over 1 h. After complete addition the heterogeneous mixture was stirred rapidly at room temperature for 24 h under approximately 1 atm of carbon monoxide. After being filtered, the resulting crude product mixture was analyzed by gas chromatography using nonane as the internal standard.

Acknowledgment. I thank Texaco Inc. for permission to publish this paper, Drs. W. M. Cummings and H. Chafetz for helpful discussions, and J. Broas, Jr., for experimental assistance.

Registry No. $PhCH_2Br$, 100-39-0; $PhCH_2Cl$, 100-44-7; $MeO^-{\cdot}K^+$, 865-33-8; $EtO^-{\cdot}Na^+$, 141-52-6; t-$BuO^-{\cdot}K^+$, 865-47-4; Na_2CO_3, 497-19-8; i-$BuO^-{\cdot}Na^+$, 13259-29-5; Al_2O_3, 1344-28-1; CH_3OH, 67-56-1; i-BuOH, 78-83-1; $PhCH_2CO_2CH_3$, 101-41-7; $PhCH_2CO_2CH_2CH(CH_3)_2$, 102-13-6; methyl benzyl ether, 538-86-3; benzyl isobutyl ether, 940-49-8; carbon monoxide, 630-08-0; dicobalt octacarbonyl, 10210-68-1.

Reactions of Hexanitroethane with Alcohols[1]

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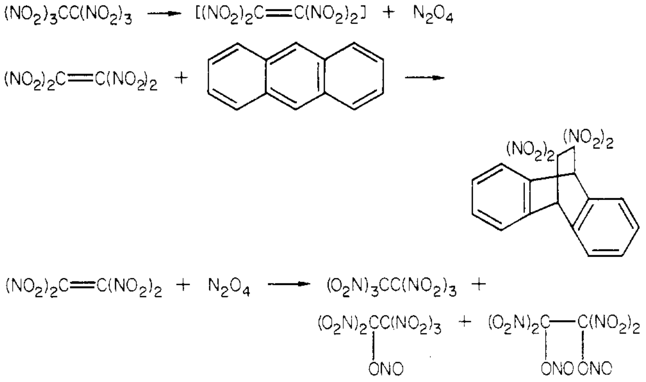
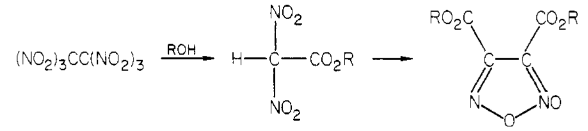
Received July 6, 1983

Olefins highly substituted with electron-withdrawing substitutents are of general interest, and tetranitroethylene, an extreme example of this class, remains a challenge in that its isolation has not been reported. We reported recently that hexanitroethane undergoes extrusion of dinitrogen tetroxide in refluxing benzene, and in the presence of a diene or anthracene, the Diels–Alder adduct derived from tetranitroethylene is obtained.[2] Other geminal tetranitro compounds also underwent this extrusion to give stable *vic*-dinitro olefins.[3] In the absence of a trapping agent, however, only gaseous decomposition products were obtained from hexanitroethane. The results were rationalized on the basis of readdition to tetranitroethylene of the ambident NO_2 radical at its oxygen center to give unstable dinitro–nitrite structures. To explore whether tetranitroethylene can be trapped by other reagents, we investigated reactions of hexanitroethane with alcohols.

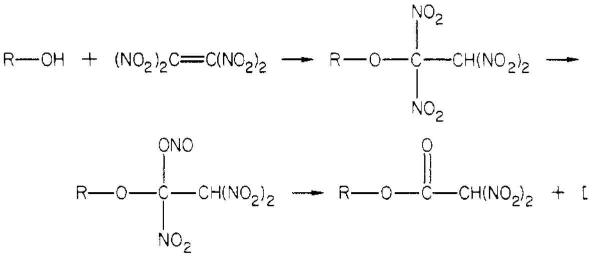


Heating a solution of hexanitroethane in refluxing methanol for 3 h resulted in the isolation of methyl dinitroacetate in 48% yield. The material was identified by its spectral properties[4] and by its quantitative transformation on standing at room temperature to give 3,4-bis(methoxycarbonyl)furazan 2-oxide.[4-6] Ethyl dinitroacetate and isopropyl dinitroacetate were obtained similarly from hexanitroethane with ethanol and 2-propanol, in 53% and 52% yield, respectively, and were likewise converted to the furazan oxides.



R = CH_3, CH_3CH_2, $(CH_3)_2CH$

The conditions at which these reactions take place are similar to those under which the tetranitroethylene Diels–Alder adducts are obtained from hexanitroethane.[2] The dinitroacetate esters might be formed by the addition of alcohols to tetranitroethylene to give the unstable 1-alkoxy-1,1,2,2-tetranitroethane structures. The formation of the carbonyl group could take place by the inversion of a nitro group to a nitrite group, followed by the loss of the elements of N_2O_3. Other examples of the isomerization of nitro groups to nitrites have been reported.[7] Alternatively, the nitro groups adjacent to the alkoxy could be hydrolyzed by trace amounts of water in the system, and equilibration of the resulting nitrous acid to oxides of nitrogen would regenerate the water. The formation of dinitroacetates from hexanitroethane and alcohols provides additional evidence for the transitory existence of tetranitroethylene.



Experimental Section

NMR spectra were obtained with a Varian T-60 spectrometer, with tetramethylsilane as an internal reference. Infrared spectra were recorded with a Perkin-Elmer 700 spectrophotometer and mass spectra with an AEI MS-9 instrument at a potential of 70 eV. Elemental analysis was carried out by Galbraith Laboratories, Inc. Knoxville, TN.

Caution: Because of the explosive nature of many polynitro compounds, experimental manipulations should be performed behind safety shielding.

Methyl Dinitroacetate. A mixture of 1.50 g (5.0 mmol) of hexanitroethane and 100 mL of methanol was heated at reflux with stirring for 3 h. Methanol was removed at reduced pressure with a rotary evaporator. The residue was dissolved in 15 mL of methylene chloride and was extracted with 20 mL of 0.2 N aqueous sodium hydroxide, and the aqueous layer was washed with two 10-mL portions of methylene chloride. The aqueous layer was acidified to pH 2–4 and was extracted with three 15-mL portions of methylene chloride. These three organic layers were combined, dried over sodium sulfate, and stripped of solvent to give 0.39 g (48%) of methyl dinitroacetate. NMR and IR spectral data were identical with reported[4] values.

Ethyl dinitroacetate was obtained in 53% yield by the above procedure: NMR ($CDCl_3$) δ 6.65 (s, 1 H), 4.43 (q, 2 H, J = 7 Hz), 1.40 (t, 3 H, J = 7 Hz); IR (CCl_4) 1765 (C=O), 1580 (NO_2) cm^{-1}.

Isopropyl dinitroacetate was obtained in 52% yield by the above procedure: NMR ($CDCl_3$) δ 6.57 (s, 1 H), 5.20 (sept, 1 H,

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[1] This work was supported by the U.S. Army Research Office.
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$J = 6$ Hz), 1.35 (d, 6 H, $J = 6$ Hz); IR (CCl_4) 1765 (C=O), 1580 (NO_2) cm^{-1}.

3,4-Bis(methoxycarbonyl)furazan 2-Oxide. A 0.40-g sample of methyl dinitroacetate was stored at room temperature for 1 week. The liquid was dissolved in 20 mL of methylene chloride, washed with two 10-mL portions of 0.2 N sodium hydroxide, and dried over sodium sulfate. Removal of the solvent gave 0.236 g (96%) of 3,4-bis(methoxycarbonyl)furazan 2-oxide, identical with the previously reported[4] material: NMR ($CDCl_3$) δ 3.95 (s, 3 H), 4.00 (s, 3 H); IR (CH_2Cl_2) 1750, 1740 (C=O), 1625 (NO) cm^{-1}.

3,4-Bis(ethoxycarbonyl)furazan 2-oxide was obtained similarly in 92% yield, identified on the basis of reported[8] spectral properties: NMR ($CDCl_3$) δ 4.38, 4.33 (overlapping quartets, $J = 7$ Hz), 1.40, 1.35 (overlapping triplets, $J = 7$ Hz); IR (CH_2Cl_2) 1750, 1740 (C=O), 1625 (NO) cm^{-1}.

3,4-Bis(isopropoxycarbonyl)furazan 2-oxide, a liquid, was obtained similarly in 93% yield: NMR ($CDCl_3$) δ 5.23, 5.18 (overlapping septets, $J = 6$ Hz each), 1.42 1.37 (doublets, $J = 6$ Hz); IR (CCl_4) 1740 (C=O), 1620 (NO) cm^{-1}.

Anal. Calcd for $C_{10}H_{14}N_2O_6$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.36; H, 5.37; N, 11.05.

Registry No. Hexanitroethane, 918-37-6; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; methyl dinitroacetate, 25160-76-3; ethyl dinitroacetate, 87711-32-8; isopropyl dinitroacetate, 87711-33-9; 3,4-bis(methoxycarbonyl)furazan 2-oxide, 18322-90-2; 3,4-bis(ethoxycarbonyl)furazan 2-oxide, 18417-40-8; 3,4-bis(isopropoxycarbonyl)furazan 2-oxide, 61678-01-1.

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A Simple Synthesis of Pyracylene[1]

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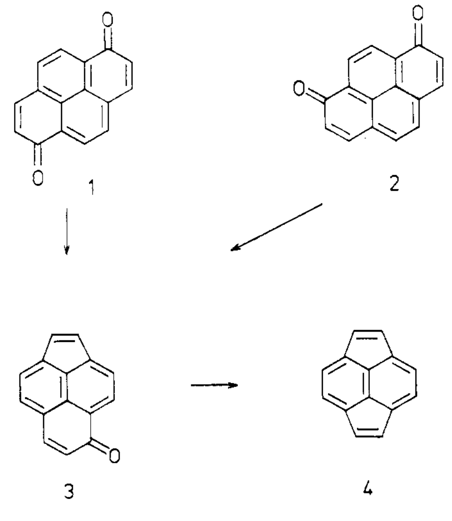
Received October 26, 1982

Pyracylene (cyclopent[*fg*]acenaphthylene, **4**) is an interesting compound owing to its π-electron system. It is regarded as a [12]annulene perturbed by the internal vinyl cross-link. As a 4n π-system, it is of limited stability. Its synthesis and spectral properties have been described by Trost,[2] however, the synthesis of **4** still remained complicated.



It has been found that cyclic carbonyl compounds eliminate CO upon flow pyrolysis,[3] leading to the corresponding ring-contracted products. If one starts from a six-membered carbonyl system, the corresponding five-membered ring can be obtained.[4] Though flow pyrolysis usually takes place at high temperatures, it can be a suitable method for the synthesis of unstable systems.[3b] There are two six-membered carbonyl systems corresponding to **4**: 1,6-pyrenedione (**1**) and 1,8-pyrenedione (**2**). Both compounds are accessible easily by oxidation of pyrene.[5]

Flow pyrolysis of **1** and **2** led to a product, which showed in the gas chromatogram–mass spectrum a peak with a molecular weight corresponding to that of **4**. The reaction conditions were optimized by using gas chromatography, and subsequently the substance was isolated by careful column chromatography. By comparison of its spectra with the data given by Trost,[2a] it was shown that the substance really was pyracylene (**4**).

In addition, the primary pyrolysis product, corresponding to the elimination of one CO, 5*H*-cyclopenta[*cd*]phenalen-5-one (**3**) could be isolated. This substance is a model compound for perturbed [13]annulenones; it was obtained before also only by a multistep synthesis.[6]

After it was shown that both quinones **1** and **2** behaved identical upon pyrolysis and led to the same products, a mixture of **1** and **2**, as it was obtained by the oxidation of pyrene, was used. The same results were observed, so it was shown that the expensive separation of the two isomers is unnecessary for this purpose.

Experimental Section

The flow pyrolyses were performed in the apparatus described already,[4b] using a quartz tube (diameter 16 mm, length 250 mm). The pyrolysis zone was filled with a bundle of seven small quartz tubes to increase the contact surface. The reactions were studied in the temperature range of 1000–1200 °C, 1100 °C resulted as the optimum temperature. The pressure measured after the cold trap was 2×10^{-3} mbar; a two-stage rotary pump (displacement swept 40 m^3 h^{-1}) was necessary to maintain the pressure.

The gas chromatographic steel column was 2-m long, 3.2 mm in diameter, and filled with 2.5% OV 17 on Chromosorb G-AW-DMCS 80–100 mesh. The oven temperature started at 150 °C and was programmed at 15°/min to 200 °C. Pyracylene (**4**) was eluted within 4 min; **1** and **2** remained on the column. A Varian 111 mass spectrometer was used. NMR spectra were run on a Varian T-60 instrument at 50 °C, UV spectra on a Beckman ACTA M VI at 25 °C, and IR spectra on a Perkin-Elmer 521 instrument.

Pyracylene (Cyclopent[*fg*]acenaphthylene, 4) and 5*H*-Cyclopenta[*cd*]phenalen-5-one (3). 1,6-Pyrenedione (**1**), 1,8-pyrenedione, or a mixture of both, as obtained by the oxidation of pyrene[5] (232 mg, 1 mmol), was sublimed through the pyrolysis tube. The products were condensed on a trap cooled with liquid nitrogen. The pyrolysate was dissolved from the cold trap with cold acetone–cyclohexane (1:1) and evaporated in vacuo to 10 mL (evaporation to dryness has to be avoided because **4** decomposes easily). The products were chromatographed twice on a column of neutral alumina (diameter 2 cm, length 20 cm, activity grade 3). Elution with light petroleum ether and crystallization from CCl_4 gave 46 mg (0.26 mmol, 26%) of slowly decomposing crystals of **4**. The NMR (in CCl_4) and the UV (in ethanol) were in accordance with ref 2a; GC–mass spectrum, *m*/*e* (relative intensity)

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[1] Presented at the 5th International Symposium on Analytical Pyrolysis, Vail, CO, Sept. 27, 1982. Part 10 of the series "Short Time Pyrolysis and Spectroscopy of Unstable Compounds". Part 9: ref 4b; part 8: ref 4c.

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