylmethyl Cation and Isobutene[1]

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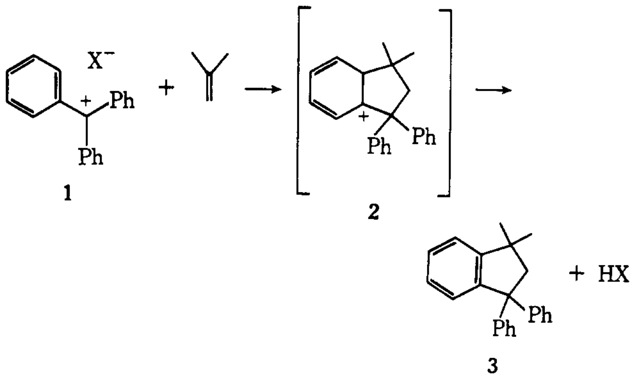
Addition of isobutene to solutions of salts of the triphenylmethyl cation (**1**) in organic solvents led to formation of 1,1-dimethyl-3,3-diphenylindan (**3**). This reaction represents a direct intermolecular addition of a carbonium ion to an aliphatic alkene to form a new ring. There has previously been evidence for indan formation as a termination step in cationic polymerizations of α-methylstryene and of other aryl olefins.[4,5] In addition, indans have been observed as products of cationic dimerizations of α-methylstyrene and of other aryl olefins.[5]



$X = ClO_4^-$ or BF_4^-

Varying amounts of an oil, presumably oligomeric isobutene, also were obtained from the reactions. The amount of this material relative to the indan seemed to decrease with decreasing rate of addition of isobutene. The polymerization of isobutene was perhaps initiated

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[1] Taken in part from the Ph.D. Thesis of R. K. L., The Pennsylvania State University, 1966.

[2] Alfred P. Sloan Foundation Research Fellow, 1964–1968.

[3] National Institutes of Health Predoctoral Fellow, 1964–1966.

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[5] S. Bywater in "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., The Macmillan Co., New York, N. Y., 1963, Chapter 7.