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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[15] G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 28 (1963).

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

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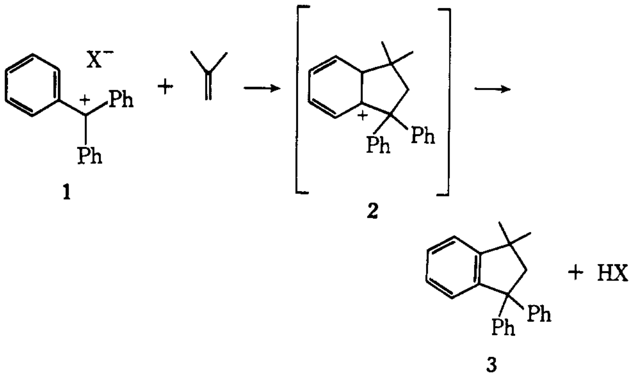
Addition of isobutene to solutions of salts of the triphenylmethyl cation (**1**) in organic solvents led to formation of 1,1-dimethyl-3,3-diphenylindan (**3**). This reaction represents a direct intermolecular addition of a carbonium ion to an aliphatic alkene to form a new ring. There has previously 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.

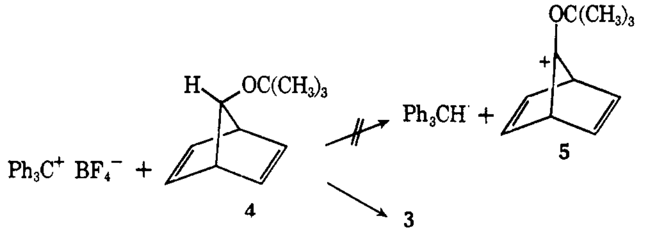
[3] National Institutes of Health Predoctoral Fellow, 1964–1966.

[4] D. C. Pepper in "Friedel-Crafts and Related Reactions," Vol. 2, part 2, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 30.

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

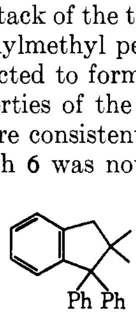
by the triphenylmethyl cation itself. Salts of this cation are thought to initiate polymerizations of reactive olefins.[4] Alternatively, the initiation may have been by the acid generated in the cyclization reaction or by catalysts generated by hydrolysis of the carbonium ion salts (**1**) due to adventitious traces of water.[6] Little oligomer was obtained from a reaction mixture which contained equimolar amounts of collidine and of **1**. Indans similar to **3** were not obtained from preliminary experiments with *cis*-2-butene or with 2,3-dimethyl-2-butene.

Indan **3** was also a product of reactions of salts of the triphenylmethyl cation with *t*-butyl ethers. In fact, **3** was first obtained from a reaction of 7-*t*-butoxynorbornadiene (**4**) and triphenylmethyl fluoroborate.



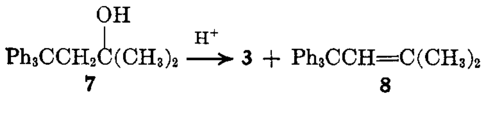
It was hoped that hydride transfer would lead to the 7-norbornadienyl cation (**5**) or products derived from its decomposition. However, triphenylmethane was not isolated as a product of this reaction. Presumably **3** was formed by reaction of the triphenylmethyl cation with isobutene that was generated from **4** (or species derived from **4**) by attack of the triphenylmethyl cation or of acids. Triphenylmethyl perchlorate and methyl *t*-butyl ether also reacted to form **3**.

The spectral properties of the hydrocarbon product of these reactions were consistent with the assignment of structure **3**, though **6** was not rigorously excluded.



6

The assignment of structure **3** was confirmed by an independent synthesis. A reaction of 4,4,4-triphenyl-2-methyl-2-butanol (**7**) in trifluoroacetic acid led to quantitative formation of **3**. Heating benzene solutions



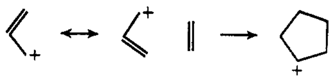
$$\underset{\mathbf{7}}{Ph_3CCH_2\overset{OH}{\overset{|}{C}}(CH_3)_2} \xrightarrow{H^+} 3 + \underset{\mathbf{8}}{Ph_3CCH{=}C(CH_3)_2}$$

of **7** containing small amounts of *p*-toluenesulfonic acid furnished reaction mixtures which contained both **3** and olefin **8**, a dehydration product of **7**; olefin **8** was slowly converted into **3** under these reaction conditions. Formation of indans by cyclizations of alcohols or olefins such as **7** and **8** is well known.[7]

The mechanism of indan formation from isobutene and the triphenylmethyl cation probably involves two bond formation steps: addition of the triphenylmethyl cation to isobutene to form **9**, the same intermediate

$$Ph_3C^+ + CH_2{=}C(CH_3)_2 \longrightarrow \underset{\mathbf{9}}{[Ph_3CCH_2C^+(CH_3)_2]} \longrightarrow [2] \longrightarrow \mathbf{3}$$

carbonium ion presumably responsible for the cyclizations of **7** and **8**, followed by cyclization of **9** to **2**. It is also conceivable that both new C–C bonds are formed simultaneously in a concerted cycloaddition. Such a reaction would be analogous formally to the unknown concerted cycloaddition of an allyl cation to an alkene, an addition that is predicted on the basis of the orbital



symmetry arguments of Woodward and Hoffmann to be unfavorable thermally (if "*cis–cis*" in stereochemstry).[8,9]

Experimental Section[10]

Reaction of Triphenylmethyl Fluoroborate with 7-*t*-Butoxynorbornadiene (4).—Triphenylmethyl fluoroborate[11] (7.80 g, 0.024 mol) and **4** (1.50 g, 0.091 mol) were dissolved in 90 ml of acetonitrile and the solution was allowed to stand at 50° for 24 hr. Dilute sodium carbonate solution was added, and the resulting mixture was extracted with six 20-ml portions of water and three 10-ml portions of saturated sodium chloride solution. The solution was dried (Na_2SO_4), and the residue obtained after evaporation of the solvent was extracted exhaustively with petroleum ether (bp 30–60°). The petroleum ether was evaporated leaving 1.85 g of solid which was dissolved in 5 ml of warm chloroform and chromatographed on a 2.5-cm column packed with 100 g of alumina (Fisher A-540, acid washed). Elution with 500 ml of petroleum ether afforded 0.74 g (0.0025 mol, 10%) of **3**. Two recrystallizations from 95% ethanol and sublimation at 60° (5 mm) gave a sample of mp 105.5–107.5°; nmr (CCl_4) τ 2.91 (m, 15, aryl H's), 7.15 (s, 2, CH_2), and 8.85 (s, 6, CH_3) ppm; uv (95% ethanol) 272 mμ max (log ϵ 3.09), 265 max (3.12), 263 shoulder (3.09), and 259 shoulder (3.05); mass spectrum (70 eV) *m/e* (rel intensity) 298 (100), 283 (86), 221 (95), 205 (33), 143 (38), 105 (26), 91 (92), and 77 (60).

Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43; Found: C, 92.75; H, 7.43.

Further elution with 150 ml of petroleum ether gave 0.30 g of resinous material. Elution with 150 ml of benzene–petroleum ether (1:1) gave 0.20 g of material which displayed a phenyl absorption pattern between 5 and 6 μ, and elution with 200 ml of ethyl ether gave 0.30 g of triphenylcarbinol and 0.05 g of an orange oil. Triphenylmethane was not noted.

Reaction of Triphenylmethyl Perchlorate with Methyl *t*-Butyl Ether.—A solution of 2.1 g (0.024 mol) of methyl *t*-butyl ether in 6 ml of acetonitrile was added over 60 min to a solution maintained at 65° of 4.0 g (0.012 mol) of triphenylmethyl perchlorate[11] dissolved in 50 ml of acetonitrile. The reaction mixture was stirred for 16 hr at 70°. A further quantity of 0.9 g (0.010 mol) of the ether in 5 ml of acetonitrile was added in one portion and stirring was continued for another 10 hr. Water was added, and the mixture was extracted with four 20-ml portions of ether. The ether extracts were washed with water and with a saturated sodium chloride solution. Evaporation of solvent from the dried (Na_2SO_4) extracts afforded 2.85 g of material which was chromatographed on a 2.5-cm column packed with 80 g of alumina (Fisher F-20, neutral grade). Elution with pentane gave 0.71 g

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(6) P. H. Plesch in "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., The Macmillan Co., New York, N. Y., 1963, Chapter 4.

(7) L. R. C. Barclay in "Friedel-Crafts and Related Reactions," Vol. 2, part 2, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 22.

(8) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(9) Apparent examples of the *cis–cis* cycloaddition of an allyl cation to a conjugated diene considered favorable[8] have recently been observed [H. M. R. Hoffmann, D. R. Joy, and K. A. Suter, *J. Chem. Soc., B*, 57 (1968)].

(10) Melting points were determined in capillary tubes with calibrated thermometers. Analyses were done by Midwest Microlab. Nmr spectra were calibrated with internal tetramethylsilane.

(11) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(0.0024 mol, 20%) of crude **3**, which after recrystallization was identical with that obtained from the reaction with **4**. Elution with benzene gave 0.13 g of a yellow oil; elution with ether gave 1.37 g of triphenylcarbinol; and elution with chloroform gave 0.08 g of an oil from which N-*t*-butylacetamide sublimed on standing. Triphenylmethane was not noted.

Reaction of Triphenylmethyl Cation Salts with Isobutene.—Isobutene (40 g, 0.71 mol) was bubbled slowly over 6 hr into a solution of 4.1 g (0.012 mol) of triphenylmethyl perchlorate[11] in 45 ml of acetonitrile in a flask equipped with a gas inlet tube, a Dry Ice–acetone condenser, a magnetic stirrer, and a drying tube. The solution was maintained at 30° during the first hour and subsequently at 60°. Dilute aqueous sodium carbonate was added, and the solution was concentrated on a steam bath. The aqueous mixture was extracted with three 20-ml portions of petroleum ether and five 20-ml portions of ether. The extract was washed with two 10-ml portions of water and three 10-ml portions of saturated sodium chloride solution. The solution was dried (Na_2SO_4), and the solvent was evaporated, leaving 3.4 g of semicrystalline material which was chromatographed on a 2.5-cm column packed with 80 g of alumina (Fisher F-20, neutral grade). Elution with pentane gave 1.5 g of **3** contaminated with a small amount of a viscous liquid. Recrystallization from 95% ethanol gave 1.0 g (0.0034 mol, 28%) of **3**. Further elution with ether gave a mixture (1.2 g) of triphenylcarbinol and N-*t*-butylacetamide.

More rapid addition of the isobutene led to formation of much more of the liquid product without altering significantly the yield of **3**. The liquid material was isolated free of **3** by careful chromatography: nmr (neat) τ 8.2 (m, 1, CH_2), 9.0 (m, 3, CH_3), 5.0 (m, weak) ppm.

In another reaction, isobutene was bubbled slowly into an acetonitrile solution containing equimolar portions of triphenylmethyl perchlorate and of collidine. Little of the liquid oligomer was isolated, though **3** still was formed in about the same yield.

Slow addition of isobutene to acetonitrile and dichloromethane solutions of triphenylmethyl fluoroborate also furnished comparable yields of **3**.

Attempted Reactions of Triphenylmethyl Perchlorate with Other Olefins.—*cis*-2-Butene (15 g, 0.27 mol) was added slowly to a solution of 3.9 g (0.011 mol) of triphenylmethyl perchlorate in 50 ml of acetonitrile as described for the reaction with isobutene. The reaction mixture was worked up in the same manner, but little material was obtained by elution with pentane–benzene.

A reaction was attempted with 2,3-dimethyl-2-butene in the same manner except that the olefin was introduced through a dropping funnel and the acetonitrile solution of triphenylmethyl perchlorate contained an equimolar amount of collidine. No material was eluted with pentane–benzene.

4,4,4-Triphenyl-2-methyl-2-butanol (7).—A solution of 1.82 g (0.0058 mol) of methyl 3,3,3-triphenylpropionate[12] in 20 ml of ether and 20 ml of benzene was added to a Grignard solution prepared from 0.4 g (0.0016 mol) of magnesium and 7 g (0.0049 mol) of methyl iodide in 40 ml of ether. The mixture was stirred and warmed for 1 hr and then left overnight at room temperature. The mixture was poured onto 100 g of ice. The layers were separated, and the ether layer was washed several times with a saturated sodium chloride solution and then with water. The solution was dried (Na_2SO_4) and evaporated, leaving 1.16 g (0.037 mol, 64%) of crude product. Recrystallization from methanol gave an analytical sample of **7**: mp 122–123° (lit.[13] mp 116–119°); nmr τ 2.75 (m, 15, aryl H's), 7.12 (s, 2, CH_2), 9.08 (s, 6, CH_3), and 9.28 (broad singlet, 1, OH) ppm.

Preparation of 1,1-Dimethyl-3,3-diphenylindan (3) from 7.—A sample of **7** (50 mg) was added in small portions to 4 ml of trifluoroacetic acid, and 1 ml of dichloromethane was added. The solvent was evaporated after the reaction had stood overnight at room temperature. The nmr spectrum of the crude, solid residue was identical with that of pure **3**. Recrystallization from 95% ethanol gave **3**, mp 109.5–110.5°. The ir and nmr spectra of this solid were identical with those of the solids obtained from reactions of triphenylmethyl cation salts with isobutene and with *t*-butyl ethers.

In an alternate reaction, a solution of 0.36 g of **7** and 17 mg of *p*-toluenesulfonic acid in 5 ml of benzene was refluxed for 2.5 hr. The solution was washed with 1 ml of a sodium chloride–sodium carbonate solution. The solution was dried ($MgSO_4$), and the solvent was evaporated. The solid residue was recrystallized twice from 95% ethanol to give **8** as white plates: mp 141–144°; nmr (CCl_4) τ 2.90 (s, 15, aryl H's), 3.75 (m, 1, =CH—), 8.15 (m, 3, CH_3), and 8.95 (m, 3, CH_3) ppm. Since elemental analyses were not obtained, the physical constants may be slightly off. The ir and nmr spectra of the crude product before recrystallization also exhibited absorptions of **3**. The spectra of the crude solid obtained from a similar reaction in which the solution was refluxed for 16 hr showed it to be a mixture of **3** and **8** containing significantly more **3** than the mixture from the preceding reaction; nearly pure **3** was obtained as a second crop during recrystallization of the crude product from 95% ethanol. Refluxing a similar benzene solution of *p*-toluenesulfonic acid and **8** led to slow formation of **3**.

Registry No.—Isobutene, 115-11-7; **1**, 14699-91-3; **3**, 10271-32-6.

Acknowledgement.—We are grateful for support of this research by the National Science Foundation and by funds made available by the Alfred P. Sloan Foundation. We are pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Varian A-60 nmr spectrometer and the Nuclide Analysis Associates 12-90-G1 mass spectrometer used in this research. H. R. wishes to thank the John Simon Guggenheim Memorial Foundation for a Fellowship and members of the Department of Chemistry at the University of California at Berkeley for their hospitality at the time that this Note was prepared. We thank Jean Martin and Samuel Wilson for experimental assistance.

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[12] S. M. McElvain and H. F. McShane, Jr., *J. Amer. Chem. Soc.*, **74**, 2662 (1952).

[13] N. C. Deno and E. Sacher, *ibid.*, **87**, 5120 (1965).

The Formation and Reactions of Ferrocenylphenylglyoxal[1]

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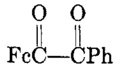
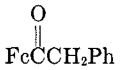
Received July 29, 1968

In this Note, we wish to report the preparation and characterization of ferrocenylphenylglyoxal (**1**) and to discuss briefly some of its chemical reactions.



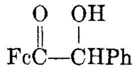
$\mathrm{Fc}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph}$

1



$\mathrm{Fc}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2Ph}$

2



$\mathrm{Fc}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh}$

3

The oxidation of benzyl ferrocenyl ketone (**2**) with activated manganese dioxide[2] in refluxing methylcyclohexane produced variable yields (20–50%)[3] of diketone **1**. A more satisfactory synthesis (95%) of **1** involved the oxidation of mandeloylferrocene (**3**) (from a mixed benzoin condensation of formylferrocene and benzaldehyde)[4] with activated manganese dioxide in refluxing chloroform solution. Although the oxidation of the acyloin **3** proceeded in uniformly higher

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[1] Organometallic π Complexes. XV. Part XIV: M. D. Rausch and A. Siegel, *J. Organometal. Chem.*, **11**, 317 (1968).

[2] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Helms, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

[3] The yields of diketone **1** were dependent upon the activity of manganese dioxide used. Samples of the latter which remained exposed to air for prolonged periods resulted in diminished yields of **1**.

[4] G. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).