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Disodium and dipotassium derivatives of 1,6-dinitrocyclooctatetraene (substrates) react with benzenediazo compounds (reagents) in THF to yield bis(azo)- or nitro(azo)-cyclooctatetraenes, the first cyclooctatetraene arylazo derivatives. Structures of the azo compounds are established by conventional methods and confirmed by X-ray crystallography. Together with the main products of electrophilic substitution, products of substrate-to-reagent electron transfer are formed. The electron-transfer products predominate with DMSO instead of THF as a solvent. The difference is apparently a result of ion-pair disintegration in the case of the substrate reactions when DMSO, a strong dissociating solvent, is used.

Introduction

The present work describes the study of alkali metal compounds of nitro and azoxy derivatives which exhibit distinct organometallic character and differ fundamentally in reactivity from their respective anion-radicals and dianions which have separate alkali-metal counterions.^{2,3} Here we focus on the disodium and dipotassium derivatives of 1,6-dinitrocycloocta-1,3,5,7-tetraene **1**.

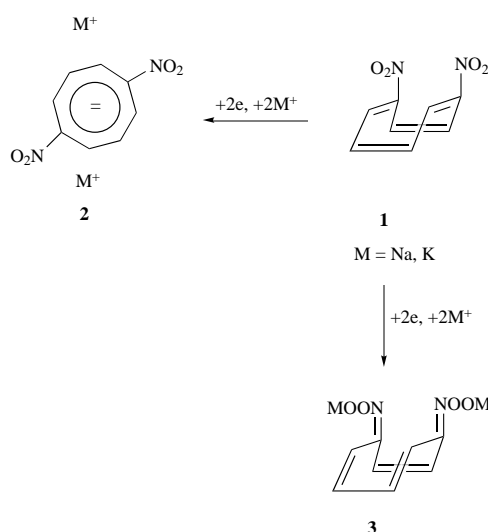
The neutral molecule of **1** has a boat conformation with the two nitro groups located above the boat.⁴

For the di(Na/K) derivative of **1**, planar and non-planar structures are theoretically possible. The planar form **2** is characterized by delocalization of the two excess electrons in the eight-membered ring. The same manner of delocalization is characteristic for the di(Na/K) derivative of unsubstituted cyclooctatetraene (COT) and dimethyl-COT.⁵ The non-planar form **3** requires fixation of the two excess electrons at the two nitro groups blocked by two alkali metals (see Scheme 1).

Conditions for existence of forms **2** and **3**

The di(Na/K) derivatives of **1** were prepared by means of interchange between **1** and di(Na/K) derivatives of COT in tetrahydrofuran (THF). An alternative approach consisted of treatment of 1,4-dinitrocycloocta-2,5,7-triene with (Na/K) methoxides in methanol.

By means of spectral [IR, NMR (¹H, ¹³C)] methods, we earlier found that form **3** became stable in non-dissociating solvents.⁵ In other words, the salts of the dianion of **1** exist in the form of ion pairs, and the excess negative charges are localized primarily on the nitro groups. In dissociating solvents, the ion pairs are broken up, and free ions are formed. This leads to a considerable shift of electron density in the eight-membered ring, see structure **2**.⁶ We had concluded in our earlier work⁶ that the difference between forms **2** and **3** must be reflected in their reactivity. The increase in delocalization of the excess electrons, which is a consequence of dissociation of the ion pairs, must lead to an increase in the level of the donor properties of the substrates. Thus, when the free dianion **2** is treated with electrophiles, it will more readily give up electrons than it will enter into electrophilic substitution. The characteristic reaction of electrophilic substitution of an *aci*-nitro group (NOO⁻M⁺), in contrast, should proceed more readily in non-dissociating solvents, when the substrates act as the ion pairs **3**.⁶



Scheme 1

The aim of our present study was to verify the prediction for the case of azo coupling and, if successful, to obtain new arylazo derivatives of cyclooctatetraene.

Interaction between di(Na/K) derivatives of **1** and benzenediazo cations

In THF or 1,2-dimethoxyethane (DME) the disodium or dipotassium derivative of **1** reacts with benzenediazo cations in two ways. One of them, the minor, is one-electron reduction of the cations. It results in N₂ evolution and formation of **1** and benzene derivatives RC₆H₅ (see Scheme 2 and Table 1).

This reaction proceeds to 10–20% only, whereas the main route is the formation of bis(azo) and nitro(azo) derivatives of COT. All appearances suggest that the key stage of the reaction is ipso-coupling, with intermediates **4** and **5** probably being formed (see Scheme 3).

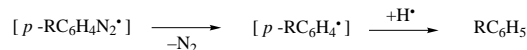
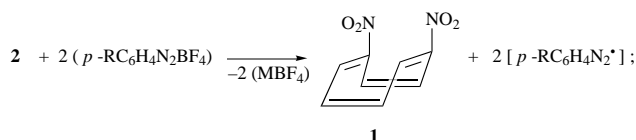
Alkali nitrite is cleaved from the intermediate **4**, while dinitrogen tetroxide is liberated from the intermediate **5**. At the same time, the cyclooctatriene ring is transformed into a cyclooctatetraene ring to give the final products **6** and **7**. Transformation of **5** into **6** is also possible (with elimination of *p*-RC₆H₄N₂NO₂).

Mono **6a–c** and bis(azo) derivatives **7a–c** are obtained together, irrespective of the stoichiometric relationship between the reagents and the substrate. Under similar conditions, yields

† This work was initially presented in the VI International Conference on Organic Synthesis.¹

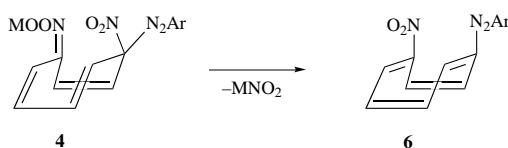
Table 1 Interaction between disodium 1,6-dinitrocyclooctatetraene and tetrafluoroborates of diazo cations with general formula p -RC₆H₄N₂BF₄ (substrate:reagent ratio, 1:2; reaction temperature is 25 °C)

Reagent (R)	Solvent	Yield (%)				
		N ₂	RPh	1	6	7
NMe ₂	THF	8	6	4	88	0
	DMSO	42	21	36	27	0
OMe	THF	12	4	5	57	26
SCN	THF	18	15	14	38	34
NO ₂	THF	22	18	14	30	39
	DMSO	71	53	52	6	4



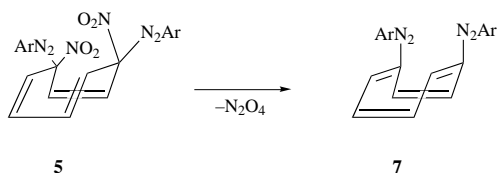
M = Na, K; R = NO₂, SCN, OMe, NMe₂

Scheme 2



Ar = p -RC₆H₄

M = Na, K; R = a, NO₂; b, SCN; c, OMe; d, NMe₂



Ar = p -RC₆H₄

R = a, NO₂; b, SCN; c, OMe;

Scheme 3

of nitroazo compounds **6** increase and yields of bis(azo) compounds **7** decrease along with a decrease in the acceptor ability of the substituent R in the benzenediazo cation. Where R = NMe₂, only monosubstitution takes place with formation of product **6d**. All the above mentioned data are collected in Table 1. The coupling activity of aryldiazo cations drops with a change of R from acceptor to donor.

The 1-nitro-6-benzeneazo derivatives **6a–d** and 1,6-bis(benzeneazo) derivatives **7a–c** formed are crystals with bright colours from yellow to brown. They are air-stable, soluble in organic solvents (acetone, benzene, chloroform) and have sharp mps (see Tables 2 and 3).

Elemental analytical results are compatible with the structural formulae of **6** and **7**. The mass spectra of all the compounds prepared show molecular ion peaks (M⁺) with intensities in the range 0.4–5% of the total ion current. The major fragmentation pathways for the M⁺ are related to cleavage of the bonds between the nitrogen and carbon atoms of the

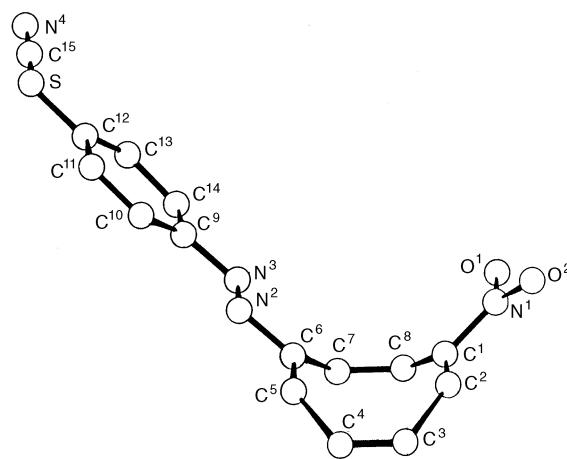


Fig. 1

COT rings; this corresponds to elimination of (M-NO₂)⁺ and (M-RC₆H₄N₂)⁺ fragments. Peaks of the (RC₆H₄)⁺ ion are the most intense in each case.⁷ Our preliminary work⁷ gives a full interpretation of the mass spectra of compounds **6** and **7**.

From the ¹H NMR spectra of compounds **6** and **7**, it was possible to identify the AA', BB' signals of the phenyl protons with their characteristic 9 Hz coupling; similarly signals from the proton-containing benzene substituents were also identifiable (see Table 2). The eight-membered ring protons, however, showed broad signals in the region of δ 6–8. The line widening resulted from very fast interchange between the 1,6- and 1,4-valence isomers at ambient temperature (25 °C).

To complete the structural proof, an X-ray analysis was performed for 1-nitro-6-(4-thiocyanatobenzeneazo)cycloocta-1,3,5,7-tetraene as a typical example. Published separately,⁴ the structure is depicted in Fig. 1.

The formation of the products in Scheme 3 have also been demonstrated. Sodium or potassium nitrite was shown to be present by IR spectroscopy in the residue from the reaction. The presence of dinitrogen tetroxide in the reaction mixture leads to formation of tarry products as minor components. The formation of N₂O₄ was revealed by the radical nitration of a minor electron-transfer product when disodium 1,6-dinitrocyclooctatetraene reacted with p -methoxybenzenediazonium tetrafluoroborate (in air, THF as a solvent) to give a new nitro compound (see Scheme 4).

Product **8** was isolated in 6% yield, and its structure was established by X-ray analysis.⁸ p -Methoxyphenyl radicals (produced by electron transfer to the diazo cation from the disodium derivative of **1**) are likely to form p -methoxyphenol after aerial oxidation. This then scavenges dinitrogen tetroxide to give 4-methoxy-2-nitrophenol **8**. *ortho*-Nitration with respect to the hydroxy group rather than the methoxy group is preferred because of stabilization of the final product **8** by intramolecular hydrogen bonding between the NO₂ and OH. If the reaction is conducted under argon, nitro-product formation is suppressed.

It is unnecessary to conduct the reaction between the dialkali compound **1** and a diazo salt under an argon atmosphere. Moreover, without an argon flow, it is possible to collect and estimate the volume of nitrogen evolved. The reaction was considered to be complete when the evolution of nitrogen gas had ceased.

As seen from Table 1, the maximum yield of nitrogen (22%) is observed for the substrate p -NO₂C₆H₄N₂BF₄ whilst the minimum (8%) occurs for the substrate p -Me₂NC₆H₄N₂BF₄. Substrates with *para* substituents, OMe and SCN, occupy a middle position (12 and 18%). All comparisons are referred to with THF as the solvent.

With DMSO instead of THF there is a sharp increase in nitrogen elimination along with yields of RC₆H₅. At the same

Table 2 Cyclooctatetraene azo compounds obtained according to Table 1

Azo compound	R	Mp/°C [solvent]	Found (%)	Empirical formula	Calc. (%)	δ_{H} /ppm
6a	NO ₂	170 [benzene]	C 56.17 H 3.41 N 18.80	C ₁₄ H ₁₀ N ₄ O ₄	C 56.37 H 3.53 N 18.79	8.44 (AA', 2H) 8.00 (BB', 2H)
6b	SCN	131.5 [benzene]	C 58.00 H 3.00 N 17.98 S 10.26	C ₁₅ H ₁₀ N ₄ O ₂ S	C 58.06 H 3.23 N 18.06 S 10.32	7.94 (AA', 2H) 7.80 (BB', 2H)
6c	OMe	122.5 [diethyl ether]	C 63.54 H 4.40 N 14.80	C ₁₅ H ₁₃ N ₃ O ₃	C 63.60 H 4.59 N 14.84	7.83 (BB', 2H) 7.08 (AA', 2H) 3.93 (OMe, s, 3H)
6d	NMe ₂	152.5 [ethyl acetate]	C 64.72 H 5.22 N 18.89	C ₁₆ H ₁₆ N ₄ O ₂	C 64.86 H 5.41 N 18.92	7.56 (BB', 2H) 6.80 (AA', 2H) 3.10 (NMe ₂ , s, 6H)
7a	NO ₂	186 [benzene]	C 59.69 H 3.41 N 20.88	C ₂₀ H ₁₄ N ₆ O ₄	C 59.70 H 3.48 N 20.90	8.42 (AA', 4H) 8.00 (BB', 4H)
7b	SCN	201 [acetone]	C 61.86 H 3.10 N 19.69	C ₂₂ H ₁₄ N ₆ S ₂	C 61.97 H 3.29 N 19.72	7.92 (AA', 4H) 7.80 (BB', 4H)
7c	OMe	178, with decomp. [benzene]	C 70.90 H 5.26 N 15.89	C ₂₂ H ₂₀ N ₄ O ₂	C 70.97 H 5.38 N 15.05	7.82 (BB', 4H) 7.08 (AA', 4H) 3.93 (OMe × 2, s, 6H)

Table 3 Absorption bands in the electronic spectra of cyclooctatetraene azo compounds obtained according to Table 1

Azo compound	R	λ_{max} /nm	$\epsilon \times 10^4/\text{l mol}^{-1} \text{cm}^{-1}$
6a	NO ₂	306, 356	2.20, 1.42
6b	SCN	236, 323	0.88, 1.06
6c	OMe	248, 342	1.74, 1.95
6d	NMe ₂	257, 460	1.46, 2.10
7a	NO ₂	304, 364	3.60, 2.04
7b	SCN	236, 322, 398	1.76, 2.22, 1.25
7c	OMe	250, 342, 400	2.22, 3.06, 2.76

time, substitution is suppressed. There is a significant difference in the dissociating power of these two solvents (relative permittivities at 293 K are equal to 7.4 and 49, respectively).

Experimental

Preparation of dipotassium (disodium) 1,6-dinitro-COT

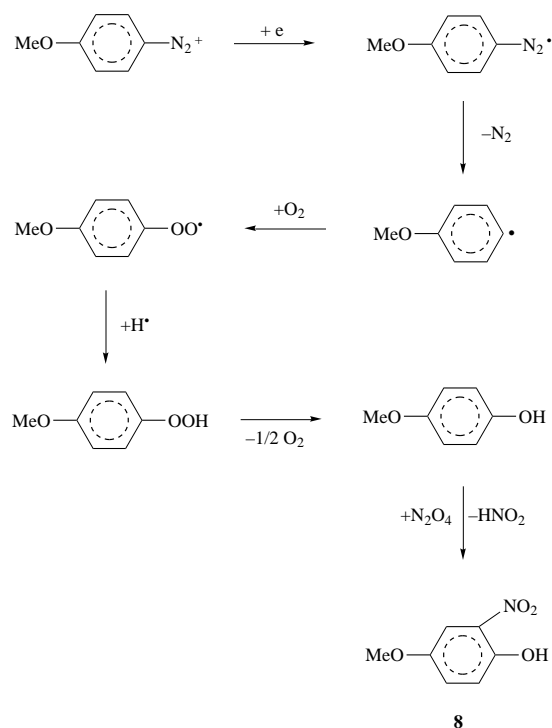
Method 1. A filtered solution of freshly prepared dipotassium COT [from COT (1.04 g) and K (0.95 g)] in THF (40 ml) was added to a solution of 1,6-dinitro-COT (1.94 g, 0.01 mol)⁹ in THF (20 ml) at -40°C under argon. The reaction mixture was stirred at -40°C for 30 min after which the temperature was raised to 25°C . A yellow precipitate of **3** was formed and this was filtered off, washed twice with cold THF, and dried *in vacuo* over phosphorus pentoxide to yield a dry solid (2.6 g) (Found: C, 35.30; H, 2.24; N, 10.22; K, 28.05. Calc. for C₈H₆K₂N₂O₄: C, 35.12; H, 2.32; N, 10.14; K, 27.71%).

The disodium derivative of 1,6-dinitro-COT was obtained in the same manner from disodium COT (Found: C, 40.22; H, 2.31; N, 11.53; Na, 18.92. Calc. for C₈H₆N₂Na₂O₄: C, 40.00; H, 2.50; N, 11.67; Na, 19.17%).

Method 2. A solution of 1,4-dinitrocycloocta-2,5,7-triene¹⁰ (1.96 g, 0.01 mol) in THF (40 ml) was stirred with dry potassium methoxide (1.41 g, 0.02 mol) at -20°C for 20 min and then warmed to 25°C over 30 min. Dipotassium 1,6-dinitro-COT was formed as a bright yellow precipitate which was treated as described above. The dry solid was obtained in 94% yield (2.55 g). The disodium analogue was prepared with sodium methoxide.

The elemental composition and spectra of the (Na/K) derivatives obtained by methods 1 and 2 were identical.

In method 2, 1,4-dinitrocyclooctatriene used as a starting

**Scheme 4**

material was synthesized by nitration of COT with N₂O₄. The resultant compound was purified by procedures given in ref. 10 to give white crystals which were dried *in vacuo* (no more than 1 h).

Interaction between the dipotassium or disodium derivative of 1,6-dinitro-COT and benzenediazonium tetrafluoroborates: a typical procedure

A dry tetrafluoroborate (0.01 mol) was slowly added to a suspension of the dipotassium derivative **3** (1.36 g) or disodium derivative **3** (1.20 g, 0.05 mol) in THF or DME (40 ml). When DMSO was used as a solvent, 10 ml were utilized to dissolve substrate **3** and 20 ml to dissolve the diazo salt. The reaction mixture was stirred over 30 min at 25°C . Nitrogen was evolved in the course of the reaction and when this ceased the reaction

mixture was stirred for a further 30 min and then filtered; a small quantity of this filtrate was examined by GLC (see below). The remaining filtrate was concentrated to 25% of its original volume. The resulting precipitate was collected and, in solution, subjected to chromatography (22 × 600 mm silica gel column; eluent hexane–ethyl acetate, 3 : 1).

The solid resulting from filtration of the reaction mixture was treated with cold acetone (3 × 10 ml), dried and analysed by means of IR spectroscopy and qualitative analytical methods. The salts MNO_2 and MBF_4 (M = Na, K) were shown to be components of the solid, although their yields were not determined.

The yields of 1,6-dinitro-COT **1**, its azo derivatives **6** and **7**, nitrogen gas, and benzenes, RC_6H_5 , are given in Table 1. Tables 2 and 3 show the analytical data upon which identification of the azo products **6** and **7** was established.

Quantities of RC_6H_5 were determined by a GLC method with authentic standard materials introduced into the mixtures being analysed. Nitrogen was used as a carrier gas in all cases. For anisole and *N,N*-dimethylaniline, a stainless-steel column (3 × 3700 mm) was used. The stationary phase was PEG-20M on silanized Chromatone N-AW, 40–60 mesh. For phenyl thiocyanate and nitrobenzene, a glass column (2 × 2000 mm) was employed. In this case, the stationary phase was 5% SE-30 on silanized Chromatone N-AW-DMCS, 20–25 mesh.

^1H NMR Spectra were obtained on a Bruker WP-200 instrument, using $(\text{CD}_3)_2\text{CO}$ as a solvent with SiMe_4 as a standard.

Electronic absorption spectra were recorded using a Specord UV-VIS spectrometer and a cuvette of 1 cm diameter with MeOH as solvent and with 10^{-3} mol l^{-1} concentrations of the azo compounds.

References

- 1 Z. V. Todres, G. Ts. Hovsepyan, in Abstracts of papers of the VI International Conference on Organic Synthesis, August 10–15, 1986, Moscow, Russia.
- 2 Z. V. Todres, *J. Organomet. Chem.*, 1992, **441**, 349.
- 3 Z. V. Todres, S. P. Avagyan and D. N. Kursanov, *J. Organomet. Chem.*, 1975, **97**, 139.
- 4 Z. V. Todres, G. Ts. Hovsepyan, V. I. Bakhmutov, A. Yu. Kosnikov, S. V. Lindeman and Yu. T. Struchkov, *Zh. Org. Khim.*, 1989, **25**, 75 (in Russian) (*Chem. Abstr.*, 1989, **111**, 77532t).
- 5 G. J. Fray and R. G. Saxton, *The Chemistry of Cyclo-octatetraene and Its Derivatives*, Cambridge University Press, London, 1978, p. 48.
- 6 Z. V. Todres, G. Ts. Hovsepyan, I. A. Garbuzova, I. V. Stankevich and V. I. Bakhmutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1969 (in Russian) (*Chem. Abstr.*, 1988, **108**, 204147m).
- 7 D. V. Zagorevskii, G. Ts. Hovsepyan and Z. V. Todres, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1182 (in Russian) (*Chem. Abstr.*, 1988, **108**, 204118c).
- 8 Z. V. Todres, G. Ts. Hovsepyan, A. Yu. Kosnikov, S. V. Lindeman and Yu. T. Struchkov, *Zh. Org. Khim.*, 1988, **24**, 2567 (in Russian) (*Chem. Abstr.*, 1989, **111**, 96744e).
- 9 Podgornova, E. S. Lipina and V. V. Perekalin, *Zh. Org. Khim.*, 1975, **11**, 213 (in Russian) (*Chem. Abstr.*, 1975, **82**, 139464r).
- 10 H. Shechter, J. J. Gardikes, T. S. Cantrell and G. V. D. Tiers, *J. Am. Chem. Soc.*, 1967, **89**, 3005.

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