0.0094 mol) dissolved in CCl_4 (50 ml) was brominated and decomposed as in method C. The heterogeneous mixture was then refluxed for 2 days, after which the supernatant liquid was examined by infrared, nmr, and gas chromatography. Comparison of these spectra with the corresponding spectra of an authentic sample revealed that the only carbonyl compound produced was methyl isopropyl ketone. The yield of the ketone (38%) was determined by integration of the gas chromatographic peaks. Compounds 31, 33, and 35–36, Table I, were similarly treated, with the results stated therein.

Registry No.—Phenyl trityl ketone, 466-37-5; tetraphenylethylene, 632-51-9; phenyl benzhydryl ketone, 1733-63-7; triphenylethylene, 58-72-0; 2-phenylpropionaldehyde, 93-53-8; *trans*-1-phenyl-1-propene, 873-66-5; methyl isopropyl ketone, 563-80-4; 2-methyl-2-butene, 513-35-9.

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Notes

Synthesis of *dl*-Muscone from Exaltone (Cyclopentadecanone)

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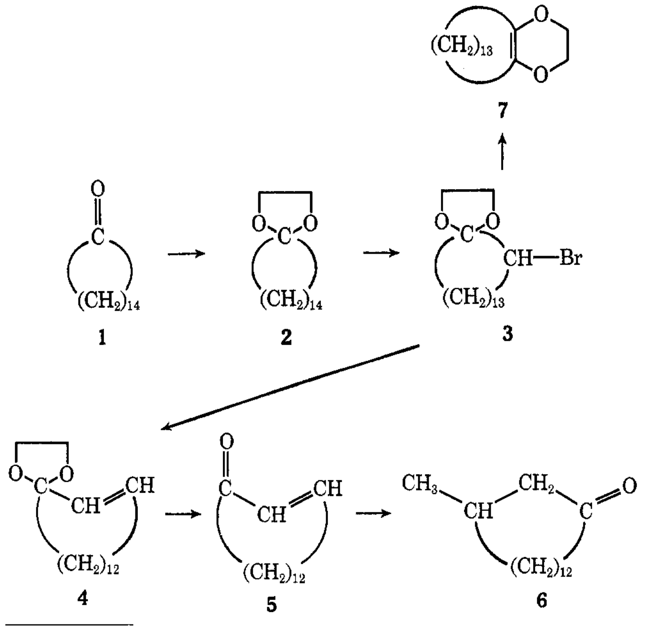
Muscone (6) and exaltone (1) are two similar compounds. The difference is that the former is a natural product;[1] the latter lacks a β-methyl group. Though there is a plethora of publications[2] for the synthesis of 6 from various starting materials, only Ruzicka and Stoll[3] have described the preparation of 6 from 1 in poor yield, The present paper reports an alternate five-step synthesis of *dl*-muscone (6) from exaltone (1) in an overall yield of 60%.



Treatment of 1 with ethylene glycol and *p*-toluenesulfonic acid monohydrate[4] in benzene afforded ketal 2 (98%) which was brominated with phenyltrimethylammonium tribromide[4,5] in tetrahydrofuran for 2 hr at 0° to give 2-bromo ketal 3 (≈100%). Though the treatment of 3 with potassium *tert*-butoxide in either *tert*-butyl alcohol or dimethyl sulfoxide[6] gave only dioxin 7, dehydrobromination of 3 with 1,5-diazabicyclo[4.3.0]non-5-ene[7,8] at 110° for 64 hr furnished the α,β-unsaturated ketal 4 (70%). Mild acid hydrolysis of 4 gave cyclopentadecenone (5) (100%) which on treatment with methyl Grignard in the presence of cuprous chloride and ether[2,9] was smoothly converted to *dl*-muscone (6) (81%).

Experimental Section

Melting points are uncorrected. Gas–liquid chromatography (glc) analyses were performed on an F & M 810 instrument using 5% Carbowax 20M and 5% silicone SE-30 coated on Anakrom ABS (80–100 mesh) packed in stainless steel columns (25 ft × 0.25 in.). The following spectrometers were used: infrared, Beckman IR-5A or Beckman IR-4; nuclear magnetic resonance, Varian HA-100 (CCl_4, TMS as internal standard); mass spectra, CEC Model 21-103 C, and AEI MS 9 for high-resolution spectra. Major mass spectral fragmentation peaks were recorded in decreasing order of intensity except for the molecular ion $(M)^+$ peak which is listed first. Five per cent deactivated silicic acid made by adding 5 ml of water to 95 g of silicic acid (Grace, 100–200 mesh) was used for column chromatography. Anhydrous magnesium sulfate was used as drying agent. Exaltone was purchased from Firmenich, New York, N. Y.

Ethylene Ketal of Cyclopentadecanone (2).—A mixture of 1 (50 g, 0.22 mol), *p*-toluenesulfonic acid monohydrate (4.2 g, 0.022 mol), freshly distilled ethylene glycol (444 ml), and anhydrous benzene (2.7 l.) was refluxed with constant removal of water. After 14 hr of reflux, 14 ml of water was collected. The mixture was cooled, the ethylene glycol layer was separated, and the benzene layer was washed successively with saturated sodium bicarbonate solution and sodium chloride solution and

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[1] Muscone is the principal constituent (1%) of musk pod obtained from the male deer *Moschus moschiferus*.

[2] B. D. Mookherjee, R. Trenkle, and R. R. Patel, *J. Org. Chem.*, **36**, 3266 (1971), and references cited therein.

[3] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, **17**, 1308 (1934).

[4] W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

[5] A. Marquet, M. Dvolaitzky, H. Kagan, L. M. C. Quannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1822 (1961).

[6] P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962).

[7] H. H. Wasserman, D. D. Ketih, and J. Nadelson, *ibid.*, **91**, 1264 (1969).

[8] H. Oediger, H. Kabbe, F. Muller, and K. Either, *Chem. Ber.*, **99**, 2012 (1966).

[9] M. Stoll and K. Commarmont, *Helv. Chim. Acta*, **31**, 554 (1948).

dried. Removal of solvent gave 60.9 g (100%) of **2** which solidified on standing, mp 29.5–30°. Glc (silicone SE-30) showed one major peak (98.4%, **2**) and one minor peak (1.6%, **1**): ir of **2** (neat) 3.4, 3.5, 6.83, 7.2, 7.29, 7.39, 8.0, 8.29, 8.42, 8.6, 8.99, 9.1, 9.25, 9.35, 9.55, 10.55, 10.9, 12.1, 12.7, 14.1 μ; nmr δ 1.32 and 1.5 [two s, 28, $-(CH_2)_{14}-$], 3.89 (s, 4, $-OCH_2CH_2O-$); mass spectrum *m/e* 268 $(M)^+$, 99, 225, 155, 55, 84, 41.

Anal. Calcd for $C_{17}H_{32}O_2$: *m/e* 268.2402. Found: *m/e* 268.2403.

Ethylene Ketal of 2-Bromocyclopentadecanone (3).—To a cold (0°) stirred solution of **2** (60.9 g, 0.228 mol, from the above experiment) in anhydrous tetrahydrofuran (1.5 l.) was added rapidly phenyl trimethylammonium tribromide (85.7 g, 0.228 mol). An orange color was developed which gradually disappeared after 1 hr. The stirring was continued for an additional 1 hr at 0°. The mass was poured into saturated sodium bicarbonate solution (600 ml) and was stirred for 30 min. Most of the tetrahydrofuran was removed under reduced pressure without heating. The aqueous layer was extracted with ether. The ethereal solution was washed with saturated sodium chloride solution and dried. Removal of solvent gave 83 g (107%) of crude bromide **3**. Glc (silicone SE-30) showed a major peak and a minor peak due to **1** and **2**, respectively. Bromide **3** did not elute from the glc column: ir of **3** (crude) 5.89 (C=O of regenerated **1**) and 9.5 μ (–COC– of ketal **3**); nmr δ 1.1–2.1 (broad m with s at 1.32 and a shoulder at 1.3), 2.66 (small t), 3.42 (small t), 3.68 (small t), 3.8–4.36 (m, –CHBr and $-OCH_2CH_2O-$), 4.5–4.7 (small m); mass spectrum *m/e* 346 $(M)^+$ and 348 $(M + 2)^+$.

Anal. Calcd for $C_{17}H_{31}O_2Br$: *m/e* 346.1507. Found: *m/e* 346.1508.

Ethylene Ketal of 2-Cyclopentadecen-1-one (4.)—A 2.5-l. flask equipped with stirrer, reflux condenser, thermometer, and a nitrogen inlet tube was charged with crude bromide **3** (83 g, 0.2 mol, from the previous experiment) and 1,5-diazabicyclo[4.3.0]non-5-ene (89.28 g, 0.72 mol). The mixture was heated at 110° for 64 hr, cooled, and poured into water. The aqueous mixture was extracted with ether. The combined ether extracts were washed successively with water and saturated sodium chloride solution and dried. Removal of solvent gave 56.5 g of crude oil which was chromatographed on deactivated silicic acid (600 g); 10–20% ether in hexane (1.5 l. per fraction) eluted 47.1 g (74.6%) of **4**. Glc (Carbowax 20M) analysis showed one major peak (88%, **4**) and two minor peaks due to **1** (5%) and **2** (7%): ir of **4** (neat) 3.45, 3.5, 6.0, 6.85, 6.9, 7.2, 7.3, 7.4, 7.65, 7.79, 7.99, 8.49, 8.9, 9.5, 10.25, 10.55, 12.4, 13.4, and 13.85 μ; nmr δ 1.1–2.3 (major s at 1.3, and broad m at 1.7 and 2.1, 24, $-CH_2-$), 3.9 (s, 4, $-OCH_2CH_2O-$), 5.1–6.0 (d at 5.3, 1 and m at 5.7, 1, –CH=CHCOO); mass spectrum *m/e* 266 $(M)^+$, 125, 99, 55, 41.

Anal. Calcd for $C_{17}H_{30}O_2$: *m/e* 266.2247. Found: *m/e* 266.251.

2-Cyclopentadecen-1-one (5).—A solution of **4** (46.1 g, 0.17 mol, from the previous experiment) and *p*-toluenesulfonic acid monohydrate (6.65 g, 0.035 mol) in water (100 ml) and acetone (50 ml) was stirred for 16 hr at room temperature. Most of the acetone was removed under reduced pressure, and the residue was poured into water. The aqueous mixture was extracted with ether. The ether extracts were washed successively with water and saturated sodium chloride solution and dried. Removal of solvent under reduced pressure yielded 38.5 g (100%) of crude **5**. Glc analysis (silicone SE-30) showed one major peak (74%, **5**) and one minor peak (26%, **1**): ir of **5** (neat) 3.4, 3.5, 5.82, 5.9, 5.99, 6.15, 6.77, 6.82, 6.9, 7.2, 7.4, 7.8, 8.25, 8.75, 8.85, 9.25, 9.55, 10.2 μ; nmr δ 1.1–2.0 (m, 20 with a s at 1.3, $-CH_2-$), 2.1–2.54 (m, 4, $-CH_2COC{=}CCH_2$), 6.08–7.0 (d, at 6.16, 1 and m at 6.8, 1, –CH=CHCO); mass spectrum *m/e* 222 $(M)^+$ 41, 55, 81, 67, 68.

Anal. Calcd for $C_{15}H_{26}O$: *m/e* 222.1983. Found: *m/e* 222.1986.

***dl*-Muscone (6).**—A solution of **5** (37.5 g, 0.169 mol, from the previous experiment) in anhydrous ether was added slowly over a period of 1 hr to a stirred mixture of methylmagnesium bromide (62 ml, 0.185 mol) and cuprous chloride (11.16 g) in anhydrous ether (750 ml) at 10°. After the addition was completed, the reaction mixture assumed a dark grayish-green color and stirring was continued for 2 hr at 10°. Cold aqueous 10% hydrochloric acid (200 ml) was added slowly, and the organic phase was separated. The aqueous layer was extracted with ether. The combined ethereal solutions were washed successively with saturated sodium bicarbonate solution, water, and saturated sodium chloride solution (50 ml) and dried. Removal of solvent under reduced pressure gave 40.2 g of crude oil which was chromatographed on deactivated silicic acid (600 g): 5% and 7.5% ether in hexane (1 l. per fraction) eluted 32.2 g (81.1%; an overall 61.5% from exaltone **2**) of muscone (**6**). Glc analysis (Carbowax 20M and silicone SE-30) showed one peak. This material was further distilled to obtain 27 g of **6**: bp 100–101° (0.09 mm); ir of **6** (neat) 3.41, 3.5, 5.84, 6.82, 7.09, 7.29, 7.8, 8.35, 8.85, 9.2, 9.45, 9.8, and 14.0 μ; nmr δ 0.92 (d, J = 6 Hz, 3, CH_3CH-), 1.1–2.0 (m, 23, with s at 1.3), 2.1–2.5 (m, 4, $-CH_2COCH_2$); mass spectrum *m/e* 238 $(M)^+$, 41, 55, 85, 69, 71, 43.

(All these spectral data were superimposable with those of natural muscone and also with synthetic *dl*-muscone made from 1,9-cyclohexadecadiene.[2])

Anal. Calcd for $C_{16}H_{30}O$: *m/e* 238.2296. Found: *m/e* 238.2298.

Reaction of 3 with Potassium *tert*-Butoxide.—A mixture of **3** (1.15 g, 0.0033 mol), potassium *tert*-butoxide (1.11 g, 0.01 mol), and anhydrous *tert*-butyl alcohol (20 ml) was refluxed for 20 hr. Most of the solvent was removed under reduced pressure, water (20 ml) was added, and the mixture was extracted with ether. The combined ether extracts were washed with saturated sodium chloride solution and dried. Evaporation of solvent under reduced pressure gave 0.8 g of yellow oil. Glc (Carbowax 20M) gave one major peak due to **7**: ir (neat) 3.42, 3.5, 5.92, 6.9, 7.4, 7.82, 8.09, 8.3, 8.6, 8.7, 9.02, 9.32, 9.85, 10.8, and 11.15 μ; nmr δ 1.2–1.8 (m, 22, with s at 1.35, $-CH_2$), 2.04 (m, 4, $-CH_2C{=}CCH_2$), 3.98 (s, 4, $-OCH_2CH_2O-$); mass spectrum *m/e* 266 $(M)^+$, 99 (base peak).

A solution of **3** (1.15 g) and potassium *tert*-butoxide (1.11 g) in dimethyl sulfoxide (20 ml) was refluxed for 10 hr. After usual work-up, a crude oil (1 g) was obtained. Glc showed a major peak due to **7**.

Anal. Calcd for $C_{17}H_{30}O_2$: *m/e* 266.2295. Found: *m/e* 266.2248.

Registry No.—**1**, 502-72-7; **2**, 184-41-8; **3**, 32247-06-6; **4**, 32247-07-7; **5**, 32247-08-8; **6**, 956-82-1; **7**, 32304-18-0.

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Transannular Ring Closure by Reduction of Cyclooctane-1,5-diones. Synthesis of a Bisnoradamantan-1-ol

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A reasonable approach to the synthesis of the series of theoretically interesting bridgehead olefins **3**[1] appeared to be double bond formation from the glycols **2**, by one of a number of known reactions.[2–4] More-

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[1] For a recent example of a polycyclic molecule with a similar "strained" double bond, see N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968).

[2] E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).

[3] J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, 1593 (1968).

[4] F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, 5223 (1970).