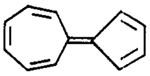
The Reductive Dimerization of Tropylium Ion by Cyclooctatetraene Dianion

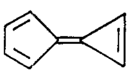
R. W. Murray and M. L. Kaplan

Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey

Received October 7, 1965

An extension of the principles which have led to the prediction of special stability for sesquifulvalene (I)[1] and calicene (II)[2] suggests that an analog involving seven- and eight-membered rings should also receive attention. The compound 5,8-bis(cycloheptatrienylidene)cyclooctatriene-1,3,6 (III) represents such a system. Presumably such a compound would have significant contributions from the polar structure, IV. There appear to be no reports of the prediction or attempted synthesis of III in the literature.


I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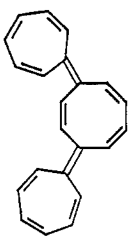
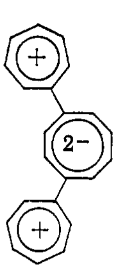
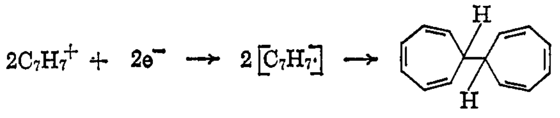

III



IV

We have attempted a synthesis of III involving the reaction of cyclooctatetraene (COT) dianion[3] and 2 moles of tropylium ion as a first step. The synthetic scheme would then involve bromination and dehydrobromination of the anticipated product, 5,8-bis(7-cycloheptatrienyl)cyclooctatriene-1,3,6 (V). The reaction of COT dianion and tropylium bromide afforded, instead, 7,7′-ditropyl (VI) in good yield. This product presumably arises from the reductive dimerization of tropylium ion by COT dianion.



VI

The product was characterized by comparing its properties with those of authentic ditropyl prepared by the method of Doering and Knox.[4] The nmr spectrum of VI consists of a triplet at 3.46,[5] a multiplet at 3.83, a multiplet at 4.83, and a multiplet at 8.16. These absorptions are assigned to the 3,4,3′,4′ olefinic, the 2,5,2′,5′ olefinic, the 1,6,1′,6′ olefinic, and the methine protons, respectively.

Conrow and Radlick have reported[6] another case in which COT dianion apparently acts as a reducing agent. In this case 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-4H-pyran was the product of the reaction of COT dianion and the 2,4,6-trimethylpyrylium cation. These two examples suggest that COT dianion may have general utility as an organic reducing agent.

We are presently attempting other synthetic routes to III, the proposed, new, nonbenzenoid aromatic compound.

Experimental Section

Preparation of 7,7′-Ditropyl. Method A.—Cyclooctatetraene (1.30 g, 0.0125 mole, Aldrich) was added at once to potassium metal (0.78 g, 0.020 g-atom) in 40 ml of tetrahydrofuran (Matheson Coleman and Bell, distilled from CaH_2, bp 66.0–66.5°) and the mixture was magnetically stirred at room temperature, in a N_2 atmosphere, for 45 min. The potassium metal dissolved completely and the resulting solution was violet. Tropylium fluoborate (3.5 g, 0.020 mole) was added as a slurry in 30 ml of tetrahydrofuran. A slight exothermic reaction was observed and stirring was continued until the now pale orange solution had returned to room temperature. Water (25 ml) was added and the reaction mixture was extracted with two 50-ml portions of petroleum ether (bp 30–60°). The combined organic layers were dried ($MgSO_4$) and concentrated on a rotary evaporator. Chromatography on a neutral alumina column (15 g, Woelm) gave 1.31 g (72%) of white, crystalline ditropyl. After one recrystallization from pentane, the infrared and nmr spectra, the melting point (62–63°, Kofler block), and mixture melting point of this substance were essentially identical with authentic ditropyl prepared by the method of Doering and Knox,[4] *i.e.*, the reduction of tropylium ion with zinc metal. The nmr spectrum was taken in carbon tetrachloride solution on a Varian A-60 spectrometer.

Method B.—Cyclooctatetraene (1 g, 0.0104 mole, Aldrich) in 10 ml of dry ethyl ether was magnetically stirred at reflux temperature, under N_2, for 1 hr with lithium powder (0.121 g, 0.0175 g-atom). After all the lithium had dissolved, the solution was cooled to room temperature, tropylium bromide (3.0 g, 0.0175 mole) was added, and the mixture was allowed to stir for 15 hr at room temperature. Hydrochloric acid (25 ml, 1 *N*) was added to the ice-cold reaction mixture. The brown organic layer was separated and the aqueous layer was extracted twice with 25-ml portions of ethyl ether. The combined ether layers were washed once with aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated on a rotary evaporator. Chromatography on an alumina (neutral, Woelm) column gave 0.46 g (29%) of ditropyl, which was characterized as in method A.

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(1) J. F. Tinker, *J. Chem. Phys.*, **19**, 981 (1951). A report of the synthesis of I is given by H. Prinzbach and W. Rosswog, *Angew. Chem.*, **73**, 543 (1961).

(2) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952). Although derivatives of II have been prepared [see, for example, H. Prinzbach, D. Seip, and U. Fischer, *Angew. Chem.*, **77**, 258 (1965)], the synthesis of the parent compound has not been reported.

(3) (a) W. Reppe, O. Schlichting, K. Klagen, and T. Toepel, *Ann.*, **560**, 1 (1948); (b) A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950); (c) T. J. Katz, *ibid.*, **82**, 3785 (1960).

(4) W. v. E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(5) Chemical shift values given are τ values with tetramethylsilane as external standard.

(6) K. Conrow and P. C. Radick, *J. Org. Chem.*, **26**, 2260 (1961).

Amine Haloboranes. The Reaction of N-Halosuccinimide with Amine Boranes

James E. Douglass[1]

Department of Chemistry, University of Kentucky,
Lexington, Kentucky

Received September 14, 1965

While several methods for the preparation of amine haloboranes have been reported[2–4] in the past several years, each procedure requires either a not too readily

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(1) Department of Chemistry, Marshall University, Huntington, W. Va. 25701.

(2) H. Noth and H. Beyer, *Ber.*, **93**, 2251 (1960).

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(4) N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1064 (1964).