The Reductive Dimerization of Tropylium Ion by Cyclooctatetraene Dianion

R. W. MURRAY AND M. L. KAPLAN

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

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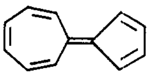
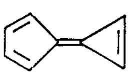
An extension of the principles which have led to the prediction of special stability for sesquifulvalene (I)[1] and calicene (II)[2] suggests that an analog involving seven- and eight-membered rings should also receive attention. The compound 5,8-bis(cycloheptatrienylidene)cyclooctatriene-1,3,6 (III) 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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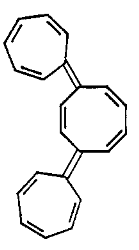
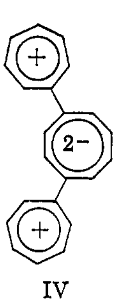
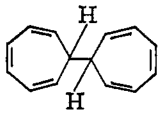

III



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.

$$2C_7H_7^+ + 2e^- \rightarrow 2[C_7H_7\cdot] \rightarrow$$



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

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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).

[3] B. M. Mikhailov, T. A. Shchegoleva, and V. D. Sheludyakov, *Izv. Akad. Nauk USSR, Otd. Khim. Nauk*, 816 (1963).

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

TABLE I

AMINE HALOBORANES, $R_3N\text{-}BH_2X$

Compound	R_3N	X	Mp, °C	ν_{BH}, cm^{-1}	Formula	B, % Calcd	B, % Found	N, % Calcd	N, % Found	X, % Calcd	X, % Found
IIa	$(CH_3)_3N$	Cl	83[a]	2440 2340							
IIb	$(CH_3)_3N$	Br	66–67[b]	2460 2330							
IIc	$C_6H_5CH_2N(CH_3)_2$	Cl	76–77	2420 2340	$C_9H_{15}BClN$	5.90	6.05	7.64	7.63	19.32	19.64
IId	$C_6H_5CH_2N(CH_3)_2$	Br	66	2450 2350	$C_9H_{15}BBrN$	4.75	4.88	6.15	6.31	35.06	34.82
IIe	$C_5H_{10}NCH_3$	Cl	49–50	2420 2360	$C_6H_{15}BClN$	7.32	7.21	9.50	9.46	24.04	23.70
IIf	$C_5H_{10}NCH_3$	Br	38–40	2420 2360	$C_6H_{15}BBrN$	5.64	5.37	7.30	7.34	41.64	41.47

[a] Lit.[2] mp 85°. [b] Lit.[2,3] mp 67°.

available starting material or the use of strong acids or high temperatures. We wish to report that the reaction of N-bromo- or N-chlorosuccinimide with amine boranes (I) in benzene affords a convenient method for preparing amine haloboranes (II) under relatively mild conditions (eq 1).

$$\underset{\text{I}}{R_3NBH_3} + (CH_2CO)_2N\text{—}X \xrightarrow{C_6H_6} \underset{\text{II}}{R_3NBH_2X} + (CH_2CO)_2NH \quad (1)$$

As a typical example, N-bromosuccinimide reacts quite rapidly with trimethylamine borane at room temperature to give trimethylamine bromoborane in yields of 65–70%.[5] The B-chloro and B-bromo derivatives of N,N-dimethylbenzylamine borane and N-methylpiperidine borane were also synthesized, and were characterized by their infrared spectra and elemental analyses (Table I).

It is well established that allylic and benzylic bromination with N-bromosuccinimide is a free-radical chain reaction[6] in which the bromine atom functions as the chain carrier.[7] In the present work, however, it seems unlikely that a radical mechanism is involved, for the following reasons: (1) there is no detectable induction period; and (2) the reaction proceeds rapidly without irradiation or added peroxide. An ionic mechanism (eq 2 and 3), with N-halosuccinimide serving

$$X_2 + H\text{—}BH_2NR_3 \longrightarrow HX + X\text{—}BH_2NR_3 \quad (2)$$

$$(CH_2CO)_2N\text{—}X + HX \longrightarrow (CH_2CO)_2NH + X_2 \quad (3)$$

as a source for a low steady-state concentration of halogen, is proposed as a working hypothesis. Circumstantial evidence for the presence of molecular halogen as an intermediate is the appearance of a transient yellowish orange color when a solution of N-bromosuccinimide is added to a solution of an amine borane.

The only limitation of the reaction encountered so far is the failure of aromatic heterocyclic amine boranes, such as those of pyridine and quinoline, to react cleanly with N-halosuccinimides. A mixture of products results, the composition of which is being investigated.

Experimental Section[8]

Materials.—N-Bromo- and N-chlorosuccinimide were purified by rapid recrystallization from hot water, followed by drying over phosphorus pentoxide in a vacuum desiccator. Trimethylamineborane was purified by vacuum sublimation.

N,N-Dimethylbenzylamine Borane.—Diborane (*ca.* 0.06 mole) was passed into a solution of N,N-dimethylbenzylamine (15 g, 0.012 mole) dissolved in 100 ml of dry tetrahydrofuran. After stripping off the solvent from the reaction mixture on the rotary evaporator, the solid residue was recrystallized twice from benzene–Skellysolve B to afford 11.7 g (69%) of fine white needles melting at 104–105°.

Anal. Calcd for $C_9H_{16}BN$: B, 7.26; N, 9.40. Found: B, 7.41; N, 9.49.

N-Methylpiperidine Borane.—Following the procedure given above and starting with 9.9 g (0.11 mole) of N-methylpiperidine, 9.7 g (86%) of product was obtained boiling at 105–107° at 14 mm, fp 23.5°.

Anal. Calcd for $C_6H_{16}BN$: B, 9.57; N, 12.37. Found: B, 9.32; N, 12.47.

Preparation of Amine Haloboranes IIa–f.—To a solution of 20 mmoles of the amine borane in 25 ml of dry benzene was added slowly a solution of 20 mmoles of N-halosuccinimide dissolved in 150 ml of dry benzene. After the addition was complete, the mixture was refluxed gently for 2 hr during which time a white precipitate formed. The precipitate was filtered off from the cooled reaction mixture, washed with benzene, and dried. The material was identified as succinimide by its melting point and infrared spectrum. The filtrate was reduced to *ca.* one-third its original volume, and the additional small amount of succinimide which crystallized was filtered off. The total yield of succinimide was 90–95%.

Evaporation of the remaining solvent left a white solid residue, which was recrystallized from carbon tetrachloride–hexane; yields of pure amine haloboranes were 60–75%. See Table I for physical properties and elemental analyses.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation.

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[5] It was found to be desirable to use sufficient solvent to dissolve all of the N-halosuccinimide, otherwise much reduced yields were obtained.

[6] H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863, 5404 (1959); *J. Org. Chem.*, **24**, 1577 (1959).

[7] (a) F. L. J. Sixma and R. H. Riem, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **B61**, 183 (1958); (b) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961); (c) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963); (d) G. A. Russell and K. M. Desmond, *ibid.*, 3139 (1963); (e) R. E. Pearson and J. C. Martin, *ibid.*, 3142 (1963).

[8] Melting points were determined on a calibrated Fisher-Johns block; boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 21 instrument. Elemental analyses were performed by Crobaugh Laboratories, Charleston, W. Va.