to yield the second-order rate constants k_2 (Table VI).

9. Thermolysis of the Cycloadducts 3a,b, 4a,b, and 5a,b. One of the cycloadducts **3a,b–5a,b** and dodecylbenzene (standard) were dissolved in toluene, distributed to several vials (flushed with N_2), and placed into a thermostated oil bath. The mixtures, which were removed from the thermostat after various times, were analyzed by HPLC as described above. For results see Table V.

Acknowledgment. We thank W. Hellebrandt for experimental assistance, R. Koschinsky and T.-P. Köhli for taking the NMR spectra, and A. Riemann for running the mass spectra. The conformational analysis of **5a** was carried out with support of Dr. C. Wolff (low-temperature NMR spectroscopy) and of Dr. A. Sawaryn (molecular mechanics calculations). We, furthermore, thank Prof. E. U. Würthwein (Münster) and Dr. E. Bäuml for discussions, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Registry No. 1, 1137-96-8; **2a**, 96806-52-9; **2b**, 20968-70-1; **2c**, 513-81-5; **2d**, 2288-18-8; **2e**, 68036-69-1; **2f**, 23611-15-6; **3a**, 123186-95-8; **3b**, 123186-99-2; **3c**, 123187-03-1; **3d**, 123187-05-3; **3d'**, 123187-08-6; **3e**, 123187-10-0; **3f**, 123187-12-2; **4a**, 123186-96-9; **4b**, 123187-00-8; **4c**, 123187-04-2; **4d**, 123187-06-4; **4d'**, 123187-09-7; **4e**, 123187-11-1; **4f**, 123187-13-3; **5a**, 123186-97-0; **5b**, 123187-01-9; **5c**, 123206-03-1; **5d**, 123187-07-5; **6a**, 123186-98-1; **6b**, 123187-02-0; **6c**, 19029-47-1; **7a**, 110373-09-6; **8a**, 110373-08-5; **9**, 123187-14-4; **11a**, 110373-11-0; **11a**·$HClO_4$, 123187-20-2; **12**, 123187-16-6; **13**, 123187-18-8; **13**·HCl, 123187-19-9; **14**, 123187-21-3; $PhNH_2$, 62-53-3; PhNO, 586-96-9; (±)-PhCHClOMe, 66873-72-1; 1-(*N*-anilinomethyl)-2-(2-methoxy-2-phenylethyl)-3,3,4,4,5,5-hexamethylcyclopentene, 123187-17-7.

Supplementary Material Available: IR, ^1H NMR (200 MHz), ^{13}C NMR (50 MHz), mass spectra (EI), and microanalytical data of all compounds listed in Table I and of compound **9** (8 pages). Ordering information is given on any current masthead page.

Oxidation of Primary Amines by Dimethyldioxirane[1]

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Dimethyldioxirane oxidizes primary amines rapidly, and generally in high yield, to the corresponding nitro compounds. The method can also be used to synthesize polynitro compounds.

Introduction

Many nitro compounds are difficult to synthesize by direct nitration methods. However, some success has been achieved by direct oxidation of the corresponding amines using either peracids or hydrogen peroxide.[2-6] We earlier reported[7] that dimethyldioxirane (**1**) oxidizes some primary amines to nitro compounds. We have now followed up our earlier work by oxidizing a variety of primary amines to the corresponding nitro compounds through the use of dimethyldioxirane.[8] This reagent is more convenient to use than other oxidants and generally leads to higher yields of the desired nitro compounds. Included in the current results are several examples of the use of **1** to prepare polynitro compounds.

This work is part of a comprehensive program on the chemistry of dioxiranes. We first reported the successful isolation in solution of **I** and related dioxiranes in 1985.[8] Since that time Adam and co-workers[9] and Curci et al.[10,11] have described similar experiments. Dioxiranes are powerful and unique oxidants that oxidize substrates ranging from more reactive species such as the amines used in the present work to the generally unreactive saturated hydrocarbons.[11,12] Our work on the oxidation of amines includes the primary amines described here and in our earlier report[7] as well as secondary and tertiary amines. We recently reported[13] that oxidation of appropriate secondary amines by **1** leads to a convenient, high yield route

Table I. Oxidation of Primary Amines by Dimethyldioxirane

amine	yield,[a] % isolated	yield,[a] % GC	method
o-nitroaniline		65	*c*
m-nitroaniline		97	*b*
3,5-dinitroaniline	94		*c*
p-aminobenzonitrile		90	*b*
p-aminobenzoic acid	95		*b*
p-chloroaniline		97	*b*
p-toluidine		98	*b*
p-aminoacetophenone		95	*b*
2,6-difluoroaniline		96	*b*
2,4,6-trichloraniline		97	*b*
p-nitroaniline		98	*b*
1-naphthylamine		42[e]	*c*
p-aminobenzotrifluoride		93	*c*
1,4-diaminocubane	80		*b*
1,3,5,7-tetraamino-adamantane	91		*d*
1,6-hexanediamine	20		*b*
1,6-hexanediamine	60		*b, d*
p-phenylenediamine	82		*b, d*
o-phenylenediamine		85	*c*
endo-2-aminonorbornane	58		*b, d*
exo-2-aminonorbornane	80.8		*b*

[a] In all cases the product is the nitro compound corresponding to the amine. [b] Amine added to dioxirane solution. [c] Dioxirane added to amine. [d] Amine hydrochloride used. [e] Accompanied by 2-hydroxy-1-nitronaphthalene (20%).

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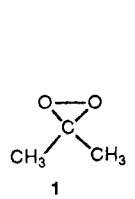
0022-3263/89/1954-5783$01.50/0

to nitroxides. Additional examples of the oxidation of secondary and tertiary amines will be the subject of future papers.

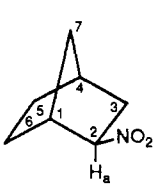
Results and Discussion

Acetone solutions of 1 were prepared as described earlier.[8] A series of aromatic primary amines were reacted with 1 to give the corresponding nitro compounds. Acetone solutions of the amines were used in order to facilitate workup. With only a few exceptions the yield of nitro compound obtained was greater than 90% (Table I). In most cases the reactions were carried out by adding the amine solution to the solution of 1. In our earlier report[7] we provided some evidence that the conversion to nitro compound proceeds through a succession of three individual oxygen transfers from 1. The intermediate compounds produced in this process can react with each other or the starting amine to reduce the yield of nitro compound. The results obtained demonstrate that the use of 1 leads to high yields even in the presence of strong electron-withdrawing groups such as *p*-nitro and *p*-trifluoromethyl. In the case of 1-naphthylamine the product 1-nitronaphthalene was formed in 42% yield but it was accompanied by a small amount (20%) of 2-hydroxy-1-nitronaphthalene. This latter material may arise from the rearrangement of a 1-naphthylamine 1,2-oxide produced by reaction of 1 with the starting amine. We had earlier shown[14] that 1 reacts with naphthalene to give *anti*-naphthalene 1,2:3,4-dioxide.

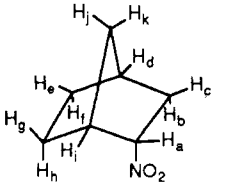
A particularly interesting application of the oxidation reaction is the synthesis of *endo*- and *exo*-2-nitronorbornane from the respective amino compounds. The structures of the nitro compounds were established by their method of synthesis as well as an analysis of the ^1H and ^{13}C NMR data (Experimental Section). These NMR data are the first reported for these compounds. Many of the proton and carbon assignments could be made fairly readily. In other cases the assignments required further NMR analysis or comparison with related compounds. In the exo isomer 2, for example, chemical shift assignments for carbons 5, 6, and 7 were made by comparison with other norbornane derivatives containing electron-withdrawing groups in the 2-exo position.[15] A similar approach was used to make the assignments for the 5, 6, and 7 carbons in the endo isomer 3.[15] In the proton NMR spectrum of 2 some of the absorptions could not be assigned uniquely. Thus multiplets at δ 1.5–1.7 and 1.2–1.3 are assigned to H_k and H_j, but without individual assignment. Likewise multiplets at δ 1.0–1.2 and 1.4–1.55 are due to $H_h + H_f$ and $H_e + H_g$, but without specific pairwise assignment. In all other cases the ^1H NMR absorptions in 2 could be readily assigned. Proton assignments in isomer 3 were much more difficult to make because of overlapping absorptions. Nevertheless assignments are given for H_a, H_i, and H_d.



1

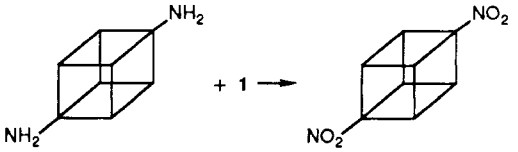


2



3

The use of 1 to prepare polynitro compounds began with the preparation of 1,4-dinitrocubane (4), a compound of some theoretical and practical significance. The synthesis of the required 1,4-diaminocubane (5) followed in most respects the earlier synthesis of Eaton and co-workers.[16] The synthesis began with the hydrolysis of cubane-1,4-dicarboxylic acid dimethyl ester to the required cubane-1,4-dicarboxylic acid using NaOH in methanol–water. The diacid was then converted to 1,4-bis[(*tert*-butoxycarbonyl)amino]cubane using the method of Yamada et al.[17] as modified by Eaton and co-workers. The carbamate was then hydrolyzed and the diamine 5 isolated as the dihydrochloride. The diamine was then freed from the hydrochloride salt and immediately oxidized to the dinitro compound with 1. When a 9-fold excess of 1 is used, then the dinitro compound can be obtained in 80% yield. The immediate oxidation of the free diamine was dictated by its instability as experienced by us and earlier workers.[16] Interestingly enough Eaton subsequently showed[18] that the dihydrochloride can be directly oxidized by 1 to the dinitrocubane in even better yield than that obtained with the free amine. This modification avoids isolation of the sensitive diamine as well as reducing the complications of side products arising from reaction of intermediates produced in the oxidation with starting diamine. As described below we have taken advantage of this modification using the hydrochloride in some of our preparations of polynitro compounds. Eaton and Wicks have also shown[18] that isocyanates can be converted to nitro compounds with 1 in wet acetone, including the oxidation of 1,4-diisocyanatocubane to 1,4-dinitrocubane in 85% isolated yield. The syntheses of the dinitrocubane using 1 are all superior to the earlier one that used *m*-chloroperbenzoic acid.



5 4

We next took advantage of the powerful oxidizing ability of 1 to synthesize 1,3,5,7-tetranitroadamantane (6). This compound is of interest because of its superior properties as a high explosive. Compound 6 was first prepared by Sollot and Gilbert in 1980.[19] Their preparation, which was followed in most details in the present work, involves the preparation of 1,3,5,7-tetrabromoadamantane, conversion to the corresponding tetraiodo compound by halogen exchange, and then a photochemical Ritter-type reaction in acetonitrile to give 1,3,5,7-tetraacetamidoadamantane tetrahydrate. In the Sollot and Gilbert procedure the tetraamide was hydrolyzed to the tetraamine and then this latter material oxidized by permanganate to the desired 6 in 45% yield. In the current work the tetraamine hydrochloride that results from the hydrochloric acid catalyzed hydrolysis of the tetraamide was reacted directly with 1. The oxidation was carried out by adding an aqueous solution of the tetrahydrochloride to a ca. 2.5 M excess acetone solution of 1 at room temperature. Under these conditions the tetranitro compound 6 was formed in 91% yield. This procedure, which takes advantage of the Eaton modification of using the amine salt rather than using the free amine, is especially useful in the current case. In addition to avoiding the complication of side reactions, the

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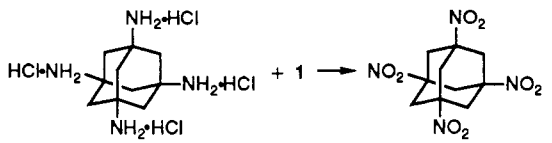
procedure eliminates the need to first free the amine from its salt, which is the form available in the tetraamide hydrolysis step. Sollot and Gilbert have shown[20] that **6** exhibits high explosive energy and combines this property with excellent impact and thermal stability.



6

In order to provide a direct comparison between the amine hydrochloride and free amine procedures, we next oxidized 1,6-hexanediamine and 1,6-hexanediamine dihydrochloride with **1** under comparable conditions. The free amine procedure gave 1,6-dinitrohexane in 20% yield, while the use of the dihydrochloride gave a 60% yield. While these yields are probably not optimal, they do permit a comparison of the two procedures under controlled conditions. As seen in the examples cited earlier, use of the amine salt leads to a good yield of the desired nitro compound.

Finally *o*- and *p*-phenylenediamine were oxidized by **1** to 1,2-dinitrobenzene and 1,4-dinitrobenzene, respectively. In the case of the ortho compound, the free amine was used while in the para case the dihydrochloride was used. The yields were 85% for 1,2-dinitrobenzene and 82% for the 1,4-dinitrobenzene. These yields should be regarded as roughly comparable since in the case of the 1,2-dinitro derivative the yield is based on GPC while the yield is that of isolated material for the 1,4 compound.

These results as well as those reported earlier[7] demonstrate the usefulness of the dioxirane method in the production of nitro compounds. The work of Eaton and Wicks[18] indicates that **1** can be used to form nitro and dinitro compounds in high yields from isocyanate precursors as well. Zabrowski and co-workers[21] have also used **1** to prepare nitro derivatives from substituted anilines. Since this group was interested in large-scale synthesis they used the in situ method[22] for the preparation of **1** under phase-transfer conditions. These conditions led to the formation of the desired nitro compounds in good to excellent yields. In those cases where the yields were lower the nitro compound was accompanied by the corresponding nitroso compound. In such cases it is likely that a change in reaction conditions would increase the yield. We had earlier demonstrated[7] that the nitroso compound is a precursor to the nitro derivative.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectral data were obtained on a Varian XL-300 NMR spectrometer. All NMR data are reported in ppm or δ values downfield from TMS, using either TMS, $CDCl_3$, or DMSO-d_6 as an internal reference. IR spectra were taken on a Perkin-Elmer 783 IR spectrophotometer. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Gas chromatography was performed on a Perkin-Elmer Sigma 2000 gas chromatograph (equipped with a flame ionization detector) and interfaced with a Shimadzu Chromatopac C-R3A integrator. Mass spectra were obtained on an Associated Electronics Industries Model MS-1201 B mass spectrometer.

Gas chromatography was performed with a J & W fused silica capillary column. The liquid phase used was DB-210: film thickness 0.5 μm; column dimensions 30 m × 0.311 mm. Helium was used as the carrier gas. Chromatographic peaks were identified both by comparison of retention times with those of authentic samples and by co-injection. When GPC was used to determine yields, the yields were calculated by multiplying the peak area by a conversion factor determined immediately prior to each analysis using authentic samples of the materials being analyzed and tetradecane as internal standard. Preparative TLC was performed on Analtech 1000 μm, precoated silica gel plates.

Materials. Acetone (Aldrich reagent grade) was fractionally distilled over anhydrous potassium carbonate. *p*-Chloroaniline, *p*-chloronitrobenzene, *p*-toluidine, *p*-nitroaniline, *p*-nitrotoluene, 2,4,6-trichloroaniline, *m*-nitroaniline, *p*-nitrobenzoic acid (all obtained from Eastman Kodak Co.), *o*-phenylenediamine, *p*-phenylenediamine, *p*-aminobenzoic acid (all obtained from Fisher Scientific), *p*-aminoacetophenone, *p*-nitroacetophenone, 2,6-difluoroaniline, 1,4-dinitrobenzene, *o*-nitroaniline, 1,2-dinitrobenzene, 3,5-dinitroaniline, 1,3-dinitrobenzene, *p*-aminobenzonitrile, *p*-nitrobenzonitrile, *p*-iodonitrobenzene, *p*-aminobenzotrifluoride, *p*-nitrobenzotrifluoride (all obtained from Aldrich Chemical Co.), and 1-naphthylamine (Mallinckrodt) were recrystallized or redistilled before use. Bromine (Fisher), $AlCl_3$ (Fisher), Al powder (Fisher), methylene iodide (Aldrich), sodium sulfite (Kodak), acetonitrile (Fisher), and 1,6-hexanediamine (Aldrich) were used without any further purification. Adamantane (Aldrich) was recrystallized from acetone prior to use, mp 267–268 °C (sealed tube) [lit.[23] mp 269.6–270.8 °C (sealed tube)]. Oxone (DuPont) ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was obtained from Aldrich and used as such. Hexanes (Fisher) and ethyl acetate (Fisher) were used without further purification. Ethanol (Fisher), triethylamine (Aldrich), and *tert*-butyl alcohol (Fisher) were fractionally distilled before use. Methanol was purified by using Mg/I_2. Diphenyl phosphorazidate (Aldrich) was distilled before use (bp 160 °C/0.2 mm). Methylene chloride was distilled over CaH_2. Cubane-1,4-dicarboxylic acid dimethyl ester was provided by Geo-Centers, Inc.

Caution. Dimethyldioxirane is a toxic material and should be used in a hood. While we have not experienced any explosions in several hundred preparations, **1** is a peroxide and should be treated accordingly.

1,2-Dinitrobenzene. *o*-Nitroaniline (0.0305 g, 0.22 mmol) was dissolved in 5 mL of acetone. To this solution was added 30 mL of a 0.06 M solution of **1**. The solution was stirred at room temperature while being protected from light. The solution was sampled periodically and a GC analysis run in order to determine the extent of reaction. The maximum yield of *o*-dinitrobenzene (65%; GC) was reached in 6 h. GC conditions: temperature 1 60 °C, time 1 5 min, rate 1 20 °C/min; temperature 2 200 °C, time 2 5 min, injection temperature 220 °C, inlet P 20 psi. The product was isolated by TLC, mp 117–118 °C [lit.[24] mp 118.5 °C].

1,3-Dinitrobenzene. *m*-Nitroaniline (0.046 g, 0.33 mmol) was dissolved in 5 mL of acetone and this solution added to a solution of **1** in acetone (0.06 M, 30 mL). The combined solution was then stirred for 30 min at 22 °C. GC analysis indicated that the yield of *m*-dinitrobenzene was 97.3%. GC conditions: temperature 1 60 °C, time 1 5 min, rate 1 20 °C/min; temperature 2 210 °C, time 2 5 min, injection temperature 250 °C, detection temperature 250 °C, inlet P 30 psi. The solvent was removed on a rotary evaporator to give the solid product, mp 89–90 °C [lit.[25] mp 90 °C].

1,3,5-Trinitrobenzene. 3,5-Dinitroaniline (0.0301 g, 0.165 mmol) was dissolved in 5 mL of acetone. A solution of **1** in acetone (30 mL, 0.06 M) was added to the amine solution. The solution was stirred at room temperature for 3 h, at which time the reaction solution still showed traces of the amine. The reaction solution was stirred overnight and the solvent removed on the rotary evaporator. The solid residue was chromatographed on a silica gel TLC plate with CH_2Cl_2–hexane (1:1) as developing solvent.

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The product was removed from the plate by using CH_2Cl_2 containing 5% methanol. Evaporation of the solvent gave a 94.2% yield of 1,3,5-trinitrobenzene, mp 121–122 °C [lit.[26] mp 121–122 °C].

p-Nitrobenzonitrile. A solution was made of *p*-aminobenzonitrile (0.033 g, 0.28 mmol) in 5 mL of acetone. This solution was added to a solution of 1 in acetone (30 mL, 0.05 M) dropwise and with stirring. Stirring was continued at 22 °C for 30 min. GC analysis indicated that the yield of *p*-nitrobenzonitrile was 90%. The reaction mixture was concentrated on the Rotovap and dried. The mass spectrum of the product shows a parent peak at 148 *m/e*. The IR spectrum of this material was identical with that of authentic *p*-nitrobenzonitrile.

p-Nitrobenzoic Acid. A solution of *p*-aminobenzoic acid (0.041 g, 0.3 mmol) in 5 mL of acetone was added to a solution of 1 (30 mL, 0.05 M) in acetone with stirring. Stirring was continued for 30 min at 22 °C. Solvent was removed on the rotary evaporator to give a 95% yield of *p*-nitrobenzoic acid, mp 239–240 °C, mixture mp 239–240 °C. The product had infrared and mass spectral data identical with those of the authentic material.

p-Nitrochlorobenzene. A solution of *p*-chloroaniline (0.0384 g, 0.3 mmol) in 5 mL of acetone was added to an acetone solution of 1 (0.05 M, 30 mL) with stirring. Stirring was continued at 22 °C for 30 min. GC analysis of the solution indicated a 97% yield of *p*-nitrochlorobenzene. The solvent was evaporated on the Rotovap and the solid obtained was dried, mp 82–83 °C [lit.[27] mp 83.6 °C].

p-Nitrotoluene. A solution of *p*-toluidine (0.032 g, 0.3 mmol) in 5 mL of acetone was added to a solution of 1 (30 mL, 0.05 M) in acetone with stirring. Stirring at 22 °C was continued for 30 min. GC analysis of the solution indicated a 98% yield of *p*-nitrotoluene. The solvent was removed on the Rotovap to give solid *p*-nitrotoluene, mp 52–53 °C, mixture mp 52–53 °C.

p-Nitroacetophenone. A solution of *p*-aminoacetophenone (0.042 g, 0.3 mmol) in 5 mL of acetone was added to a solution of 1 (30 mL, 0.05 M) in acetone with stirring. Stirring was continued at 22 °C for 30 min. GC analysis of the solution indicated a 95% yield of *p*-nitroacetophenone. The solvent was evaporated to give solid *p*-nitroacetophenone, mp 78–79 °C, mixture mp 78–79 °C.

1-Nitro-2,6-difluorobenzene. A solution of 2,6-difluoroaniline (0.018 g, 0.14 mmol) in 5 mL of acetone was added to a solution of 1 (20 mL, 0.05 M) in acetone with stirring. Stirring was continued at 22 °C for 10 h. GC analysis of the reaction mixture indicated a 96% yield of 1-nitro-2,6-difluorobenzene. The reaction mixture was concentrated on the Rotovap. The residue was subjected to preparative GC (column 15% OV-25, 8 ft × $^1/_4$ in; 80–100-mesh; injection temperature 125 °C, detection temperature 120 °C, collection temperature 100 °C, column temperature 125 °C; flow rate 100 mL/min). The sample collected showed a parent peak (159 *m/e*) for 1-nitro-2,6-difluorobenzene in its mass spectrum.

1-Nitro-2,4,6-trichlorobenzene. A solution of 2,4,6-trichloroaniline (0.0506 g, 0.26 mmol) in 5 mL of acetone was added to a solution of 1 (30 mL; 0.05 M) in acetone. The solution was stirred at 22 °C for 10 h. GC analysis indicated a 97.5% yield of 1-nitro-2,4,6-trichlorobenzene. The solvent was removed on the Rotovap and the residue recrystallized from ethanol to give the solid product with mp 69 °C [lit.[28] mp 71 °C]. The solid also showed a parent peak (225 *m/e*) for 1-nitro-2,4,6-trichlorobenzene in the mass spectrum.

1,4-Dinitrobenzene. A solution of *p*-nitroaniline (0.0418 g, 0.3 mmol) in 5 mL of acetone was added to a solution of 1 (30 mL, 0.05 M) in acetone. The solution was stired at 22 °C for 30 min. GC analysis indicated a 98% yield of 1,4-dinitrobenzene. The solvent was evaporated on the Rotovap to give the solid product, mp 171–172 °C, mixture mp 171–172 °C.

1-Nitronaphthalene. A solution of 1-naphthylamine (0.041 g, 0.3 mmol) in acetone was prepared. To this solution was added a solution of 1 (30 mL, 0.05 M) in acetone with stirring. Stirring at room temperature was continued for 30 min. GC analysis indicated a 42% yield of 1-nitronaphthalene. Repeating the reaction with a higher ratio of 1 to the amine did not improve the yield. The reaction mixture was concentrated and the residue was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on silica gel TLC plates. When developed with CH_2Cl_2–hexane (1:1), the plates indicated the presence of several products. The two major products were identified as 1-nitronaphthalene, mp 58–59 °C [lit.[29] mp 61.5 °C], and 2-hydroxy-1-nitronaphthalene (20%), mp 103 °C [lit.[30] mp 104 °C].

p-Nitrobenzotrifluoride. A solution of *p*-aminobenzotrifluoride (0.054 g; 0.33 mmol) in 5 mL of acetone was prepared. To this solution was added a solution of 1 (30 mL, 0.06 M) in acetone. Stirring at room temperature was maintained while the reaction mixture was periodically sampled in order to determine the extent of the reaction. After 2 h the yield (GC) of *p*-nitrobenzotrifluoride was 92.6% with no further increase observed. The mass spectrum of the product showed a parent peak at 191 *m/e*.

Cubane-1,4-dicarboxylic Acid. To a 50 mL, three-necked round-bottom flask equipped with a condenser and a magnetic stirring bar were added cubane-1,4-dicarboxylic acid dimethyl ester (0.500 g, 2.27 mmol), NaOH (3.00 g, 75 mmol), in 20 mL of H_2O, and 15 mL of methanol. This reaction mixture was heated at reflux for 8 h. After being cooled to room temperature, the solution was slowly acidified (litmus) with 60% HCl (pH = 2.0). The resulting solution, containing a white solid, was cooled in an ice bath for 15 min. The solid was filtered off, washed with 200 mL of distilled water and 10 mL of hexane, and vacuum dried to give 0.39 g (89.36%) of the diacid as a white solid: mp 231 °C dec [lit.[31] mp 226 °C dec]. The aqueous filtrate was extracted with ethyl acetate (6 × 30 mL). The combined organic layers were dried ($MgSO_4$, 10 min), filtered, and concentrated in vacuo. The white solid obtained was washed with 50 mL of H_2O and dried under vacuum to give 30 mg (6.8%) of acid, mp 232 °C dec. The overall yield was 96.16%. IR (KBr): 3300–2400 (OH, CH), 1690–1670 cm^{-1} (C=O). ^1H NMR (DMSO-d_6): δ 4.09 (s).

1,4-Bis[(*tert*-butoxycarbonyl)amino]cubane. To a 15 mL, flame-dried, three-necked round-bottom flask equipped with a magnetic stirring bar and rubber septum connected to a nitrogen inlet was added a solution of cubane-1,4-dicarboxylic acid (0.20 g, 1.04 mmol), triethylamine (0.22 g, 0.3 mL, 2.1 mmol), and diphenyl phosphorazidate (0.57 g, 0.45 mL, 2.10 mmol) in *tert*-butyl alcohol (3.5 mL). This mixture was refluxed for 12 h. The reaction mixture was then cooled to room temperature and was poured into a saturated, aqueous sodium bicarbonate solution (approximately 12 mL). The precipitate formed was cooled in an ice bath for about 10–15 min and was filtered under vacuum. The gray-colored precipitate was washed with 200 mL of distilled water (or until the filtrate was almost neutral to pH paper) and 3 mL of ether. Overnight air drying at reduced pressure gave 0.26 g (75.11%) of 1,4-bis[(*tert*-butoxycarbonyl)amino]cubane: mp 218 °C dec [lit.[16] mp >220 °C]. IR (KBr): 3290, 1700–1660 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.45 (s), 3.8–4.1 (br s).

1,4-Diaminocubane Dihydrochloride. To a 10-mL beaker, equipped with a magnetic stirrer, was added 0.100 g (0.300 mmol) of 1,4-bis[(*tert*-butoxycarbonyl)amino]cubane in 2 mL of methanol. This suspension was stirred for 10–15 min and then was cooled in a $CHCl_3/N_2$ bath (–61 °C). Hydrogen chloride gas was bubbled through the suspension until the mixture was completely saturated with HCl. At this point a clear brown-colored solution was obtained. This solution was allowed to warm to room temperature, which caused a slight turbidity. The turbidity was removed by filtration. The filtrate obtained was evaporated to dryness on a rotary evaporator to give a dark brown oil. This oil solidified after being kept under vacuum overnight. The solid was washed with cold ethanol and yielded 50 mg (81%) of a pale brown solid. Recrystallization from methanol gave light brown needles, mp >350 °C [lit.[16] mp >260 °C]. IR (KBr): 3100–2500

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cm^{-1} (br). ^1H NMR (D_2O): δ 4.21 (s).

1,4-Diaminocubane. In a 15-mL beaker equipped with a magnetic stirrer was prepared a solution of NaOH (0.023 g, 0.583 mmol) in 1.7 mL of H_2O. To this was added solid 1,4-diaminocubane dihydrochloride (0.056 g, 0.271 mmol). The suspension obtained was stirred for 10 min and then filtered. The filtrate was extracted with 6 × 20 mL of CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ (15 min), filtered, and concentrated in vacuo to give 0.023 g (58%) of 1,4-diaminocubane as a yellow solid. ^1H NMR ($CDCl_3$): δ 3.50 (s).

1,4-Dinitrocubane. To a 100-mL round-bottom flask equipped with a magnetic stirrer was added an acetone solution of dimethyldioxirane (42 mL, 0.045 M). A solution of 1,4-diaminocubane (0.005 g, 0.036 mmol) in 5.0 mL of CH_2Cl_2 was added slowly through a dropping funnel over a period of 20 min. The reaction mixture was stirred at room temperature for 48 h. The solvent was removed on the rotary evaporator. The material obtained was diluted with 30 mL of CH_2Cl_2 and then dried over anhydrous $MgSO_4$ (10 min) and filtered. The solvent was removed in vacuo. The white solid obtained was separated on a silica gel (5 g, 70–230 mesh, Aldrich) column by using CH_2Cl_2 solvent, which gave 5.7 mg (80%) of white solid, mp 259 °C (lit.[16] mp 260 °C). IR ($CHCl_3$ solution): 1520, 1510, 1500, 1400 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.68 (s).

1,3,5,7-Tetrabromoadamantane. To a 100-mL, three-necked, flame-dried round-bottomed flask equipped with a water condenser, magnetic stirrer, and a rubber septum connected to a nitrogen inlet, were added bromine (21 mL, 65.14 g, 40.37 mmol) and anhydrous aluminum chloride (4.95 g, 36.69 mmol). This mixture was cooled to 5–10 °C with an ice bath. Adamantane (5.0 g, 36.69 mmol) was added over a period of 30 min with constant stirring. The mixture was then refluxed at 70 °C for 24 h, which led to vigorous HBr evolution. Excess bromine was distilled off. The residue was treated with aqueous sodium sulfite and then stirred with 50 mL of a 6 M HCl solution. The solid precipitate was filtered off, washed several times with water, and then air dried. Recrystallization from hot glacial acetic acid gave 8.6 g (52%) of 1,3,5,7-tetrabromoadamantane, mp 246–247 °C [lit.[19] mp 245–247 °C]. IR (KBr): 2940–2960, 1450, 1440, 1385, 1320, 1210, 990, 840, 720 cm^{-1}. ^1H NMR (DMSO-d_6): δ 2.77 (s).

1,3,5,7-Tetraiodoadamantane. Methylene iodide (24 mL, 79.8 g, 297.9 mmol) and aluminum powder (2 g, 7.44 mmol) were added to a round-bottomed flask equipped with a magnetic stirrer and a water condenser. Bromine (0.13 mL, 3.77 mmol) was added to this mixture and the combined mixture stirred for 35 min in an oil bath at 80–82 °C. 1,3,5,7-Tetrabromoadamantane (2 g, 4.42 mmol) was added in one portion and allowed to react for 15 min at the same temperature. The reaction mixture was poured into 40 mL of cold water with constant stirring. Sodium sulfite was added to remove any color of bromine. The methylene iodide layer was separated and washed with 2 × 50 mL of H_2O. The solvent was removed by vacuum distillation. The solid residue was washed successively with 10 mL each of chloroform and acetone. The off-white colored solid obtained was recrystallized from toluene to give 1.8 g (64%) of the product as shiny white needles, mp > 360 °C [lit.[19] mp 370–371 °C]. IR (KBr): 1440, 1390, 1320, 1200, 980–990, 830, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.22 (s).

1,3,5,7-Tetraacetamidoadamantane Tetrahydrate. Into a 650-mL quartz reaction vessel equipped with a mechanical stirrer was placed 1,3,5,7-tetraiodoadamantane (1 g, 1.56 mmol) in a mixture of acetonitrile (105 mL) and water (0.13 mL). The heterogeneous mixture was stirred at room temperature for 10 min and then was photolyzed for 65 h in a Rayonet photochemical reactor (16 lamps, 0.09 W at 1849 Å and 8 W at 2537 Å). A dark brown-black solid was obtained after filtration. The solid was washed several times with fresh acetonitrile (total 100 mL) and dried. The solid was dissolved in warm methanol to remove any unreacted starting material. The solution was then filtered off and evaporated to dryness. The solid obtained was dissolved in hot water (90 mL) and the solution neutralized with dilute NaOH, which caused a color change from yellow to colorless. The solution was filtered and the filtrate evaporated to dryness. The white solid obtained was rinsed with acetone (1 mL), acetone–water (1 mL, 1:1) and acetone (1 mL). Recrystallization from water gave 0.32 g (48%) of 1,3,5,7-tetraacetamidoadamantane tetrahydrate, mp > 340 °C [lit.[19] no melting to 360 °C]. IR (KBr): 3280, 1660, 1540, 1450, 1430, 1385, 1370, 1350, 1330, 1305, 1280, 1230, 680 cm^{-1}. ^1H NMR (DMSO-d_6): δ 1.71 (s), 2.02 (s), 3.35 (s), 7.53 (s). ^{13}C NMR (DMSO-d_6): 23.63, 43.26, 52.36, 168.95 ppm.

1,3,5,7-Tetraaminoadamantane Tetrahydrochloride. Into a 10-mL round-bottomed flask equipped with a water condenser and magnetic stirrer was added 1,3,5,7-tetraacetamidoadamantane tetrahydrate (0.14 g, 0.319 mmol) in 35 mL of 18% HCl. The reaction mixture was refluxed for 3 h and then cooled. The solid that precipitated was filtered off, washed with acetone, and then dried. The yield of the tetrahydrochloride was 0.081 g (76%), mp > 360 °C [lit.[19] mp > 360 °C]. IR (KBr): 3430, 2950, 2880, 1590, 1550, 1540, 1490, 1375, 1365, 1310, 1080, 1020, 960, 950 cm^{-1}.

1,3,5,7-Tetranitroadamantane. An acetone solution of 1 (0.05 M, 34 mL, 1.70 mmol) was placed in a 100-mL round-bottomed flask equipped with a magnetic stirrer. A solution of tetraaminoadamantane tetrahydrochloride (17 mg, 0.056 mmol) in 2 mL of water was added to the dioxirane solution over a period of 12 min, during which time the color of the solution changed from yellow to pale blue. The reaction solution was stirred at room temperature for 4 h at which time the solution was colorless. The solvent was removed on the rotary evaporator to give a white powder. The crude product was recrystallized from acetone/water to give 16 mg (91%) of the tetranitro compound, mp > 340 °C [lit.[19] mp > 360 °C]. IR (KBr): 1550–1560, 1460, 1365, 920, 845, 730–750 cm^{-1}. ^1H NMR (DMSO-d_6): δ 2.89 (s). ^{13}C NMR (DMSO-d_6): 41.34, 85.6 ppm.

1,6-Hexanediamine Dihydrochloride. Into a 250-mL Erlenmeyer flask was placed 1,6-hexanediamine (2 g, 17.24 mmol) in 75 mL of benzene. The solution was cooled to 0 °C and HCl bubbled through until saturation was reached. The white solid obtained was filtered off and washed with benzene. Recrystallization of the solid from methanol gave 2.7 g (90%) of the dihydrochloride, mp 255–256 °C [lit.[32] mp 248 °C].

1,6-Dinitrohexane. Method 1. An acetone solution of 1 (0.062 M, 85 mL, 5.29 mmol) was placed into a 100-mL round-bottomed flask equipped with a magnetic stirrer. A solution of 1,6-hexanediamine (0.017 g, 0.143 mmol) in 1.5 mL of water was added dropwise to the dioxirane solution over a period of 4 min. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed on the rotary evaporator and the residue was dissolved in 2 mL of chloroform and subjected to TLC using hexane/ethyl acetate (1:1) as eluent. The band at R_f 0.7 was extracted with $CHCl_3$ (2 × 50 mL), and the solvent was evaporated to give solid 1,6-dinitrohexane (4 mg, 20%), mp 35–36 °C [lit.[33] mp 36.5–37.5 °C]. ^1H NMR ($CDCl_3$): δ 1.47 (m), 2.04 (m), 4.40 (t). ^{13}C NMR ($CDCl_3$): 25.73, 27.05, 75.40 ppm. **Method 2.** A solution of 1 (0.053 M, 100 mL, 5.29 mmol) was placed in a 100-mL round-bottomed flask equipped with a magnetic stirrer. A solution of 1,6-hexanediamine dihydrochloride (0.028 g, 0.147 mmol) in 1.5 mL of water was added dropwise to the solution of 1 over a period of 4 min. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed on the rotary evaporator and the residue dissolved in chloroform (2 mL) and then subjected to TLC using hexane/ethyl acetate (1:1) as eluent. The band at R_f 0.7 was extracted with $CHCl_3$ (2 × 50 mL). The solvent was evaporated to give 15 mg (60%) of 1,6-dinitrohexane, mp 35–36 °C [lit.[33] mp 36.5–37.5 °C]. ^1H NMR ($CDCl_3$): δ 1.49 (m), 2.1 (m), 4.42 (t). ^{13}C NMR ($CDCl_3$): 25.72, 27.05, 75.40 ppm.

1,4-Diaminobenzene Dihydrochloride. Into a 250-mL Erlenmeyer flask were added *p*-phenylenediamine (2.5 g, 23.15 mmol) and 125 mL of ether. The solution was stirred for 10 min and then was saturated with HCl gas at ice-bath temperature. The solid that precipitated was filtered off, dried, and recrystallized from methanol to give 3.59 g (86%) of the dihydrochloride as a pink-white solid, mp > 290 °C dec.

1,4-Dinitrobenzene. An acetone solution of 1 (0.03 M, 60 mL, 1.8 mmol) was placed in a 100-mL round-bottomed flask equipped with a magnetic stirrer. A solution of *p*-phenylenediamine dihydrochloride (0.22 g, 0.12 mmol) in 1.5 mL of water was added to the dioxirane solution over a period of 5 min. The reaction mixture was stirred at room temperature for 23 h. The solvent was removed on the rotary evaporator and the solid obtained

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recrystallized from methanol to give 0.015 g (82%) of 1,4-dinitrobenzene, mp 172–174 °C [lit.[34] mp 172–173 °C].

1,2-Dinitrobenzene. *o*-Phenylenediamine (0.022 g, 0.20 mmol) was dissolved in 5 mL of acetone. To this solution was added 30 mL of 0.06 M 1 at room temperature with stirring. Stirring was continued for several hours while the reaction solution was sampled and GPC analysis used to follow production of the dinitro compound. After 6 h the yield had reached 85% and there was no further increase in yield with time.

***endo*-2-Nitronorbornane.** An acetone solution of 1 (145 mL, 0.036 M, 5.22 mmol) was placed into a 250-mL round-bottomed flask equipped with a magnetic stirrer. A solution of *endo*-2-aminonorbornane hydrochloride (0.051 g, 0.348 mmol) in 1 mL of water was added slowly to the dioxirane solution at 21 °C over a period of 3 min. The reaction mixture was stirred at room temperature for 7 h. The reaction mixture was diluted with 60 mL of water and then extracted with 4 × 50 mL of CH_2Cl_2. The combined organic solution was washed with 100 mL of water and dried over anhydrous Na_2SO_4 for 8 h. The solvent was evaporated in vacuo to give a yellow oil. Chromatography of the oil using a Chromatotron with a silica gel plate (2 mm) and eluting with CH_2Cl_2 (200 mL) gave, after concentration, a viscous oil, which solidified upon refrigeration to give 31 mg (58%) of *endo*-2-nitronorbornane as a white powder, mp 59–63 °C [lit.[35] mp 64–67 °C]. ^1H NMR ($CDCl_3$): δ 1–1.6 (m, 6 H), 1.7–2.0 (m, 1 H), 2.0–2.22 (m, 1 H), 2.3–2.5 (br s, 1 H, H_d), 2.8–3.0 (br s, 1 H, H_i), 4.7–4.9 (m, 1 H, H_a). ^{13}C NMR ($CDCl_3$): ppm 23.02 (C_6), 28.21 (C_5), 33.24 (C_7), 36.69 (C_4), 38.83 (C_3), 42.84 (C_1), 87.42 (C_2).

***exo*-2-Nitronorbornane.** An acetone solution of 1 (190 mL, 0.061 M, 11.59 mmol) was placed into a 250-mL round-bottomed flask equipped with a magnetic stirrer. A solution of *exo*-2-aminonorbornane (0.215 g, 1.93 mmol) in 25 mL of acetone was added slowly to the dioxirane solution over a period of 4 min. The reaction mixture was stirred at room temperatue for 30 min. The solvent was removed in vacuo. Fresh CH_2Cl_2 (150 mL) was added and the solution dried ($MgSO_4$, 30 min) and then filtered, and the solvent was removed in vacuo. The yellow oil obtained was diluted with 1 mL of CH_2Cl_2 and then subjected to TLC using hexane/ethyl acetate (4:1) as eluent. The band at R_f 0.68 was extracted 3 times with $CH_3COCH_3/CH_2Cl_2/CH_3OH$ (1:1:0.2) and the solvent evaporated to give a yellow oil. Bulb-to-bulb distillation of the oil gave 0.22 g (80.8%) of *exo*-2-nitronorbornane as a pale yellow liquid, bp 125–127 °C/2 mm. ^1H NMR ($CDCl_3$): δ 1.0–1.2 (m, 2 H, $H_h + H_f$), 1.4–1.55 (m, 2 H, $H_e + H_g$) (latter two assignments may be interchanged), 1.2–1.3 (m, 1 H, H_j), 1.5–1.7 (m, 1 H, H_k) (latter two assignments may be interchanged), 1.7–1.8 (m, 1 H, J = 13, 8, 2 Hz, H_b), 2.10–2.25 (m, 1 H, J = 13, 7, 5, 4 Hz, H_c), 2.25–2.48 (br s, 1 H, H_d), 2.7–2.82 (d, 1 H, J = 4.3 Hz, H_i), 4.25–4.4 (dd, 1 H, J = 6, 3 Hz, H_a). ^{13}C NMR ($CDCl_3$): ppm 26.20 (C_6), 27.91 (C_5), 35.65 (C_4), 35.69 (C_7), 36.85 (C_3), 43.50 (C_1), and 87.97 (C_2).

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Photochemistry of Some Extended π-Systems: Type A and Aryl Rearrangements of Systems with Extended Conjugation Related to Cyclohexadienones and Cyclohexenones. Mechanistic and Exploratory Organic Photochemistry[1]

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6,6-Diphenyl-2(6*H*)-naphthalenone and 5,6,6-triphenyl-2(6*H*)-naphthalenone were synthesized as extended relatives of 4,4-diphenylcyclohexadienone and their photochemistry was investigated. In the case of the diphenylnaphthalenone, irradiation resulted in a regioselective phenyl migration and formation of 5,6-diphenyl-2-naphthol whether the photolysis was in methanol or in benzene. Irradiation of the triphenylnaphthalenone in methanol or isopropyl alcohol afforded a product in which one molecule of solvent and one molecule of molecular oxygen were incorporated. Photolysis in acetonitrile led instead to a tricyclic photoproduct in a process reminiscent of the type A rearrangement of 2,5-cyclohexadienones. This tricyclic photoproduct itself was photochemically reactive and rearranged regioselectively to afford 5,7,8-triphenyl-2-naphthol. By trapping, a tricyclic zwitterion was shown to play a role in the rearrangement of the triphenylnaphthalenone. The photochemistry of both naphthalenones was shown by quenching to result from triplet excited states. Lack of reactivity on sensitization suggested the photochemistry derives from T_n. The quantum efficiencies were shown to be lower and the triplet reaction rate slower in a comparison with the monocyclic 4,4-diphenylcyclohexadienone. Finally, enone analogues were investigated. Both 6,6-diphenyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone and 6,6-diphenyl-4,4a,5,6,10,10a-hexahydro-2(3*H*)-anthracenone were synthesized. Only the former was reactive; phenyl migration resulted in formation of four stereoisomeric tricyclic ketones whose structures were established by X-ray analysis. For all of the various reactions, mechanisms are provided and discussed along with MNDO-CI computations.

Introduction

The photochemistry of 2,5-cyclohexadienones and 4-aryl-substituted cyclohexenones has been the object of a number of investigations at Wisconsin.[2,3] Thus, we found that the dienones undergo a "type A" rearrangement[2] while

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