washed with concentrated ammonium hydroxide solution; the tube was sealed under vacuum and placed in an oil bath at 110 °C for 17 h. Analysis by NMR and IR showed recovery of the starting material intact.

Reaction of 1-Vinyl-2-methylcyclopropanol with Sulfuric Acid. To concentrated sulfuric acid (5 mL) at 0 °C was added dropwise with stirring 1-vinyl-2-methylcyclopropanol (75 mg in 75 mL of tetrahydrofuran). Stirring at 0 °C was continued for 5 min, and the mixture was poured into ice water (40 mL) and extracted with ether (4 × 25 mL). The ether phase was washed with saturated sodium bicarbonate solution (20 mL) and dried over anhydrous magnesium sulfate. Removal of the solvent at room temperature under vacuum gave the mixture of dimethylcyclobutanone isomers (20 mg, 40% overall), which was analyzed by VPC on a 10 ft × $^3/_8$ in. 20% 1,2,3-tris(β-cyanoethoxy)propane column packed on Chromosorb P (column temperature 70 °C, flow rate 60 mL of He/min). Authentic samples of the cyclobutanone isomers were synthesized according to a known method.[12] These samples were then used for comparison purposes with the products of the present experiment. The percentage of products was the following: 2,4-trans (4%), 2,4-cis (26%), 2,3-trans (24%), 2,3-cis (46%).

Reaction of 1-Vinyl-2-methylcyclopropanol with Dry HBr in Methylene Chloride. The vinyl carbinol (99 mg in 89 mg of tetrahydrofuran) was dissolved in methylene chloride (25 mL) and brought to 0 °C with an ice–water bath. Dry HBr gas from the commercial source was bubbled through the solution for 2 min. The reaction was then allowed to stand for 5 min in the cold, poured into saturated sodium bicarbonate solution (10 mL), and extracted with methylene chloride (2 × 10 mL). After the solution was dried over anhydrous magnesium sulfate, the solvent was removed under vacuum at room temperature to yield the isomeric dimethylcyclobutanones (83% overall). The compounds were analyzed by VPC as before, showing formation of 2,3-trans (75%) and 2,3-cis (25%). The other isomers were not observed. In separate control runs done on the individual isomers, the following results were obtained. With hydrogen bromide in methylene chloride, 2,3-cis went to a mixture of 2,3-trans (73%) and 2,3-cis (27%), with no 2,4 material. With hydrogen bromide in methylene chloride, 2,3-trans went to 2,3-trans (77%) and 2,3-cis (23%), with no 2,4 material. With sulfuric acid, 2,3-cis produced only a very small amount of 2,3-trans and no 2,4 material. With sulfuric acid, 2,3-trans remained totally unchanged. Neither 2,4-trans nor 2,4-cis produced any 2,3 material at all when treated with hydrogen bromide in methylene chloride. With sulfuric acid, 2,4-trans produced only a very small amount of 2,4-cis and no 2,3 material at all. With sulfuric acid, 2,4-cis underwent no significant isomerization to the trans form and gave no 2,3 material.

Acknowledgment. This work was supported by Grant GM-07874 from the National Institutes of Health.

Registry No. 1a, 13837-45-1; **2**, 22935-31-5; **2** acetate ester, 73680-08-7; **3**, 73680-09-8; **3** acetate ester, 73680-10-1; **4**, 73680-11-2; **4** acetate ester, 73680-12-3; **6**, 1517-15-3; **7** (X = Br), 73680-13-4; **7** (X = Br) 2,4-dinitrophenylhydrazone, 73680-14-5; **7** (X = Cl), 22935-33-7; **8**, 17714-43-1; **9** (X = OH), 23107-52-0; **9** (X = OAc), 73680-15-6; **9** (X = $CH_2N(CH_2Ph)_2$), 22935-34-8; **10** (X = Cl), 73680-16-7; **10** (X = OH), 73680-17-8; **11**, 24186-34-3; **13**, 19995-72-3; **14a**, 1604-99-5; **14b**, 1605-00-1; **14c**, 1942-42-3; **14d**, 28113-36-2; cyclopropanone, 5009-27-8; 2-methylcyclopropane, 19995-71-2; vinyl bromide, 593-60-2; ethyl vinyl ketone, 1629-58-9; ketene, 463-51-4; dibenzylamine hydrochloride, 20455-68-9; isobutenyl bromide, 3017-69-4; 5-hydroxy-5-methyl-3-hexanone, 59356-91-1.

Tetranitroethylene. In Situ Formation and Diels–Alder Reactions[1]

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The reaction of hexanitroethane with dienes gave the Diels–Alder adducts of tetranitroethylene. Thus, the reaction in refluxing benzene of hexanitroethane with anthracene gave 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene. Similarly, 9-methylanthracene and 9,10-dimethylanthracene gave 9-methyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene and 9,10-dimethyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene, respectively. Cyclopentadiene reacted with hexanitroethane in methylene chloride at −10 °C to give 5,5,6,6-tetranitro-2-norbornene. Reaction of the anthracene adduct of tetranitroethylene with sodium iodide gave the sodium salt of 12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one, which was protonated with acetic acid to give the corresponding nitro ketone. Treatment of the sodium salt with chlorine and bromine gave 12-chloro-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one and 12-bromo-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one, respectively.

Olefins highly substituted with electron-withdrawing substituents have been of general interest since the first synthesis of tetracyanoethylene[2] led to a broad area of useful reactions.[3] Tetranitroethylene remains an unknown extreme example of this class of compounds.[4] The existence of the unstable olefin 1,1-dinitroethylene has been demonstrated by trapping experiments,[5] and, more recently, the isolation and characterization of 1,2-dinitroethylene has been reported.[6] We now report the in situ preparation of tetranitroethylene as evidenced by its trapping as Diels–Alder adducts.

Mixing hexanitroethane[7] with an excess of anthracene in benzene gave a transient violet coloration that disappeared upon heating. Heating the solution at reflux resulted in the evolution of nitrogen oxides and the precipitation of a 63% yield of a white solid that was identified

(1) This work was supported by the U.S. Army Research Office.

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(4) The compound was claimed in a patent (Gilliland, W. L. U.S. Patent 3 257 470, 1966) without structure proof and the work could not be repeated: Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* **1979**, *44*, 1181.

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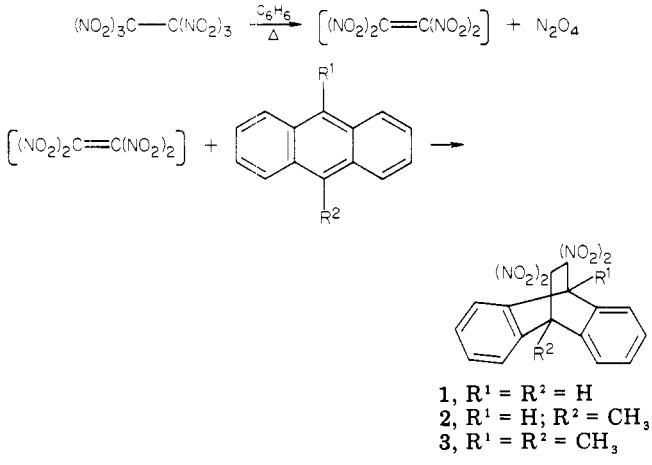
0022-3263/80/1945-2880$01.00/0

Table I. Diels-Alder Adducts of Tetranitroethylene and Anthracenes

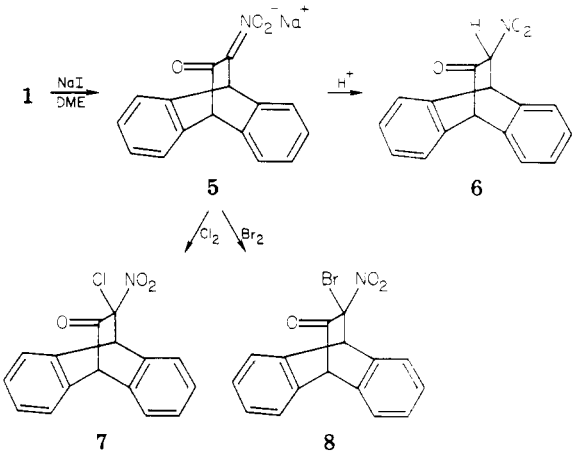
compd	IR, cm^{-1} [a]		NMR, δ [b]		
	NO_2 asym stretch	NO_2 sym stretch	aryl-H	9,10-H	9,10-CH_3
1	1580	1310	7.28 (m, 8 H)	5.40 (s, 2 H)	
2	1585	1305	7.30 (m, 8 H)	5.28 (s, 1 H)	2.30 (s, 3 H)
3	1580	1310	7.22 (m, 8 H)		2.27 (s, 6 H)

[a] 1 and 3 in KBr, 2 in $CHCl_3$. [b] 1 in acetone-d_6, 2 and 3 in $CDCl_3$.

Scheme I

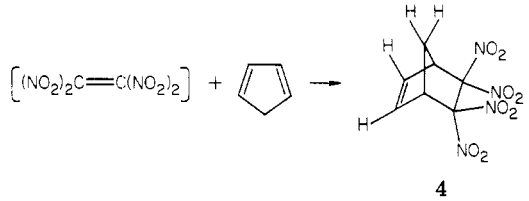


Scheme II



as 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (**1**), the Diels–Alder adduct of tetranitroethylene and anthracene. From the mother liquor, 9-nitroanthracene was isolated. Methyl-substituted anthracenes reacted similarly with hexanitroethane, but the products were soluble in benzene and the yields were lower; 9-methylanthracene and 9,10-dimethylanthracene gave the corresponding tetranitroethylene adducts, 9-methyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (**2**) and 9,10-dimethyl-9,10-dihydro-11,11,12,12-tetranitro-9,10-ethanoanthracene (**3**), in yields of 9% and 23%, respectively (Scheme I).

Cyclopentadiene was examined to explore the applicability of this reaction to aliphatic dienes. At room temperature, hexanitroethane and cyclopentadiene reacted exothermically, yielding no simple products. However, when this reaction was carried out at −10 °C in methylene chloride solution, a 15% yield of 5,5,6,6-tetranitro-2-norbornene (**4**), the Diels–Alder adduct of tetranitroethylene and cyclopentadiene, was isolated. The low yield is attributed in part to difficulties in separating this product from byprodcts arising from the reaction of nitrogen dioxide with cyclopentadiene.



4

The tetranitroethylene adducts of the anthracenes (**1–3**) are colorless crystalline compounds that all melted with decomposition at 142–143 °C. Relevant spectral data are summarized in Table I. The characteristic nitro group IR stretching frequencies are consistent with reported values for polynitroalkanes.[8] The NMR spectra are consistent with the assigned structures. In compound **1**, the 9,10 bridgehead protons appear as a sharp singlet at δ 5.40. The corresponding chemical shift for the anthracene–tetracyanoethylene adduct was reported to be δ 5.82.[9] The bridgehead CH for the 9-methylanthracene adduct **2** appears in the same region, and the bridgehead methyls of **2** and **3** appear at δ 2.27–2.30. The tetranitroethylene adduct of cyclopentadiene gave characteristic IR nitro absorptions at 1605 and 1585 cm^{-1} (asymmetric stretch) and 1310 cm^{-1} (symmetric stretch). The NMR spectrum was consistent with reported spectra for 2-norbornenes substituted at the 5 and 6 positions.[10] The bridge methylene protons gave doublets (J = 12 Hz) at δ 2.30 and 2.68, whereas the bridgehead and olefinic protons gave multiplets at δ 4.00 and 6.50, respectively.

The only previously reported compounds with more than two carbons that contain $\alpha,\alpha,\beta,\beta$-tetranitro groups are 2,2,3,3-tetranitrobutane and 3,3,4,4-tetranitrohexane, and catalytic hydrogenation was the only reported reaction of the compounds.[11] In order to provide additional characterization of this structural feature in the tetranitroethylene Diels–Alder adducts, reaction with the mild reducing agent sodium iodide was examined. This reducing agent transforms trinitromethyl groups to nitronitronate salts.[12]

The tetranitroethylene adduct of anthracene reacted at 60–65 °C with sodium iodide in dimethoxyethane to give an 87% yield of a solid that was identified spectrally as the sodium salt of 12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one, **5** (Scheme II). The NMR spectrum showed dissimilarity of the bridgehead hydrogens, and the IR spectrum showed a strong absorption at 1650 cm^{-1}, which is in the region reported for carbonyl groups of salts of α-nitro ketones.[13] Acidification of **5** with acetic acid

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(12) Glover, D. J.; Kamlet, M. J. *J. Org. Chem.* **1961**, *26*, 4734.
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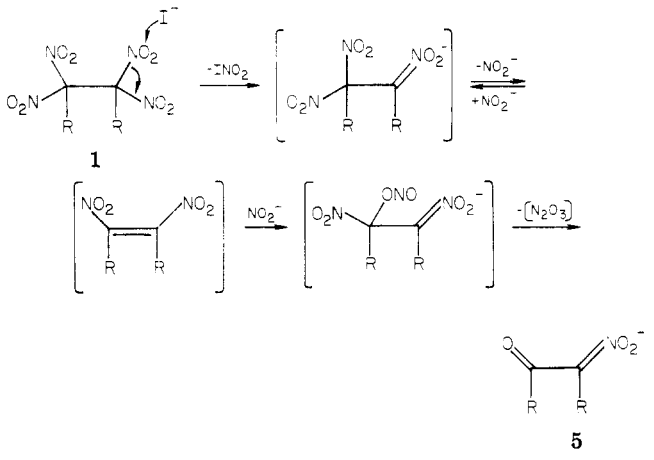
Scheme III



gave 12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (6), which was identified by elemental analysis, NMR, and IR; IR absorptions observed at 1760 and 1560 cm^{-1} are characteristic carbonyl and nitro bands of α-nitro ketones.[13a] The nitronate salt 5 was characterized further by reaction with chlorine and with bromine to give 12-chloro-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (7) and 12-bromo-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (8), respectively; halogenations of salts of α-nitro ketones have been reported previously.[13a]

This conversion of a tetranitro compound into a nitro ketone salt represents a novel type of nitro reduction. The reaction was not affected by the exclusion of oxygen, the addition of 1 equiv of water, or careful exclusion of water. Thus, a nitro group must be the source of the carbonyl oxygen. A possible pathway is shown in Scheme III. Attack of iodide on a nitro group is similar to known reductions of terminal trinitroalkanes;[12] the resulting nitryl iodide reacts with additional sodium iodide to give iodine and sodium nitrite. The loss of nitrite from the dinitronitronate salt would give a vicinal dinitro olefin, a member of a class of compounds known to be susceptible to nucleophilic attack.[6,14] Addition of nitrite ion to this olefin would give a geminal nitro nitrite, which would be converted to a carbonyl by loss of the elements of dinitrogen trioxide.[15] The ambident nature of nitrite ion in nucleophilic substitutions is well-known,[16] and recently additions of nitrite to perfluoroolefins have been shown to give products resulting from both N and O attack.[17] In the present example, N attack would merely reverse the preceding step.

The formation of tetranitroethylene from hexanitroethane may be formally represented as simply the expulsion of dinitrogen tetroxide. There is precedence for this elimination in that 1,2-dichloro-1,2-dinitroethylene has been prepared by heating 1,2-dichloro-1,1,2,2-tetranitroethane.[18] The thermolysis of hexanitroethane has been studied previously, both with the neat solid and with solutions in saturated hydrocarbon or halogenated solvents, but only simple gaseous decomposition products and solvent-oxidation products were reported.[19] This degradation in the absence of a trapping agent may be due to a reversal of the elimination by which the formation of tetranitroethylene is postulated. The addition of nitrogen dioxide to olefins gives C–O as well as C–N products,[20] and the former would degrade in the manner depicted for the nitro nitrite in Scheme III to give oxides of carbon and nitrogen.

The half-life of hexanitroethane in carbon tetrachloride at 85 °C was 8.6 h,[19] and we observed a similar order of magnitude in benzene. However, in refluxing benzene in the presence of anthracene, hexanitroethane was consumed completely within 30 min, and in the presence of cyclopentadiene, the reaction took place within 2 h at −10 °C. Assistance by the diene in the initial C–N bond breaking is indicated, possibly involving π complexes similar to those reported for reactions of tetranitromethane with unsaturated compounds.[21]

An alternative stepwise route to the adducts involves homolysis of hexanitroethane to give a pentanitroethyl radical, which would add to the diene. Homolysis at the remaining trinitromethyl group would give a diradical which would cyclize to give the observed adducts. It would be necessary, however, for the free-radical center of the initial adduct to survive long enough for the second homolysis to occur.

Experimental Section

NMR spectra were obtained with a Varian T-60 instrument with tetramethylsilane as an internal reference. Infrared spectra were recorded with a Perkin-Elmer 700 spectrophotometer. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN, and by the Analytical Facility, California Institute of Technology, Pasadena, CA. Benzene was distilled from calcium hydride and stored over molecular sieves, and 1,2-dimethoxyethane was distilled from sodium metal or from sodium benzophenone ketyl. Hexanitroethane was prepared from 1,1,1-trinitrochloroethane according to procedures described by Borgardt et al.[7] Overall yields of hexanitroethane from 1,1,1-trichloro-2-nitroethane were 20–30%.

Caution: Because of the explosive nature of many polynitro compounds, experimental manipulations should be performed behind safety shielding. In the preparation of hexanitroethane,[7] the friction-sensitive dipotassium tetranitroethane was not allowed to become dry. The wet precipitated salt was washed with methanol and then with methylene chloride and was used wet with methylene chloride in the nitration step.

11,11,12,12-Tetranitro-9,10-dihydro-9,10-ethanoanthracene (1). A mixture of 0.30 g (1.0 mmol) of hexanitroethane and 0.45 g (2.5 mmol) of anthracene in 10.0 mL of benzene was heated at reflux with stirring for 30 min under a slow stream of nitrogen. The initially violet reaction mixture became light orange at the reflux temperature, and a colorless solid precipitated. Filtration and washing with benzene gave 0.292 g (63%) of a 1:1 benzene solvate. Heating the material for 3 h at 56 °C (0.1 mm) gave benzene-free product, mp 142–143 °C dec.

Anal. Calcd for $C_{16}H_{10}N_4O_8$: C, 49.75; H, 2.61; N, 14.50. Found: C, 49.57; H, 2.83; N, 14.08.

Chromatography of the mother liquor over 10 g of silica gel (hexane–chloroform) gave 0.34 g of a yellow solid which was recrystallized from acetic acid to give 0.098 g of 9-nitroanthracene, mp 148-149 °C, identical with an authentic sample.

9-Methyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (2). A solution of 0.30 g (1.0 mmol) of hexanitroethane and 0.48 g (2.5 mmol) of 9-methylanthracene in 10.0 mL of benzene was heated for 1 h at reflux under nitrogen. Chromatography over 30 g of silica gel (hexane–CH_2Cl_2) and recrys-

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(15) Other nitro to nitrite isomerization routes can be envisioned. A referee has suggested homolysis of a C–N bond in the dinitro nitronate salt with subsequent C–O recombination of the resulting radical anion–nitrogen dioxide radical pair to give the nitro nitrite of Scheme III.

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(21) Altukhov, K. V.; Perekalin, V. V. *Russ. Chem. Rev.* **1976**, *45*, 1052.

tallization of the colorless product fraction from benzene gave 0.037 g (9%) of product, mp 142–143 °C dec.

Anal. Calcd for $C_{17}H_{12}N_4O_8$: C, 51.01; H, 3.02; N, 14.00. Found: C, 51.00; H, 2.93; N, 14.16.

9,10-Dimethyl-11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (3). A solution of 0.30 g (1.0 mmol) of hexanitroethane and 0.41 g (2.0 mmol) of 9,10-dimethylanthracene in 10.0 mL of benzene was refluxed 30 min under nitrogen. The above isolation procedure gave 0.097 g (23%) of **3**, mp 142–143 °C dec.

Anal. Calcd for $C_{18}H_{14}N_4O_8$: C, 52.18; H, 3.41; N, 13.52. Found: C, 52.39; H, 3.44; N, 13.95.

5,5,6,6-Tetranitro-2-norbornene (4). To a solution of 2.0 mL of cyclopentadiene and 2.0 mL of methylene chloride cooled to −20 °C was added, dropwise over 20 min, 0.30 g (1.0 mmol) of hexanitroethane in 2.0 mL of methylene chloride. The resulting orange solution was stirred for 2 h at −10 °C and 0.5 h at 0 °C. Concentration in vacuo of the resulting solution gave a gummy, dark residue which was chromatographed on 30 g of silica gel (hexane–methylene chloride). The colorless early fractions were rechromatographed over 10 g of silica gel (hexane–methylene chloride). Recrystallization from hexane–benzene gave 0.042 g (15%) of colorless needles, mp 127–129 °C.

Anal. Calcd for $C_7H_6N_4O_8$: C, 30.67; H, 2.21; N, 20.44. Found: C, 31.12; H, 2.28; N, 20.43.

12-Nitro-9,10-dihydro-9,10-ethanoanthracen-11-one Sodium Salt (5). A solution of 0.625 g (4.0 mmol) of sodium iodide in 5 mL of 1,2-dimethoxyethane was added to 0.484 g (1.0 mmol) of the anthracene–tetranitroethylene adduct (benzene solvate) in 3 mL of 1,2-dimethoxyethane, and the mixture was heated with stirring at 60–65 °C for 4 h. The resulting precipitate was filtered, washed with 1,2-dimethoxyethane and with methylene chloride, and air dried to give 0.288 g (87%) of an off-white solid, mp 295 °C dec, the dimethoxyethane solvate of the title compound containing 0.5 mol of solvent: IR (KBr) 3450, 1650, 1405, 1280 cm^{-1}; NMR (Me_2SO-d_6) δ 7.10 (m, 8 H, aromatic), 5.70 (s, 1 H, CH), 4.68 (s, 1 H, CH), 3.38 (s, 2 H, CH_2 of solvent), 3.20 (s, 3 H, CH_3 of solvent).

12-Nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (6). A suspension of 0.25 g (0.75 mmol) of the above sodium salt in 6 mL of methylene chloride was acidified dropwise with stirring at 5 °C with 0.048 g (0.80 mmol) of glacial acetic acid in 1 mL of methylene chloride. The mixture was stirred at 5 °C for 1 h and filtered. The filter cake was washed with methylene chloride, and the combined methylene chloride solutions were stripped of solvent under vacuum to give a solid residue which was triturated with benzene–hexane and filtered to give 0.096 g (48%) of white crystals, mp 170–174 °C dec. An analytical sample, mp 181–182.5 °C dec, was prepared by silica gel chromatography (methylene chloride) followed by recrystallization twice from benzene–hexane: IR (CH_2Cl_2) 1760, 1560, 1370 cm^{-1}; NMR ($CDCl_3$) δ 7.27 (m, 8 H), 4.95 (m, 3 H).

Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.51; H, 4.22; N, 5.25.

12-Chloro-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (7). A suspension of 0.225 g (0.68 mmol) of the nitronate salt solvate (**5**) in 15 mL of methylene chloride was chlorinated at 0 °C until the yellow chlorine color persisted in the solution. The chlorine flow was discontinued, and the mixture was stirred for 20 min at 0 °C and then filtered. The filtrate was concentrated in vacuo and the solid residue was recrystallized twice from benzene–hexane to give 0.080 g (39%) of colorless crystals: mp 161.5–162 °C; IR (CH_2Cl_2) 1760, 1570, 1460, 1340 cm^{-1}; NMR ($CDCl_3$) δ 7.27 (m, 8 H), 5.02 (s, 1 H), 4.97 (s, 1 H).

Anal. Calcd for $C_{16}H_{10}NClO_3$: C, 64.12; H, 3.36; N, 4.67; Cl, 11.83. Found: C, 64.10; H, 3.44; N, 4.56; Cl, 12.07.

12-Bromo-12-nitro-9,10-dihydro-9,10-ethanoanthracen-11-one (8). To a suspension of 0.20 g (0.60 mmol) of the nitronate sodium salt solvate (**5**) in 10 mL of methylene chloride was added, dropwise at 5 °C, 0.096 g (0.60 mmol) of bromine in 5 mL of methylene chloride with stirring over a 35-min period. The orange mixture was stirred for 30 min. The above isolation procedure gave 0.12 g (42%) of colorless crystals: mp 168–169.5 °C; IR (CH_2Cl_2) 1760, 1560, 1465, 1340 cm^{-1}; NMR ($CDCl_3$) δ 7.22 (m, 8 H), 5.15 (s, 1 H), 4.98 (s, 1 H).

Anal. Calcd for $C_{16}H_{10}BrNO_3$: C, 55.84; H, 2.93; N, 4.07; Br, 23.22. Found: C, 55.89; H, 3.22; N, 3.77; Br, 23.43.

Registry No. 1, 73804-83-8; 2, 73804-84-9; 3, 73804-85-0; 4, 73804-86-1; 5, 73804-87-2; 6, 73804-88-3; 7, 73804-89-4; 8, 73804-90-7; hexanitroethane, 918-37-6; anthracene, 120-12-7; 9-methylanthracene, 779-02-2; 9,10-dimethylanthracene, 781-43-1; cyclopentadiene, 542-92-7.

α,α-Difluoroarylacetic Acids: Preparation from (Diethylamino)sulfur Trifluoride and α-Oxoarylacetates

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Several α,α-difluoroarylacetic acids have been prepared by reaction of DAST ((diethylamino)sulfur trifluoride) with esters of α-oxoarylacetic acids and then hydrolysis of the resulting difluoro ester. Examples include the α,α-difluoro derivatives of the synthetic plant auxin, α-naphthylacetic acid, and the antiinflammatory drug, ibufenac.

We have found a convenient and high yield one-step method for preparing esters of α,α-difluoroacetic acids by the selective replacement of the α-oxo group of α-oxoarylacetates with two fluorine atoms, using the fluorinating reagent DAST[1] ((diethylamino)sulfur trifluoride). Such fluorine-containing compounds are virtually unknown, possibly because of the absence of a good general synthetic route. The only reported ester of an α,α-difluoroarylacetic acid is ethyl difluorobenzeneacetate; its six-step low-yield (13.3%) synthesis starts with the chlorination of phenylacetonitrile and involves halogen-exchange and hydrolysis steps.[2]

These rather inaccessible compounds are of interest because the presence of two fluorine atoms at the α position would be expected to modify the activity of biologically important arylacetic acids. Naturally occurring

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