A Simple Synthesis of 2,3-Homotropone

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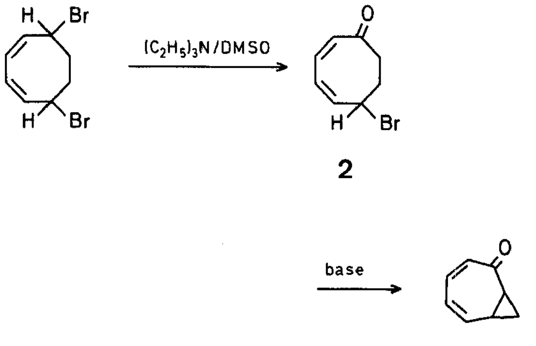
2,3-Homotropone (**1**) was first prepared by Holmes and Pettit starting from cyclooctatetraeneiron tricarbonyl in a 4 stage synthesis[1] (less than 11% over-all yield according to Paquette and Cox[2]). Formation of **1** (21% yield) was also reported as one of five products from the reaction of tropone with diazomethane[3].

We have found that 6-bromo-1-oxocycloocta-2,4-diene (**2**) readily undergoes γ-elimination of hydrogen bromide on treatment with base to give **1** in high yield; this result provides a simple method for the preparation of **1** from cyclooctadienes and 1,3,5-cyclooctatriene.

Bromination of 1,3,5-cyclooctatriene gives 1,6-dibromocycloocta-2,4-diene[4] which, on heating to reflux as crude product with triethylamine (1.1 equiv.) in dimethyl sulfoxide/dichloromethane (3:2), gives **2** in 45% yield and **1** in 7% yield.



2

1

Treatment of **2** with base under various conditions, e.g. triethylamine in dimethyl sulfoxide at 80°, 1,5-diazabicyclo[3.4.0]non-5-ene in refluxing benzene, sodium hydride in refluxing tetrahydrofuran, or potassium hydroxide in methanol at room temperature, yielded **1** in yields of more than 90%. In dimethyl sulfoxide the oxidation product, 1,6-dioxocycloocta-2,4-diene, was not detected.

Thus the isolation of **2** is not necessary for the preparation of **1**; heating of the crude dibromide with excess triethylamine in dimethyl sulfoxide gave **1** in 59% yield. Cycloocta-1,3- and -1,5-diene can also be used as starting materials. The 1,5-diene has been reported to give 1,6-dibromocycloocta-2,4-diene as major product upon treatment with *N*-bromosuccinimide[4]. The mixtures of dibromides thus obtained from the dienes gave **1** in moderate yields: 27% from the 1,3-diene and 32% from the 1,5-diene. In the former case, the major ketonic by-product was 1-oxocycloocta-2,4-diene (presumably arising from 1-bromocycloocta-2,4-diene) and in the latter case, 1-oxocycloocta-2,4,6-triene.

6-Bromo-1-oxocycloocta-2,4-diene (2):

To a solution of 1,3,5-cyclooctatriene (2.12 g, 20 mmol) in dichloromethane (5 ml) was added a solution of bromine (3.20 g, 20 mmol) in dichloromethane (5 ml) with stirring at −50° over a period of 5 min. Dried dimethyl sulfoxide (15 ml, distilled from calcium hydride) and triethylamine (2.21 g, 22 mmol) were added to the solution and the mixture heated to reflux for 1 h. The mixture was then cooled, diluted with water (40 ml), and extracted with dichloromethane (30 ml). The extract was dried with sodium sulfate, the solvent removed (rotary evaporator), and the residual yellow oil subjected to chromatography on silica gel (100 g). Elution with dichloromethane/ethyl acetate (9:1) gave **2** and **1** as a pale yellow oil together with an as yet unidentified ketonic compound (0.12 g); yield of **2**: 1.79 g (45%); yield of **1**: 0.17 g (7%).

Product **1**: The I.R., U.V., and ^{1}H-N.M.R. ($CDCl_3$ and concentrated sulfuric acid) spectra are in accord with those described in Lit.[1].

Product **2**:

I.R. (neat): $\nu_{max} = 1660, 1620, 1594, 1163, 1140, 850, 782, 730\ cm^{-1}$.

^{1}H-N.M.R. (CCl_4, 60 MHz): $\delta = 6.7$—5.8 (m, 4H), 4.70 (m, 1H), 2.9—2.1 ppm (m, 4H).

Mass spectrum: $m/e = 202$ (M^+, 7%), 200 (M^+, 7%), 160 (52%), 158 (56%), 121 (31%), 79 (100%).

2,3-Homotropone (1):

Method A: from 1,3,5-cyclooctatriene: A mixture of the crude dibromide (5.32 g), triethylamine (4.35 g, 43 mmol), and dried dimethyl sulfoxide (20 ml) was heated at 80° for 1 h. The mixture was worked up as described above and the redish residue subjected to chromatography on silica gel (50 g) using dichloromethane/ethyl acetate (95:5) as eluent to give **1**; yield: 1.41 g (59%).

Method B: from cycloocta-1,5-diene: A mixture of cycloocta-1,5-diene (32.4 g, 0.3 mol), *N*-bromosuccinimide (118 g, 0.66 mol), benzoyl peroxide (1.0 g), and carbon tetrachloride (400 ml) was heated under reflux for 2 h. The mixture was then cooled in an ice bath, the succinimide filtered off by suction, and the filtrate washed with warm water, saturated aqueous sodium hydrogen carbonate, water, and dried with sodium sulfate. The solvent was evaporated off, the residue added to dried dimethyl sulfoxide (250 ml) and triethylamine (98 ml, 0.7 mol) and the mixture heated at 80° with stirring for 2 h. The mixture was cooled, diluted with water, and extracted with chloroform (3 × 100 ml). The solvent was evaporated off and the darkish residue distilled in vacuum through a 30 cm column packed with glass tips;

fore-run: yield: 1.6 g; b.p. 35—42°/0.2 torr;

1-oxocycloocta-2,4,6-triene (identified by comparison with authentic material); yield: 2.8 g (8%); b.p. 44—46°/0.2 torr (Lit.[6]: b.p. 89—90°/6 torr;

1; yield: 11.5 g (32%); b.p. 56—57°/0.2 torr (Lit.[2]: b.p. 55 to 56°/0.15 torr).

C_8H_8O	calc.	C 79.97	H 6.71
(120.14)	found	79.69	6.63

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[1] J. D. Holmes, R. Pettit, *J. Amer. Chem. Soc.* **85**, 2531 (1963).

[2] L. A. Paquette, O. Cox, *J. Amer. Chem. Soc.* **89**, 5633 (1967).

[3] L. J. Lusko, K. N. Houk, *Tetrahedron Lett.* **1972**, 1925.

[4] A. C. Cope, C. L. Stevens, F. A. Hochstein, *J. Amer. Chem. Soc.* **72**, 2510 (1950).

[5] A. C. Cope, B. D. Tiffany, *J. Amer. Chem. Soc.* **73**, 4158 (1951).

[6] G. Büchi, E. M. Burgess, *J. Amer. Chem. Soc.* **84**, 3104 (1962).