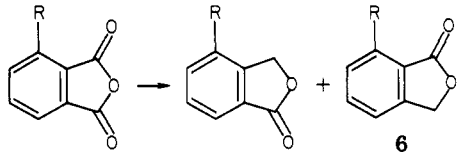
Table II. Reductions of 4



4 5 6

R	reagent	% yield (5 + 6)	% 5	% 6
OCH_3 (4a)	$NaBH_4$	80-93[a]	53 ± 3	47 ± 3
	$LiBH(Et)_3$	76	50	50
	L-Selectride	83	10	90
CH_3 (4b)	$NaBH_4$[b]	95	56	44
	L-Selectride	91	15	85

[a] Several reductions were carried out with $NaBH_4$. [b] Excess $NaBH_4$ must be avoided in this case, as it leads to overreduction to diol, in a reaction that shows some selectivity, diminishing the percentage of **5b** relative to **6b**. The value shown in the table was obtained by using the stoichiometric amount of hydride.

Analyses of lactone mixtures were carried out on the crude products by using ^1H NMR (Varian T-60). The percentage compositions were determined by integration of the sharp singlets due to the methoxy protons in **2**, **3**, **5a**, and **6a**, and the methyl protons of **5b**,**6b** and checked by comparison of the benzylic absorptions where these were distinguishable. The values given in the Tables I and II have the error limits usual to this method of analysis.

Reduction Procedures. Reactions were carried out by using 0.5 g of anhydride, added to a mixture of 1 molar equiv (100% excess) of $NaBH_4$ in 10 mL of THF, and the slurry was refluxed for 2 h. The solvent was removed by rotary evaporation, and 6 N HCl (2.5 mL) was added to decompose excess hydride. The acidic solution was extracted 3 times with small volumes of CH_2Cl_2, and the combined organic phase was dried (Na_2SO_4) and evaporated. Toluene or chlorobenzene (ca. 15 mL) was added, and distilled to effect dehydration; the last traces of solvent were removed by vacuum evaporation, the residue weighed, and a homogeneous sample taken for analysis.

L-Selectride (1 M in THF) reductions were done on the same scale in THF, usually at ambient temperature, for 2 h, using 10% excess of the hydride (a twofold excess of the reagent did not affect yield or composition of products). Approximately 2 mL of 3 N NaOH was added followed by 3 mL of 30% H_2O_2 (vigorous, ice bath needed with dropwise addition). The mixture was acidified with 6 N HCl and rotary evaporated to remove the THF. The remaining slurry/solution was saturated with NaCl and extracted with CH_2Cl_2 as above.

Lactone Identification. Individual isomers were isolated by silica gel chromatography (pentane/CH_2Cl_2) and/or recrystallization and had the following characteristics.

4-Methoxyphthalide: mp 126-128 °C (lit.[12] mp 127 °C); NMR ($CDCl_3$) δ 3.90 (OCH_3), 5.24 (CH_2); IR ($CHCl_3$) 1764 cm^{-1}.

7-Methoxyphthalide: mp 104-106 °C (lit.[13] mp 103.5-105 °C); NMR δ 4.00 (OCH_3), 5.22 (CH_2); IR 1761 cm^{-1}.

4-Methylphthalide: mp 69-70.5 °C (lit.[14] mp 69-70 °C; NMR[15] δ 2.39 (CH_3), 5.27 (CH_2); IR 1760 cm^{-1}.

7-Methylphthalide: mp 87-88 °C (lit.[14] mp 85-87 °C); NMR[15] δ 2.69 (CH_3), 5.27 (CH_2); IR 1752 cm^{-1}.

1-Methoxy-3-(hydroxymethyl)-2-naphthoic Acid γ-Lactone (3): mp 137-139 °C (lit.[16] mp 138 °C); NMR δ 4.33 (s, 3, OCH_3), 5.30 (d, J = 1.3 Hz, 2, CH_2, irradiation of this peak causes sharpening of some signals in the aromatic region), 7.35-8.45 (m, 5, arom); IR ($CHCl_3$) 1761 cm^{-1} (lit.[16] 1757 cm^{-1}); mol wt 214.0627 (calcd 214.0630). We note that our NMR and IR data do not coincide with the values given by Kraus et al.[17]

4-Methoxy-3-(hydroxymethyl)-2-naphthoic Acid γ-Lactone (2): mp 164-166 °C (lit.[16] mp 168 °C); NMR δ 4.13 (s, 3, OCH_3), 5.65 (s, 2, CH_2), 7.5-8.4 (m, 5, arom); IR 1756 cm^{-1}.

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Registry No. **1**, 60678-31-1; **2**, 79069-93-5; **3**, 33295-75-9; **4a**, 14963-96-3; **4b**, 4792-30-7; **5a**, 4792-33-0; **5b**, 2211-83-8; **6a**, 28281-58-5; **6b**, 2211-84-9.

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Synthesis and Reactions of 11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene[1]

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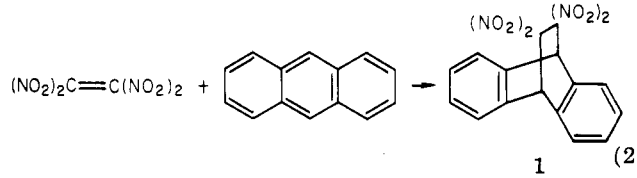
We reported recently[2] that hexanitroethane undergoes elimination of dinitrogen tetraoxide in refluxing benzene (eq 1). When this reaction was carried out in the presence

$$(NO_2)_3CC(NO_2)_3 \rightarrow [(NO_2)_2C{=}C(NO_2)_2] + N_2O_4 \quad (1)$$



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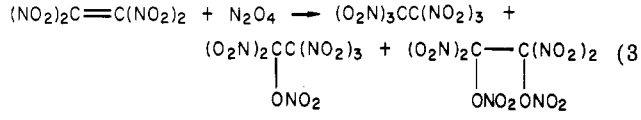

(3)

of a diene or an anthracene derivative, the corresponding Diels-Alder adduct derived from tetranitroethylene was isolated; anthracene gave 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (**1**). In the absence of such a trapping agent, hexanitroethane gives simple gaseous decomposition products.[3] The reaction of the ambident NO_2 radical with olefins is known to give both C-N and C-O products,[4] and readdition to tetranitroethylene by the latter mode would give unstable products.

It appears, therefore, that if tetranitroethylene is to be isolated directly, contact with N_2O_4 must be avoided. The Diels-Alder reaction is generally reversible, and the retro-Diels-Alder reaction has been found to be useful in synthesis.[5] With this objective we investigated the vacuum pyrolysis of the tetranitroethylene adduct of anthracene (**1**).

(1) This work was supported by the U.S. Army Research Office.
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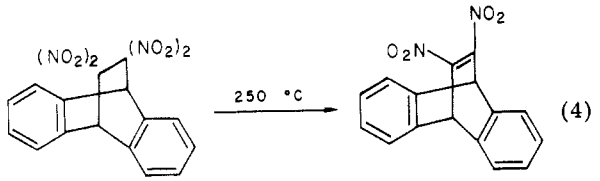
0022-3263/81/1946-4811$01.25/0

No evidence was found for the retro-Diels–Alder reaction of 1. Instead, this pyrolysis provided an additional example of the novel N_2O_4 extrusion reaction from vicinal dinitro compounds. The reaction was carried out simply by adding 1 to an evacuated flask heated at 250–260 °C. The product that sublimed immediately was contaminated by 15% of the starting material, but conversion was completed by repeating the process. The product was identified as 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2, eq 4). Its NMR spectrum was similar to that of 1, and

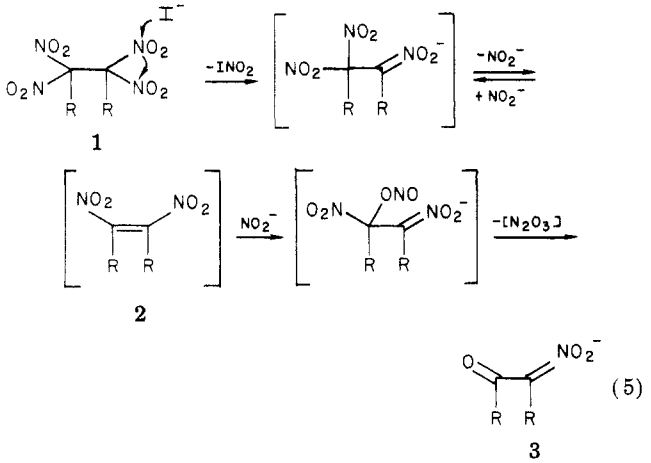


(4)

1 2

its IR spectrum showed absorption at 1540 cm^{-1}, characteristic for nitro olefins.[6]

Previously[2] we postulated that the olefin 2 was an intermediate in the reaction of 1 with sodium iodide to give the sodium salt of 12-nitro-9,10-dihydro-9,10-ethanoanthracene-11-one (3, eq 5). The nitronate salt resulting

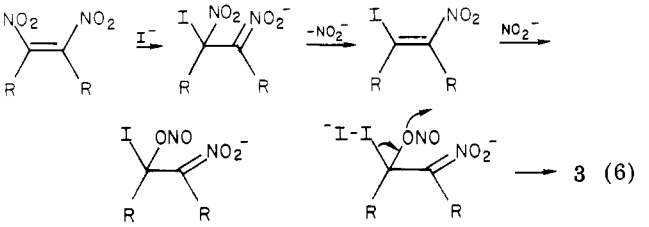


(5)

from reductive attack of iodide on a nitro group of 1 can lose nitrite ion to give 2. Readdition of nitrite at its oxygen center to the olefin 2 would give the unstable nitro nitrite, a ketone precursor. With the olefin 2 now in hand, we were able to test its role in the formation of ketone 3. Compound 3 was not formed when the olefin 2 and sodium nitrite were heated under the conditions previously used to prepare 3 from 1 (60–65 °C; 1,2-dimethoxyethane as solvent). Sodium nitrite did not dissolve, and the addition of 18-crown-6 also had no effect. However, the olefin 2 reacted with sodium iodide at room temperature to give 3, and 2 equiv of sodium iodide was required for complete consumption of the starting material.

This result suggests that the addition of iodide to the olefin 2 is involved in the formation of ketone 3 from 1. Isomerization to nitrite of the nitro group adjacent to the iodine could take place by nitrite ion elimination and readdition to the resulting vicinal iodonitro olefin. A carbonyl group could then result in several possible ways from reductive attack by a second iodide ion. One such possible route is shown in eq 6.

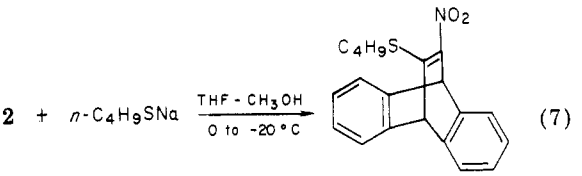
Vicinal iodonitro olefins readily undergo nucleophilic substitution; kinetic and stereochemical studies of α-iodo-β-nitrostilbenes supported an addition–elimination rather than a concerted mechanism.[7] Other vicinal dinitro



(6)

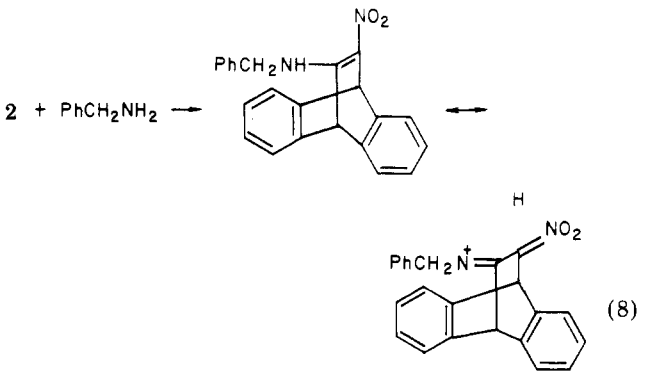
olefins have also been reported to give nucleophilic substitution products with amines, amino acids, and mercaptans.[8]

The dinitro olefin 2 underwent characteristic reactions. Sodium *n*-butylmercaptide reacted with 2 at 0 to −20 °C in tetrahydrofuran and methanol to give 11-(butylthio)-12-nitro-9,10-dihydro-9,10-ethenoanthracene (eq 7).



(7)

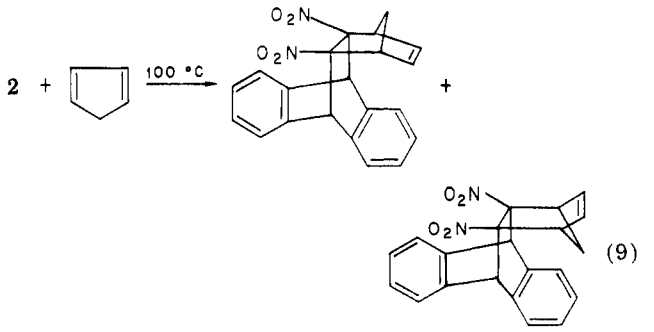
Benzylamine reacted with the dinitro olefin 2 in tetrahydrofuran. The product, 11-(benzylamino)-12-nitro-9,10-dihydro-9,10-ethenoanthracene (eq 8), exhibited



(8)

zwitterionic character. Its IR spectrum showed characteristic[9] nitronate salt bands (1350 to 1460 cm^{-1}) as well as an intense band at 1610 cm^{-1} ascribed to iminium salts.[10] The NMR signal for C=NH⁺ appeated at δ 10.5.

The dinitro olefin 2 also functioned as a dienophile in a Diels–Alder reaction with cyclopentadiene (eq 9). The



(9)

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reaction was carried out in methylene chloride solution at 100 °C in a sealed tube. The NMR spectrum indicated that the adduct consisted of an equimolar mixture of exo and endo isomers. The isomers could not be separated by TLC.

It is of interest that 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2) is the product one would obtain from the Diels–Alder reaction of anthracene with dinitroacetylene. Dinitroacetylene has not been reported, although *tert*-butylnitroacetylene[11] and phenylnitroacetylene[12] have been described recently.

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. The 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene was prepared by using previously described procedures,[2] and 1,2-dimethoxyethane was distilled from sodium benzophenone ketyl. Reactions of polynitro compounds were carried out behind safety shielding.

11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene (2). A bent tube containing 0.1–0.15 g of 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (1) was fitted to a 50-mL round-bottom flask that was partially immersed in a 250–260 °C oil bath. The flask was evacuated to 0.5 mmHg, and the solid was added rapidly by rotating the tube. A yellow solid condensed quickly on the unheated portion of the flask and in the vacuum exit; essentially no residue remained in the heated area. The flask was cooled and the product was taken up in methylene chloride. A total of 0.94 g (2.0 mmol) of the tetranitro compound was pyrolized in this way in increments. Solvent was removed from the combined solutions, and the residue was washed with hexane. The crude product, which was found to contain 15% starting material, was repyrolyzed by the above procedure. the product was recrystallized from benzene–hexane and dried for 2 h at 56 °C (0.05 mmHg) to give 0.37 g (62%) of yellow solid: mp 162–164 °C dec; IR (CH_2Cl_2) 1540, 1460, 1350 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (m, 8 H, aromatic), 5.60 (s, 2 H, bridgehead CH).

Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 65.31; H, 3.43, N, 9.52. Found: C, 65.13; H, 3.81; N, 9.32.

Reaction of 11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene (2) with Sodium Iodide. A solution of 0.56 g (0.38 mmol) of sodium iodide in 2 mL of dry 1,2-dimethoxyethane was added to a solution of 0.070 g (0.19 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene in 1 mL of 1,2-dimethoxyethane, and the resulting dark red mixture was stirred for 1 h. The precipitated product was isolated by filtration, washed with 1,2-dimethoxyethane and with methylene chloride, and air dried to give 0.030 g (48%) of the sodium salt of 12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (3) as a complex with 0.5 mol/mol of 1,2-dimethoxyethane which was identical with an authentic sample.[2]

11-(Butylthio)-12-nitro-9,10-dihydro-9,10-ethenoanthracene. A solution of 0.10 g (0.34 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2) in 4 mL of methanol and 2 mL of tetrahydrofuran was cooled to −25 °C, and a solution of 0.34 mmol of sodium *n*-butylmercaptide in 2 mL of methanol was added over a 5-min period with stirring. The reaction mixture was stirred for 15 min at −20 °C and was then warmed to 0 °C over a 30-min period. The solvent was removed in vacuo, and the residue was chromatographed over 10 g of silica gel (1:1 methylene chloride–hexane). The yellow fractions were combined, and the solvent was evaporated. Recrystallization of the residue from cyclohexane gave 0.050 g (43%) of bright yellow prisms: mp 144–145.5 °C; IR (CH_2Cl_2) 1540, 1460, 1320, 1300 cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.3 (m, 8 H, Ar), 5.93 (s, 1 H, bridgehead CH), 5.47 (s, 1 H, bridgehead CH), 3.10 (t, 2 H, CH_2S), 1.62 (m, 4 H, CH_2CH_2), 0.98 (m, 3 H, CH_3).

Anal. Calcd for $C_{20}H_{19}NSO_2$: C, 71.19; H, 5.68; N, 4.15; S, 9.50. Found: C, 71.15; H, 5.66; N, 4.09; S, 9.39.

11-(Benzylamino)-12-nitro-9,10-dihydro-9,10-ethenoanthracene. A solution of 0.10 g (0.34 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene (2) and 0.040 g (0.37 mmol) of benzylamine in 4.0 mL of dry tetrahydrofuran was allowed to stand 28 h at room temperature. The solvent was evaporated, and the residue was washed with ether–THF to give 0.075 g (63%) of crystalline product. An analytical sample was recrystallized f rom ether–THF: mp 243–244.5 °C dec; IR (CH_2Cl_2) 1610, 1460, 1410, 1370, 1350 cm^{-1}; NMR ($CDCl_3$) δ 10.5 (m, 1 H, NH), 6.8–7.4 (m, 13 H, Ar), 5.88 (s, 1 H, bridgehead), 5.20 (s, 1 H, bridgehead), 4.78 (d, 2 H, J = 6 Hz, benzyl CH_2).

Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12, N, 7.90. Found: C, 78.15; H, 5.05; N, 7.85.

Reaction of 11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene (2) with Cyclopentadiene. A solution of 0.25 mL of cyclopentadiene and 0.060 g (0.20 mmol) of 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene in 2 mL of methylene chloride was heated in a sealed tube for 1 h at 100 °C. Column chromatography (10 g of silica gel, hexane–methylene chloride) and recrystallization of the colorless middle fractions from benzene–hexane gave 0.025 g (17%) of the Diels–Alder adduct of cyclopentadiene and 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene: colorless needles; mp 167–168 °C. An analytical sample was dried for 3 h at 56 °C (0.05 mm): IR (CH_2Cl_2) 1545, 1360 cm^{-1}; NMR ($CDCl_3$) indicated a 1:1 mixture of exo and endo isomers, δ 7.17 (m, 16 H, Ar), 6.40 (m, 2 H, CH=CH), 5.27 (m, 2 H, CH=CH), 5.00 (s, 2 H, ArCHAr), 4.83 (s, 2 H, ArCHAr), 3.60 (m, 2 H, CH), 3.30 (m, 2 H, CH), 3.00, 1.88, 1.20, and 0.066 (4 d, J = 11 Hz, 1 H each, CH_2).

Anal. Calcd for $C_{21}H_{16}H_2O_4$: C, 69.99; H, 4.48; N, 7.77. Found: C, 69.89; H, 4.47; N, 7.62.

Registry No. 1, 73804-83-8; 2, 79069-90-2; 3·Na, 73804-87-2; 11-(1-butylthio)-12-nitro-9,10-dihydro-9,10-ethenoanthracene, 79083-87-7; sodium *n*-butylmercaptide, 4779-86-6; 11-(benzylamino)-12-nitro-9,10-dihydro-9,10-ethenoanthracene, 79069-91-3; benzylamine, 100-46-9; cyclopentadiene/11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene Diels–Alder adduct (endo), 79069-92-4; cyclopentadiene/11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene Diels–Alder adduct (exo), 79120-27-7.

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Stereodynamics in Benzamidoximes. A Reassignment

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In a previous work concerning the study of the stereochemistry of benzamidoximes by NMR we observed,[2] inter alia, nonequivalence for the ortho methyl groups in compounds 1 and 2 at room temperatures in Me_2SO. As at higher temperature the NMR signals of these substituents broadened and coalesced into a single peak at ca. 110 °C, the free energies of activations for the related exchange process calculated from the total line-shape study were 21.5 and 19.9 kcal/mol for 1 and 2, respectively. The internal motions which could in principle be responsible for the exchange process were thought to be the restricted rotation about the C—N single bond or the inversion of configu-

(1) (a) University of Ferrara. (b) University of Bologna. (c) Institute of CNR.
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