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(8) Traces of **12a** were also detected (tlc) but not isolated. The formation of amides **12**, as pointed out before,[6a] does not proceed by transamidation involving **2a** or **3a** and free dimethylamine. The most likely mechanism involves an exchange reaction[9] between DMF and **7**.

(9) See, for example, J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968, p 338.

(10) Under different conditions (8 hr in boiling butanol in the presence of catalytic amounts of 98% H_2SO_4), Gauger and Manecke[2d] observed limited (*ca.* 10%) conversion of **2a** to **3a**. This finding was interpreted, however, in terms of proton-catalyzed hydrolysis of **2a** by traces of water present in the system, followed by reamidation to **3a** by the mechanism postulated[3] for the direct formation of the 1,3-isomer from squaric acid, and therefore permits no conclusion regarding the relative thermodynamic stabilities and equilibration behavior of the two compounds.

(11) Although drawn in eq 2 as a tight ion pair, the salt **5** is probably fully solvent separated in the medium employed. The structural representation of **5** in Scheme I reflects this situation.

(12) Anilinosquarate anion, although carrying a formal negative charge of unity, is susceptible to nucleophilic attack at the carbon atoms of the four-membered ring, as this negative charge is most certainly localized on the oxygen atoms. In phenylsquarate anion, West and Powell's simple HMO calculations[13] suggest an overall charge density of +1.036 on the ring carbon atoms, with −2.097 units distributed over the three oxygen atoms.

(13) R. West and D. L. Powell, *J. Amer. Chem. Soc.*, **85**, 2577 (1963).

(14) Similar arguments hold for the related reaction type of aromatic nucleophilic displacement on activated substrates: J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 847.

(15) For the analogous phenylsquarate anion, a simple HMO calculation[13] suggests a net charge of +0.320 on C-3 as against +0.264 on each of the equivalent atoms C-2 and C-4.

(16) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 1793 (1960).

(17) Although attempts to monitor by ir spectroscopy the dissociation pattern of **7** in DMF solution failed because of the intrinsic solvent absorption in the critical carbonyl stretching region, we obtained the spectra of **7** and the salt **5** in the similarly aprotic dimethyl sulfoxide (1 *M* solutions). The acid **7** gave the two (asymmetric and symmetric) CO stretching bands at 1800 (m–s) and 1710 (s) cm^{-1} characteristic of the cyclobutene-3,4-dione system. In addition, two very weak bands due to its anion appeared at 1775 and 1655 cm^{-1}, indicating weak ionization. In the spectrum of **5**, the latter two peaks clearly predominated over the former two bands and became virtually the sole bands in this region when another mole of aniline was added, suggesting essentially complete dissociation in the more basic medium. The two-band absorption pattern of anilinosquarate anion at the positions indicated suggests that the vinylogous system is at least partially retained in the anion. The acidic H atom of the anilino group, allowing for powerful chelation and concomitant fixation of the double bond as shown in the structural representation of **5** in Scheme I, may account for this behavior.

(18) Melting points, uncorrected, taken in sealed capillaries. Ir spectra obtained on KBr pellets or DMSO solutions with a Perkin-Elmer Infracord spectrometer.

(19) Double-bond fixation in the 1-hydroxysquarate monoanion of **6**, brought about by strong H bonding to the olate oxygen atom at C-2, permits assignment of the two bands to the asymmetric and symmetric CO stretching vibrations, respectively.

(20) In C_{2v} symmetry of **1**, this vibration is an A_1 species (ν_9 in the notation of Baglin and Rose[21]). The absorption gains intensity in the (H bonded) hydroxysquarate anion of **6** owing to reduced symmetry.

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The Attempted Generation of Triplet Benzyne

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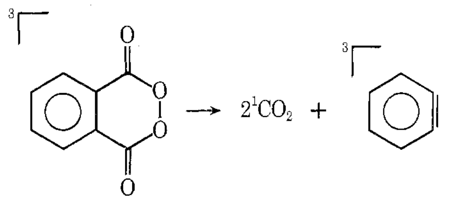
In an attempt to generate benzyne in its excited triplet state, the benzophenone-sensitized decomposition of phthaloyl peroxide (PPO) was examined. A linear Stern–Volmer diagram was obtained. Reaction with *trans*-cyclooctene gave a ratio of cycloadducts indicative of singlet benzyne.

It is generally agreed that the ground state of benzyne is a singlet.[2] Recent calculations[3] predict that the energy separation between the ground singlet and excited triplet states of benzyne may be as low as 0.72 eV.[3f] In an attempt to generate triplet benzyne we have investigated the photochemical decomposition of phthaloyl peroxide (1, PPO) from its triplet state.

Of the reported photochemical benzyne precursors[2a,4] PPO seemed best suited because of the absence of heavy atoms[5] and its solubility in organic solvents. Furthermore, Walling and Gibian have reported that photosensitized decomposition is a general process for acyl peroxides.[8] While this work was in progress, Jones and DeCamp reported that benzyne adducts with olefins can be obtained in good yield from the direct photolysis of PPO through Pyrex.[9] They concluded that the same singlet state species obtained from the thermally generated benzyne was present in the direct photolysis of PPO; they did not observe triplet state benzyne.[9]

Results and Discussion

In order to generate triplet benzyne in a photochemical reaction, the benzyne precursor should be converted into its excited triplet state. In the subsequent cleavage, triplet PPO should form benzyne in the triplet state because of the high triplet energy of carbon dioxide (E_T > 120 kcal/mol).[10] We have observed that PPO can be converted into its excited triplet state by sensitization with benzophenone. Quenching experiments with acrylonitrile[11] were run in acetonitrile using a merry-go-round apparatus. Analyzing for peroxide by iodometric titration[12] we found that PPO is decomposed photolytically (>330 nm) six times faster in the presence of benzophenone than in its absence. In the presence of benzophenone greater than 99% of the light is absorbed by benzophenone, supressing any direct photolysis. A Stern–Volmer plot of the inverse of the relative quantum yield ($1/\phi_{rel}$, loss of peroxide) *vs.* quencher concentration gave a straight line indicating that the decomposition of PPO proceeds *via* the excited triplet state (Figure 1).



1 (PPO)

In order to observe whether or not benzyne is actually generated, a trapping agent which has a higher triplet energy than the sensitizer is required. Furthermore, in order to be able to differentiate between singlet and triplet benzyne, it is desirable that two possible modes of reaction of

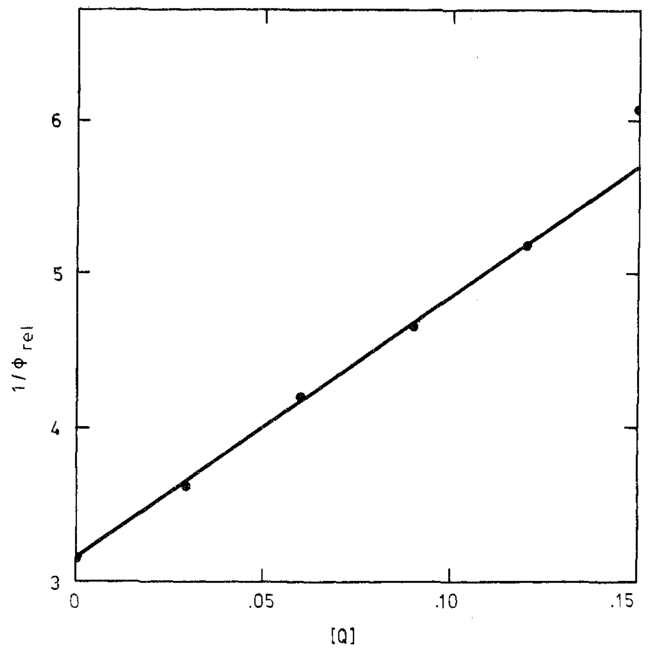
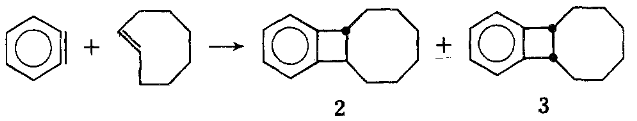


Figure 1. Stern–Volmer plot of $1/\phi_{\mathrm{rel}}$ *vs.* the concentration of acrylonitrile [Q].

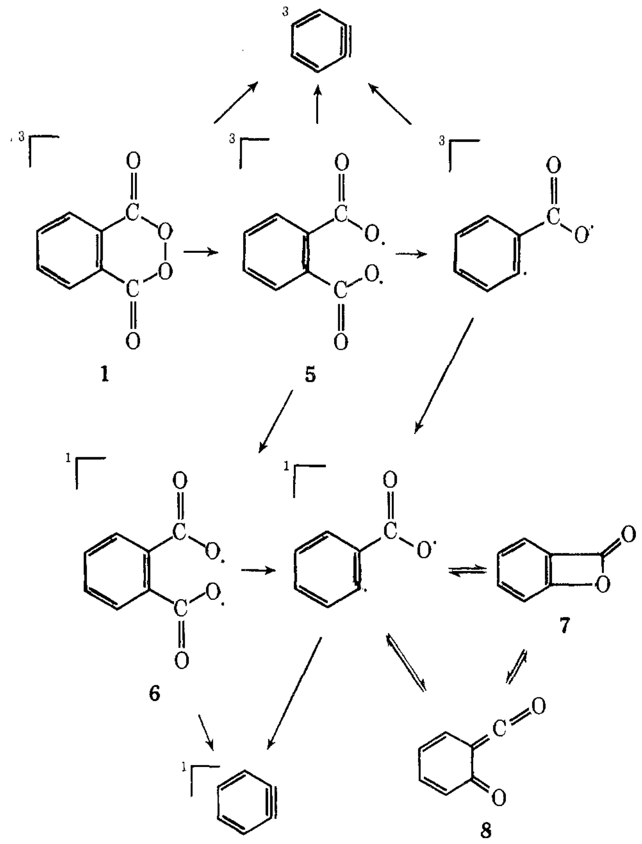
benzyne with the trapping agent exist. Whereas identical product ratios obtained from benzyne generated in different ways would suggest a common intermediate, different product ratios would suggest that the benzyne intermediates are different. Gassman and Benecke[13] have observed that when benzyne generated from benzenediazonium-2-carboxylate reacts with *trans*-cyclooctene, *trans*-**2** and *cis*-**3** [2 + 2] cycloaddition products are formed (45 and 13% yield, respectively) in a nonconcerted reaction.



Using *trans*-cyclooctene as a trapping agent we would expect that the 1,4 diradical intermediate[13] formed in the cycloaddition with triplet benzyne would have a longer lifetime than in the reaction with singlet benzyne. In the triplet reaction a spin inversion is necessary before rebonding can occur to form the cycloadduct. Hence there is more time for rotation to the more stable cis conformation to occur before rebonding takes place. It is therefore reasonable to expect an increase in the ratio of cis to trans cycloadducts relative to the ratio observed by Gassman, if a triplet state intermediate is involved (Skell's postulate).[14]

When *trans*-cyclooctene was used to trap the benzyne from the benzophenone-sensitized decomposition of PPO, the results were complicated by the observation that PPO and *trans*-cyclooctene react thermally at room temperature,[15] forming phthalic anhydride as the main product and cyclooctene oxide, neither of which forms **2** or **3**. In order to suppress this thermal reaction a solution of PPO and *trans*-cyclooctene in acetone[17] prepared at room temperature was subjected to benzophenone-sensitized photolysis at −60°. Gas chromatographic analysis of the reaction mixture still showed mainly the products of the thermal reaction, but also revealed the low yield formation of the two cycloadducts **2** and **3** in the ratio 82:18, respectively.[18] These cycloadducts were formed in the same ratio observed in the reaction of thermally (65°) generated (from benzenediazonium-2-carboxylate) singlet benzyne and *trans*-cyclooctene (81:19 for **2** and **3** respectively). More significantly singlet benzyne generated at −60° under the same conditions by direct irradiation (>330 nm) of benzothiadiazole 1,1-dioxide[19] led again to **2** and **3** in a 82:18 ratio. This result suggests that a reaction of singlet benzyne was observed in the photosensitized decomposition of PPO.[20]

Scheme I[21]



The possible stages in the decomposition of triplet PPO including spin inversion and demotion to the ground singlet states are shown in Scheme I. The present results suggest that the rate of triplet–singlet interconversion in one of the intermediates is faster than the loss of two carbon dioxide molecules which results in benzyne. It seems most reasonable that this spin inversion takes place in intermediate **5**. The spin density in this diradical should be mostly localized on the electronegative oxygen atoms which are separated from one another by four carbon atoms. Hence, in this species one might expect the energy difference between the singlet and triplet manifolds to be small, and that the spin inversion would therefore be rapid. We expect that this situation would arise with any sensitized reaction in which benzyne is generated in a stepwise process. Future attempts at the synthesis of triplet benzyne are therefore likely to be successful only if a one-step decomposition of the triplet precursor can be realized.

Experimental Section

Reagents. Phthaloyl peroxide (PPO) was prepared according to Jones[9] or Russel[24] and contained 94% active oxygen by iodometric titration.[25] Benzothiadiazole 1,1-dioxide was purified *via* its dihydro compound.[19] Benzophenone was recrystallized from ethanol. Acetonitrile and acrylonitrile were freshly distilled.

trans-**Cyclooctene.** trans-Cyclooctane-1,2-diol[26] (101 g, 0.70 mol) and ethyl orthoformate (104 g, 0.70 mol) were heated at 140–160° for 8 hr, while ethanol distilled off. Fractionation of the mixture yielded after a forerun 68.8 g (34%) 2-ethoxy-*trans*-cyclooctano[1,2-*d*]dioxolane.

This as well as the polymeric pot residue can be cleaved to *trans*-cyclooctene (*cf.* ref 27); 20.3 g of the above dioxolane was heated at 220–240°. A stream of nitrogen swept the products into a cooled receiver. The condensate (13.7 g) was fractionated. The fraction of bp 78° (72 Torr) was taken up in petroleum ether (40–

60°), washed twice with water, and with brine, dried (Na_2SO_4), and distilled giving cyclooctene (95.5% trans, 4.5% cis by vpc).

Photolysis. PPO (60.0 mg) and benzophenone (60.0 mg) were dissolved in 10 ml of acetonitrile in a 10 mm o.d. Duran tube. After degassing by four freeze–thaw cycles the tube was sealed and irradiated in a merry-go-round apparatus by a high-pressure mercury arc (Hanau-Q-700) *via* 1.5 cm of a filter solution[28] containing 650 g of $NaBr \cdot 2H_2O$ and 3.00 g of $Pb(NO_3)_2$ per liter (cut-off 330 nm). The filter system was chosen such that after 20-min irradiation 46% of PPO had been destroyed in the presence of benzophenone and <8% in the absence of benzophenone. Samples were analyzed iodometrically.[25] One sample was irradiated for 5 hr and the tube was frozen, opened, and connected to a system which swept the carbon dioxide formed into $Ba(OH)_2$ solution with nitrogen. Titration with 0.1 *N* HCl showed 73% of 2 equiv of CO_2 to be formed. The residual solution gave a negative test for peroxide.

Quenching Study. Photolyses were carried out as above (20-min irradiation). The samples contained 0.02–0.10 ml of acrylonitrile. Relative quantum yields were determined iodometrically.[25] With higher acrylonitrile content (up to 0.5 ml) total quenching was approached.

Benzyne Trapping. PPO (60.0 mg) and benzophenone (60.0 mg) were dissolved in 10 ml of acetone in a 10-mm o.d. Solidex tube. *trans*-Cyclooctene (0.255 ml) was added and the mixture was immediately degassed by three freeze–thaw cycles. The cold tube was positioned in a Liebig condenser, through the jacket of which methanol at −50 to −60° was circulated, and irradiated for 5 hr as above. After stripping the solvent, the reaction mixture was analyzed by vpc (⅛ in. × 6 ft column with 10% Apiezon on 60/80 Chromosorb R, 180°, 35 ml of N_2/min; or ¼ in. × 12 ft column with 15% polyphenyl ether OS 124 on 60/100 kieselgur, 180°, 80 ml of N_2/min). The main component was phthalic anhydride. Two minor peaks (ratio 82:18) had the same retention time as **2** and **3** prepared by the method of Gassman.[13] In our hands the latter method gave **2** and **3** in a 81:19 ratio. For final identification the sample was chromatographed on a 4 m × 3 mm glass column with 2.5% SE 52 on 80/100, Chromosorb G-AW DMCS, 160°, 25 ml of He/min. The column effluents were transferred *via* on all-glass two-stage Biemann separator to an Atlas CH4B mass spectrometer. **2** and **3** from the PPO reaction showed the same retention times and mass spectra as the authentic samples.

Photolysis of Benzothiadiazole 1,1-Dioxide. Benzothiadiazole 1,1-dioxide (9.36 mmol) in 10.0 ml of acetone (−10°) was added to *trans*-cyclooctene (0.255 ml) at −78°. After degassing, the mixture was photolyzed as above. Although decolorized after 20 min, the irradiation was continued for 4 hr. Vpc analysis (⅛ in. × 12 ft column with 4% SE 52 on Chromosorb G, 135°, 50 ml of N_2/min) showed the presence of **2** and **3** in a 82:18 ratio.

Photoisomerization of *trans*-Cyclooctene. Benzophenone (60.0 mg) and *trans*-cyclooctene (0.255 ml) were photolyzed exactly as above. Vpc analysis (300 ft × 0.01 in. capillary column with Carbowax 20M, 70°, 40 psi He) showed that 7.3% *cis*-cyclooctene had been formed.

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Registry No.—**1**, 4733-52-2; benzyne, 462-80-6; *trans*-cyclooctene, 931-89-5; *trans*-cyclooctane-1,2-diol, 42565-22-0; benzophenone, 119-61-9; benzothiadiazole 1,1-dioxide, 37150-27-9; ethyl orthoformate, 122-51-0.

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