

a σ^\pm treatment has been applied similarly before.³³ One might not expect the same sensitivity, ρ , to apply over the whole range. These interactions of excited carbonyl with amines involve partial electron and partial hydrogen transfer in the transition state.⁵ The former may dominate with electron donating and the latter with withdrawing substituents. There may in effect be a

change in mechanism over the range of substituents and the data might alternately be placed on a broken line. However, the considerations relating to applicability of σ^+ and σ^- , above, appear relevant.

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The Laser Initiated Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene¹

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Abstract: As part of a program to appraise the photochemical potential of the argon ion laser the photoaddition of *p*-benzoquinone to cyclooctatetraene has been examined. Laser irradiation of these materials in a nonacidic solvent leads to the formation of the 1,4-adduct **5**. When acetic acid is used as the solvent, **5** is not observed. Instead the acid catalyzed rearrangement products, **6** and **7**, are observed as the only products. If the irradiation is conducted in a nonacidic solvent in the presence of oxygen, the peroxide 4'a,10'a-dihydrospiro[2,5-cyclohexadiene-1,3'-cycloocta-as-trioxin]-4-one (**11**) is formed in good yield. The structure of **11** was confirmed by a single crystal X-ray study conducted with the 3-bromo derivative **13**. The mechanism of this unusual oxidative photoaddition and the advantages of the laser light source are discussed.

The anaerobic photochemistry of quinones has been studied extensively,² but only recently has the effect of oxygen upon quinone photochemistry begun to be assessed.³ Our attention has been drawn to this area for two reasons. The weak long wavelength n, π^* absorption of most quinones in the 450–500-nm region of the spectrum is well suited for excitation with an argon laser,⁴ thus constituting an ideal system for evaluating the photochemical potential of the argon laser. Furthermore, photooxidations initiated by n, π^* excited carbonyl groups have not been examined in any detail, and in particular a knowledge of quinone photooxidations might be most useful in view of the involvement of quinones in biological oxidations.⁵ Consequently, we have undertaken a general program of study intended to better define the scope and mechanistic nature of quinone-sensitized photooxidations of olefins using an argon ion laser as the exciting source. The *p*-benzoquinone (PBQ)–cyclooctatetraene (COT) system has been examined as a part of this general program, and observed to yield several novel photo-

products. Of these substances only one arises from the reaction of molecular oxygen. The structure of this material has been unequivocally determined by X-ray crystallography, and found to be that of a unique dienone–peroxide. Therefore, while the overall objectives of the general program are still under active investigation, the unusual results observed in the PBQ–COT system are reported at this time.

Results and Discussion

Anaerobic Photochemistry. Argon laser irradiation of PBQ and COT in the absence of oxygen and in a nonacidic solvent such as carbon tetrachloride, benzene, acetone, or methanol affords a single product ($\sim 77\%$). This sensitive substance has apparently been prepared previously using conventional light sources.⁶ However, it may be isolated more readily and in crystalline form from the uncomplicated laser reaction mixture. Elemental analysis and mass spectroscopy, m/e 212 (M^+), indicate that the material is a 1:1 adduct between PBQ and COT. The nmr spectrum of the adduct exhibits two overlapping doublets of doublets, (δ) 2.74 ppm, $J = 8$ Hz (1 H) and 4.67 ppm, $J = 5$ Hz (1 H). These signals had previously been assigned to the oxetane protons in the 1,2-cycloaddition product **1**.⁶ However, these two signals have been shown not to be coupled with each other in a double resonance experiment. Furthermore, in our hands Pd/C hydrogenation of this adduct yielded a phenolic alcohol **2**, mp 136.8–137.2°, which was not the same as the analogous Pd/C hydrogenation product **3**, mp 120–121°, obtained from

(1) E. J. Gardner, R. H. Squire, R. C. Elder, and R. M. Wilson, *J. Amer. Chem. Soc.*, **95**, 1693 (1973).

(2) J. M. Bruce, *Quart. Rev., Chem. Soc.*, **21**, 405 (1967).

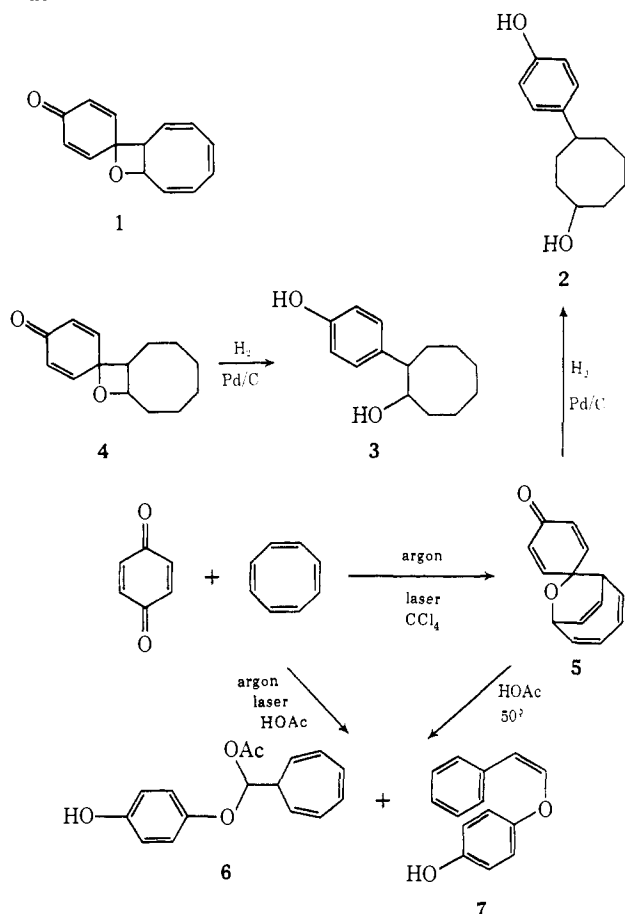
(3) (a) C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 731 (1969); (b) D. Creed, H. Werbin, and E. T. Strom, *ibid.*, **93**, 502 (1971); (c) S. Fugisawa, S. Kawabata, and R. Kamamoto, *J. Pharm. Soc. Jap.*, **87**, 1451 (1967); (d) M. Ohmae and G. Katsui, *Bitamin*, **35**, 116 (1967); (e) G. Katsui and M. Ohmae, *J. Vitaminol. (Kyoto)*, **12**, 117 (1966).

(4) The n, π^* absorption of *p*-benzoquinone, for example, has $\lambda_{\text{max}}^{\text{hexane}}$ 458 nm (ϵ 21) and 479 (11). A Coherent Radiation Model 53A argon ion laser was used in this work. This laser emits 6 W of power in the following lines: 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2).

(5) R. A. Morton, Ed., "Biochemistry of Quinones," Academic Press, New York, N. Y., 1965; T. P. Singer, "Biological Oxidations," Interscience, New York, N. Y., 1968.

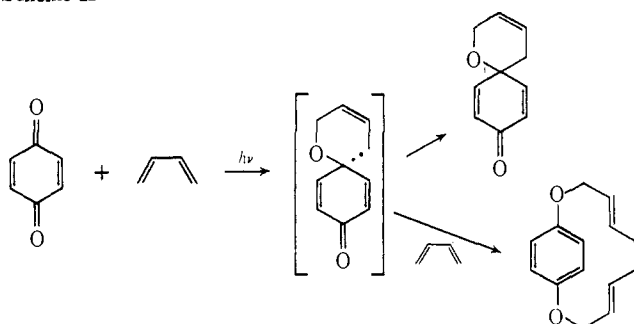
(6) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).

Scheme I



the oxetane 4 (Scheme I). These data together with the further chemistry of the adduct (*vide infra*) strongly suggest that the correct structure is the 1,4-adduct 5 rather than the 1,2-adduct 1 proposed originally. This mode of addition is not altogether unexpected since excited quinones have been previously observed to undergo 1,4-cycloadditions of this type with dienes rather than the more typical photochemically allowed 1,2-cycloaddition.^{2,7} Apparently these 1,4-additions are not concerted, but proceed through a long-lived, possibly biradical intermediate. The involvement of such an intermediate is supported by the fact that it may be trapped if the reaction is conducted using high diene concentrations (Scheme II).⁷

Scheme II

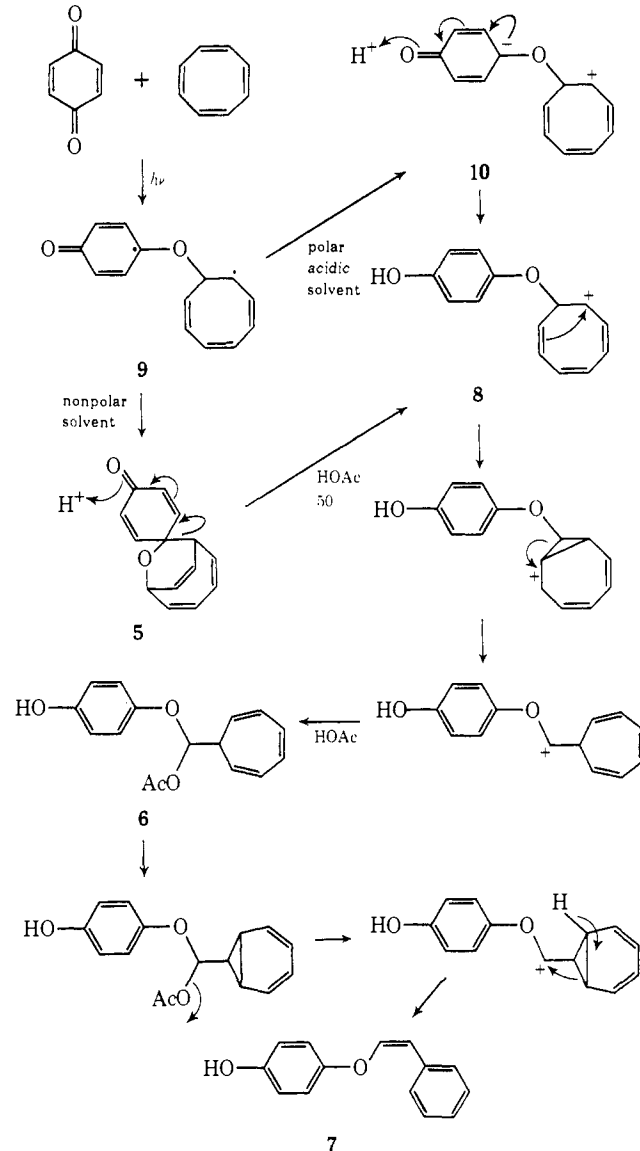


In striking contrast the photochemistry of PBQ and COT in acetic acid yields two new substances as the only products (Scheme I). The cycloheptatriene derivative 6 was isolated as an oil (58%): nmr (δ) 2.02 ppm (s, 3 H), 2.30 (d of t, 1 H, $J = 6$ and 6 Hz), 5.42 (m,

(7) J. A. Barltrop and B. Hesp, *J. Chem. Soc.*, 5182 (1965).

2 H), 6.22 (m, 2 H), and 6.65 (m, 8 H). The enol ether of phenylacetaldehyde 7 was isolated in 26% yield: mp 81.5 – 82.5° ; nmr (δ) 5.48 ppm (d, 1 H, $J = 7$ Hz), 6.48 (d, 1 H, $J = 7$ Hz), and 6.65–7.75 (m, 10 H). These same materials are also formed when the adduct 5 is warmed in acetic acid. Prolonged heating of either the adduct 5 or the cycloheptatriene 6 results in complete conversion to the enol ether 7. It is perhaps of significance that during the laser irradiation the presence of 5 was not detected by thin-layer chromatography. Therefore, it would seem that 5 is not an intermediate in the formation of 6 and 7, since the thermal rearrangement of 5 requires about 9 hr at 50° for complete consumption of 5, and the irradiation took place in 1.5 hr at ambient temperature. A rationale for the convergence of the thermal and photochemical rearrangement is outlined in Scheme III. The thermal

Scheme III

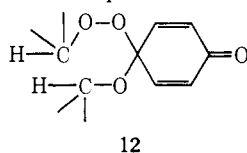


pathway probably proceeds through protonation of the dienone 5 and carbon-carbon bond cleavage to yield the stabilized carbonium ion 8. A series of ring contractions would then afford the cycloheptatriene 6 and the enol ether 7. Similar acid-catalyzed rearrangements have been reported for the epoxide of COT and certain cycloheptatriene derivatives.⁸ The photochemical for-

mation of **6** and **7** probably arises from the biradical **9**. In relatively nonpolar and nonacidic solvents this species collapses to the dienone **5**. However, solvation in a polar acidic medium would increase the energy separation between the dienone and cyclooctatrienyl orbitals of the biradical. This increased splitting might be sufficient to strongly favor the zwitterionic form **10** over the covalent form **9**.⁹ Protonation of **10** would afford ion **8** which would be common to both the thermal and photochemical pathways. One final point that must be mentioned is the assignment of the cis geometry for the enol ether double bond of **7**. This assignment is based on the olefinic proton coupling constants ($J = 7$ Hz). The trans isomer has not been observed, and the reason for this specific formation of the cis isomer is unclear.

Aerobic Photochemistry. Against this background of the anaerobic photochemistry of PBQ and COT, it was most interesting to observe the effect of oxygen upon these reactions. In any one of a variety of nonacidic solvents such as carbon tetrachloride, benzene, acetone, or methanol a new substance **11** was obtained along with the previously observed 1:1 adduct **5**. Typical yields under aerobic conditions were 49% for **11** and 31% for **5** in carbon tetrachloride. Acetic acid again proved to be an anomalous solvent yielding only **6** and **7** in the same manner as under anaerobic conditions.

This new substance **11** has mp 111.7–111.9°; ir (KBr) 1670 and 1635 cm^{-1} ; nmr (90 MHz, CCl_4) (δ) 4.88 ppm (m, 2 H), 5.70 (bt, 2 H), 6.13 (m, 4 H), 6.25 (dd, 1 H, $J = 10.8$ and 2 Hz), 6.30 (dd, 1 H, $J = 10.4$ and 2 Hz), 6.58 (dd, 1 H, $J = 10.4$ and 3.1 Hz), and 7.62 (dd, 1 H, $J = 10.8$ and 3.2 Hz); M^+ 244; positive starch-iodide test for peroxides. These data are consistent with a 1:1:1 adduct between PBQ, COT, and molecular oxygen, and suggest that the adduct is a dienone-peroxide with partial structure **12**. Un-

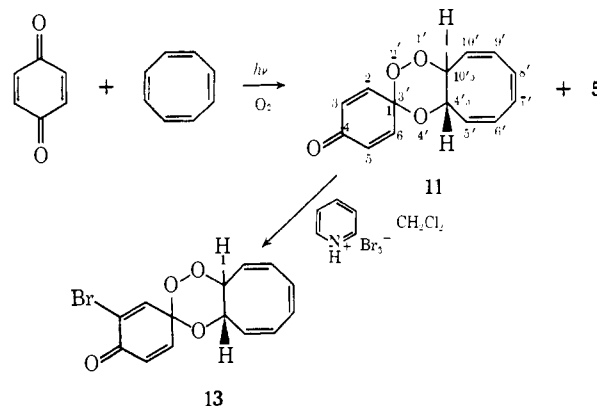


12

fortunately the data did not clearly define the nature of the COT-derived portion of the molecule, and efforts to gain further information about this aspect of the structure by chemical degradation were unsuccessful. Treatment of **11** with a variety of reagents leads either to no reaction, a plethora of products, or a straightforward and uninformative reaction at the dienone moiety. One such reaction was the bromination of **11** with pyridinium hydrobromide perbromide. This reagent converted **11** to what appeared to be, by the standard criteria of thin-layer chromatography, melting point, and elemental analysis, a single monobromide **13** in 89% yield. However, information obtained in an X-ray study of this material (see X-ray section) indicated the material is a 92:8 mixture of the 3- and 5-monobromides of **11**. This mixture had mp 138.8–139.1°; nmr (90 MHz, CDCl_3) (δ) 4.87 ppm (m, 2 H), 5.70 (m, 2 H), 6.13 (m, 4 H), 6.38 (d, 1 H, $J = 10$ Hz), 6.59 (dd, 1 H, $J = 10$ and 3 Hz), 8.04 (d, 1 H, $J =$

3 Hz); m/e M^+ 322 and 324. These data confirmed that **11** had not been brominated in the COT-derived moiety as might have been expected, but in the position α to the carbonyl in the dienone moiety (Scheme IV). The structures of **13** and the parent compound, 4'a,-

Scheme IV



10'a-dihydrospiro[2,5-cyclohexadiene-1,3'-cyclooctatrioxin]-4-one (**11**),¹⁰ were unequivocally established by a single-crystal X-ray study of the monobromide **13** (see X-ray section).

The mechanism of peroxide formation is a point of considerable interest concerning which we can offer the following observations. Peroxide formation is not a consequence of some exotic property of the laser radiation. The usual broad-spectrum ultraviolet sources emitting in the 360-nm region also produce **11**. However, **11** absorbs in this region of the spectrum, and suffers decomposition in the process such that the net result is an extremely complex polymeric reaction mixture. If one uses pure **11** as a thick-layer chromatography guide, crude **11** can be isolated from this mixture after extensive chromatography in about 4% yield. Conventional visible sources will also yield **11**, but only in small quantities after very long irradiation times. Under these conditions thermal decomposition tends to complicate the reaction mixture. The success of the laser irradiation must be attributed to nothing more than the delivery of a large amount of energy to the quinone n, π^* absorption in a short time period, and to the lack of absorption by the photoproducts at the irradiation wavelengths. Consequently, the formation of peroxide **11** should be amenable to description in conventional linear photochemical terms.

The question of the exact nature of the species which leads to peroxide formation is not completely clear. Certainly initial excitation of PBQ is favored over excitation of COT, since the quinone n, π^* absorption coincides with the laser wavelengths.⁴ In this same region of the spectrum COT exhibits only end absorption with an extinction coefficient considerably less than one. In the dilute solutions employed (*ca.* 10^{-2} M) there is no spectroscopic evidence for complexation between the PBQ and COT which might alter the absorption spectrum of either of the compounds¹¹ or

(10) We are indebted to K. L. Loening of Chemical Abstracts Service for suggesting this nomenclature.

(11) Other workers have reported anomalous bands in the ultraviolet spectra of PBQ in olefin solvents; see ref 6 and 7. In the present case the observation of PBQ in concentrated or neat COT was not possible due to the long-wavelength absorption of COT and to the thermal reaction which takes place between PBQ and COT in very concentrated solutions. This Diels-Alder reaction was not observed in the dilute solutions used for the photochemical work.

(8) C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 576 (1958).

(9) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

favor a singlet excited state reaction. Therefore, the quinone triplet is in all probability involved.¹²

The triplet energy of PBQ is well established to be about 50 kcal/mol.¹³ The triplet energy of COT is much less certain. In the formation of semibullvalene from COT, acetone ($E_t = 78$ kcal/mol) was an effective sensitizer, but acetophenone ($E_t = 74$ kcal/mol) was not.¹⁴ On the basis of these data one might place the triplet energy of COT between 78 and 74 kcal/mol. This estimate of the triplet energy of COT very possibly represents a higher triplet state, since COT has been observed to quench rose bengal ($E_t = 39.4$ kcal/mol) in sensitized photooxidations.¹⁵ Therefore, the possibility exists that PBQ might transfer its triplet energy to COT. However, quinones seem to be anomalous sensitizers in that sensitization does not always take place on a straightforward energetic basis. Instead excited-state complexes between the quinone and olefin can result, and these complexes can decay to either the triplet state of the olefin, or to a quinone-olefin adduct.^{13b, 16}

Bearing these considerations in mind one might consider three general mechanisms for the formation of the peroxide **11**. These possibilities differ in the order with which the three reactants become incorporated into **11** (Scheme V). In pathway A the triplet n, π^* of PBQ might conceivably react with oxygen to form the spirotrioxetane **14** or some related species **15**. Either of these reactive species might then add to COT in a 1,2 fashion yielding **11**. Pathway B invokes the COT dioxetane **16** which could arise either from the reaction of triplet COT with ground-state oxygen or the reaction of ground-state COT with singlet oxygen. This dioxetane might then incorporate a molecule of quinone to form **11**. Finally in pathway C an initial adduct (**9**) between PBQ and COT is envisaged. The 1,4-biradical **9** is the same as was previously invoked to explain the formation of **5**, **6**, and **7**. In the presence of oxygen this biradical might be intercepted by a molecule of oxygen to form **11**.

Using pathway A as a working hypothesis one might expect a variety of olefins to react with **15** to form trioxanes related to **11**. It has been our somewhat limited experience that nonconjugated olefins and conjugated aryl olefins such as 1,5-cyclooctadiene, norbornadiene, and stilbene react with PBQ in an uncomplicated fashion under aerobic conditions to form oxetanes and their rearrangement products. No photoproducts that have incorporated a molecule of oxygen have been detected in careful examinations of these systems. If pathway B were operating, one might expect to be able to trap **16** with a carbonyl com-

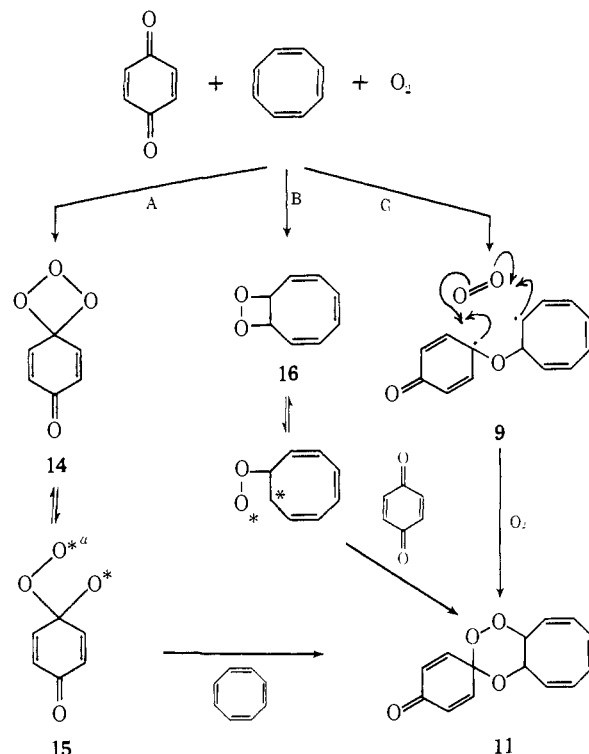
(12) In those cases where direct evidence is available, quinones usually react through the triplet states. The exception is duroquinone; see ref 2.

(13) (a) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 244; (b) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(14) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **92**, 2015 (1970).

(15) K. Gollnick, *Advan. Photochem.*, **6**, 18 (1968), and references therein.

(16) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966); J. J. Bohning and K. Weiss, *ibid.*, **88**, 2893 (1966). Energy transfer and adduct formation with PBQ are competing processes even when the triplet energy of a conformationally mobile diene is nearly 10 kcal/mol below that of PBQ: R. M. Wilson and S. W. Wunderly, unpublished results.

Scheme V^a

^a * = .., +, -.

pound other than the quinone. Several 1,2,4-trioxanes derived from acetone have been reported to be surprisingly stable substances.¹⁷ Nevertheless when PBQ and COT are irradiated under aerobic conditions in acetone as the solvent no acetone-derived trioxanes could be detected. The sole products were the usual quinone trioxane **11** and the 1:1 adduct **5**. The likelihood of **16** as an intermediate is further diminished by the inert nature of COT toward photooxidation with dye sensitizers.¹⁸

Pathway C seems to offer the best explanation for the formation of **11**. Assuming rate constants in the vicinity of the diffusion limit for the addition of triplet quinone to COT and for the quenching of triplet quinone by ground-state oxygen, the COT ($2.8 \times 10^{-2} M$) should compete favorably with oxygen ($5-1 \times 10^{-3} M$)¹⁹ for the triplet quinone. The resulting triplet **9** might then undergo spin inversion to singlet **9** which could collapse to **5**. Alternatively, either triplet or singlet **9** might be trapped by oxygen to afford **11**. The success of such a trapping process would depend upon the lifetime of the biradical **9**. Again assuming a diffusion-controlled rate constant for the trapping step and oxygen concentrations in the vicinity of $10^{-3} M$, a biradical lifetime in the range of 10^{-7} – 10^{-6} sec would be necessary in order for appreciable trapping to be realized. Clearly, biradicals similar to **9** can be trapped by dienes at high concentration (Scheme II).⁷ Biradicals

(17) G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1682 (1957); M. Schulz, *Advan. Heterocycl. Chem.*, **8**, 182 (1967); W. Adam and A. Rios, *Chem. Commun.*, 822 (1971).

(18) Our observation of the lack of photooxidation of COT is in accord with that of previous workers: G. O. Schenck and K. Gollnick, *J. Chim. Phys. Physicochim. Biol.*, **55**, 892 (1955).

(19) C. S. Parmenter and J. D. Rau, *J. Chem. Phys.*, **51**, 2242 (1969); R. Nilsson, P. B. Merkel, and D. R. Kearns, *Photochem. Photobiol.*, **16**, 109 (1972); N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49 (1972); E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973).

Table I. Fractional Atomic Coordinates^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Br ^b	1.1499 (1)	0.3654 (3)	0.2300 (1)	C(5)	1.0096 (13)	0.8335 (26)	0.0832 (8)
Br' ^c	1.1238 (18)	0.9447 (29)	0.1161 (12)	C(6)	0.9031 (12)	0.7501 (26)	0.0644 (8)
O(1')	0.7695 (7)	0.2315 (15)	0.0522 (5)	C(4'a)	0.6866 (9)	0.4172 (20)	0.1557 (6)
O(2')	0.8259 (7)	0.4279 (17)	0.0283 (5)	C(5')	0.5831 (11)	0.5096 (23)	0.1925 (7)
O	1.1808 (9)	0.7961 (21)	0.1579 (7)	C(6')	0.4665 (11)	0.5141 (22)	0.1728 (8)
O(4')	0.7578 (6)	0.5940 (14)	0.1361 (4)	C(7')	0.4004 (11)	0.4189 (25)	0.1085 (8)
C(1)	0.8585 (11)	0.5492 (23)	0.0954 (7)	C(8')	0.4032 (11)	0.2303 (29)	0.0800 (8)
C(2)	0.9423 (10)	0.4222 (24)	0.1446 (7)	C(9')	0.4844 (14)	0.0576 (24)	0.0988 (8)
C(3)	1.0519 (12)	0.5138 (23)	0.1621 (7)	C(10')	0.6040 (13)	0.0854 (23)	0.1018 (7)
C(4)	1.0870 (13)	0.7145 (25)	0.1367 (7)	C(10'a)	0.6584 (10)	0.2893 (22)	0.0848 (7)

^a Estimated standard deviations in the last digit are given in parentheses. This form is used throughout the paper. ^b Population parameter = 0.9242 (81). ^c Population parameter = 0.0868 (62).

Table II. Atom Thermal Parameters^a

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Br	529 (9)	1082 (14)	881 (12)	122 (9)	-133 (7)	303 (11)
Br'	1191 (204)	704 (159)	1443 (213)	-440 (136)	449 (153)	-182 (136)
O(1')	691 (59)	764 (68)	760 (61)	79 (53)	-121 (47)	-127 (54)
C(2')	591 (54)	1137 (89)	631 (57)	169 (57)	-52 (44)	-65 (59)
O	829 (74)	1001 (95)	1305 (94)	-161 (72)	-276 (67)	119 (81)
O(4')	448 (46)	858 (69)	659 (53)	75 (48)	43 (40)	-85 (50)
C(1)	590 (81)	780 (103)	715 (90)	143 (76)	-26 (71)	-67 (82)
C(2)	453 (74)	1078 (124)	752 (90)	179 (80)	-106 (64)	2 (86)
C(3)	755 (92)	653 (96)	661 (86)	225 (79)	19 (70)	172 (76)
C(4)	742 (101)	796 (114)	700 (93)	118 (88)	81 (79)	91 (85)
C(5)	635 (90)	988 (124)	970 (109)	103 (94)	-24 (79)	149 (100)
C(6)	706 (96)	916 (118)	879 (104)	88 (91)	80 (80)	341 (94)
C(4'a)	451 (67)	685 (91)	538 (71)	-22 (67)	18 (56)	-40 (66)
C(5')	596 (83)	751 (99)	688 (85)	-53 (74)	28 (66)	-20 (77)
C(6')	587 (82)	749 (99)	816 (94)	-7 (74)	7 (70)	72 (83)
C(7')	570 (81)	830 (114)	712 (93)	42 (78)	-9 (69)	42 (85)
C(8')	569 (83)	1100 (137)	665 (90)	-70 (93)	-108 (66)	-62 (95)
C(9')	923 (117)	784 (111)	760 (97)	-99 (94)	-84 (83)	-148 (84)
C(10')	882 (104)	762 (110)	590 (83)	47 (88)	-120 (73)	-131 (77)
C(10'a)	478 (72)	772 (98)	597 (79)	58 (70)	75 (59)	-124 (73)

^a $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$; all values have been multiplied by 10⁴.

When compared with dimeric peroxides (1,2,4,5-tetraoxanes) all trioxane angles and bond distances are in close agreement. The largest difference is the C(3')-O(4') distance of 1.41 (2) Å as compared with the average of the other C-O distances 1.46 (1) Å. The C(3')-O(4')-C(4'a) angle may be open slightly. Both of these rather minor effects could be attributed to the longer C(10'a)-C(4'a) bond.

It should be noted that the spiro carbon atom has significant deviation from typical tetrahedral angles. In an analogous dienone ring, angular variations of the spiro carbon are to be expected and have been shown to occur.²⁹ The structures of the dienone rings compare favorably.

The geometry of 1,3,5-cyclooctatriene has not been established. Here this ring does not appear to be overly strained, and is quite similar to cyclooctatetraene.³⁰ The distortions from tetrahedral geometry of C(10'a) and C(4'a) range from 113 (1) to 103 (1)°. The standard sp²-sp³ hybridized carbon bond distance observed here is an averaged 1.49 (2) Å. The usual distance is 1.51 Å. The structure of 1,3,5-trimethyl-7-methylene-1,3,5-cyclooctatriene complexed with two iron atoms has been reported.³¹ However, it is difficult

to assess the effects of the exocyclic double bond and the iron complexation on the structure.

When the structure had been refined to an *R* factor of 0.086 with anisotropic temperature parameters, a small peak, approximating one-third of a carbon atom, was discernible in the Fourier difference map. This peak was presumably due to partial bromination at the 5 position. When a model assuming a mixture of the 3- and 5-monobromides was adopted for further refinement, the *R* factor decreased to 0.073, and the isomer populations were determined to be about 92% for the 3-bromo isomer and 8% for the 5-bromo isomer (see Experimental Section).

Conclusions

On the basis of our limited experience it would seem that the argon laser shows considerable promise as a photochemical light source for the rapid preparation of both thermally and photochemically sensitive substances on the gram scale. The formation of the trioxane **11** not only illustrates this point convincingly, but provides the second photochemically prepared example of these unusual olefin-quinone-oxygen adducts to be observed. The formation of these adducts seems to be dependent upon subtle stereoelectronic factors which influence the lifetime of the oxetane precursor biradical, and stabilize this species long enough to permit trapping by oxygen. A more detailed investigation of

(29) A.-M. Pilotti, *Acta Crystallogr., Sect. B*, **28**, 2123 (1972).

(30) J. Bordner, R. G. Parker, and R. H. Stanford, Jr., *Acta Crystallogr., Sect. B*, **28**, 1069 (1972).

(31) F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **90**, 2031 (1968).

Table III. Bond Distances (Å)

Atom	Atom	Distance	Atom	Atom	Distance	Atom	Atom	Distance
Br	C(3)	1.890 (13)	C(1)	C(2)	1.523 (19)	C(4'a)	C(5')	1.495 (17)
O(1')	O(2')	1.486 (14)	C(2)	C(3)	1.417 (18)	C(4'a)	C(10'a)	1.533 (17)
O(1')	C(10'a)	1.464 (15)	C(3)	C(4)	1.424 (21)	C(5')	C(6')	1.377 (17)
O(2')	C(3')	1.467 (16)	C(4)	C(5)	1.498 (21)	C(6')	C(7')	1.490 (19)
O	C(4)	1.250 (19)	C(5)	C(6)	1.366 (20)	C(7')	C(8')	1.313 (24)
O(4')	C(4'a)	1.446 (15)	C(6)	C(1)	1.497 (21)	C(8')	C(9')	1.480 (22)
O(4')	C(1)	1.410 (15)	C(4'a)	O(4')	1.446 (15)	C(9')	C(10')	1.386 (21)
						C(10')	C(10'a)	1.484 (20)

Table IV. Bond Angles (deg)

Central atom	Atom 1	Atom 3	Angle	Central atom	Atom 1	Atom 3	Angle
O(1')	C(4'a)	C(1)	116.1 (10)	C(5)	C(4)	C(6)	118.0 (14)
O(4')	O(2')	C(10'a)	106.8 (9)	C(6)	C(1)	C(5)	123.9 (13)
O(2')	O(1')	C(1)	108.7 (8)	C(4'a)	O(4')	C(10'a)	109.3 (9)
C(1)	O(4')	O(2')	109.4 (9)		O(4')	C(5')	104.7 (10)
	O(4')	C(6)	107.8 (11)		C(10'a)	C(5')	114.8 (9)
	O(4')	C(2)	109.1 (10)	C(5')	C(4'a)	C(6')	132.5 (12)
	O(2')	C(6)	103.9 (11)	C(6')	C(5')	C(7')	131.5 (12)
	O(2')	C(2)	109.3 (11)	C(7')	C(6')	C(8')	131.2 (11)
	C(6)	C(2)	117.1 (11)	C(8')	C(7')	C(9')	128.6 (13)
C(2)	C(1)	C(3)	116.7 (13)	C(9')	C(8')	C(10')	122.0 (14)
C(3)	C(4)	C(2)	124.1 (13)	C(10')	C(9')	C(10'a)	121.8 (13)
C(4)	O	C(3)	121.9 (13)	C(10'a)	O(1')	C(4'a)	107.1 (9)
	O	C(5)	118.4 (14)		O(1')	C(10')	103.4 (11)
	C(3)	C(5)	119.7 (12)		C(4'a)	C(10')	112.7 (10)

Table V. Root Mean Square Displacements (Å)

Atom	Min	Mean	Max	Atom	Min	Mean	Max
Br	0.2164	0.2865	0.3672	C(5)	0.2351	0.2687	0.3373
Br'	0.2162	0.3055	0.3981	C(6)	0.2272	0.2491	0.3499
O(1')	0.2458	0.2464	0.2966	C(4'a)	0.1981	0.2207	0.2498
O(2')	0.2218	0.2405	0.3424	C(5')	0.2368	0.2436	0.2671
O	0.2040	0.3313	0.4073	C(6')	0.2241	0.2600	0.2827
O(4')	0.2002	0.2563	0.2855	C(7')	0.2184	0.2570	0.2830
C(1)	0.2162	0.2549	0.2841	C(8')	0.2107	0.2419	0.3308
C(2)	0.1950	0.2641	0.3162	C(9')	0.2162	0.2873	0.3040
C(3)	0.1842	0.2504	0.3101	C(10')	0.2187	0.2562	0.3128
C(4)	0.2371	0.2454	0.3024	C(10'a)	0.1898	0.2358	0.2774

these factors is underway along with further efforts to extend the photochemical usefulness of the laser.

Experimental Section

Melting points were determined with a Mettler FP-2 hot-stage apparatus. Nuclear magnetic resonance spectra were recorded with a Varian Associates A-60 or T-60, and where specified, a Brüker 90-MHz spectrometer. Chemical shifts are reported in parts per million (δ) down field from tetramethylsilane as an internal standard. Infrared spectra were recorded with a Perkin-Elmer Model 337 or 700 spectrophotometer. Ultraviolet spectra were determined with a Cary Model 14 spectrophotometer. Mass spectra were determined with a Hitachi (Perkin-Elmer) RMU-7 spectrometer at 70 eV. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thick-layer chromatography was performed with Brinkmann silica gel PF₂₅₄₊₃₆₆ and column chromatography with Brinkmann silica gel (less than 0.08 mm).

Laser Irradiations. All laser irradiations were conducted with a Coherent Radiation Laboratories Model 53A argon ion laser. The laser is rated at 6 W TEM₀₀ with lines of 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2). The laser power was monitored using a Coherent Radiation Laboratories Model 201 power meter. Irradiations were typically conducted using all lines, and power levels of 5–6 W. The beam diameter was expanded from 1.5 mm at the 1/e² points to 5 or 10 cm with a lens. The unexpanded beam could be used; however, small dark particles in the solution or moderately intense coloration of

the solution will cause flashing of the solvent in the beam, generate sharp reports at the inner surface of the reaction vessel, and occasionally burn black spots in the surface of the vessel at the point of beam entry. Beam expansion eliminates these problems, and the hazard of fire or shattered reaction vessels. A solution of the reactants was simply irradiated with magnetic stirring under an atmosphere of either air, oxygen, or argon.

Photoaddition of *p*-Benzoquinone to Cyclooctatetraene. A solution of 5.9602 g (57.3 mmol) of cyclooctatetraene and 1.5277 g (14.1 mmol) of *p*-benzoquinone in 700 ml of benzene was irradiated under argon with an argon laser for 3.5 hr. The solvent was concentrated to ca. 20 ml, filtered through Celite, and evaporated to dryness. Chromatography on a short silica gel column yielded 2.32 g (77%) of spiro[2,5-cyclohexadiene-1,8'-[7']oxabicyclo[4.2.2]-deca [2',4',9'] trien]-4-one (5). An analytical sample was prepared by several recrystallizations from 2-propanol-ether: mp 67–72° dec; ir (CHCl₃) 1660 and 1625 cm⁻¹; nmr (90 MHz, CDCl₃) 2.74 (dd, 1 H, *J* = 8 Hz), 4.67 (dd, 1 H, *J* = 5 Hz), 5.65 (dd, 1 H, *J* = 8 and 10 Hz), 6.04 (m, 7 H), 7.16 (m, 2 H); uv (absolute MeOH) λ_{\max} 199 nm (ϵ 11,400), 223 (16,200), 260 (5400); mass spectrum *m/e* 212 (M⁺). Anal. Calcd for C₁₄H₁₂O₂: C, 79.23; H, 5.70. Found: C, 79.31; H, 6.03.

Preparation of *p*-(2-Hydroxycyclooctyl)phenol (3). To a suspension of 95.8 mg of 10% Pd/C in 50 ml of absolute ethanol was added by syringe a solution of 0.2975 g (1.36 mmol) of 4 in 8 ml of ethanol. After 0.5 hr the catalyst was removed by filtration through Celite filter aid. Removal of the solvent and preparative thick-layer chromatography eluting with chloroform-ether (20:1) yielded 0.1321 g (44%) of 3 which when recrystallized from ben-

zene-ligroin had mp 120–121 °; ir (KBr) 3200 cm⁻¹; nmr (CDCl₃) 1.67 (m, 13 H), 2.70 (m, 1 H), 3.90 (m, 1 H), 6.10 (s, 1 H), 6.95 (A₂B₂, 4 H, *J* = 8 Hz); mass spectrum *m/e* 220 (M⁺).

Anal. Calcd for C₁₄H₂₀O₂: C, 76.36; H, 9.09. Found: C, 76.30; H, 9.20.

Preparation of *p*-(4-Hydroxycyclooctyl)phenol (2). To a suspension of 92.3 mg of 10% Pd/C in 50 ml of absolute ethanol was added by syringe a solution of 0.2512 g (1.185 mmol) of **5** in 8 ml of ethanol. After 1.25 hr the catalyst was removed by filtration through Celite. Removal of the solvent and preparative thick-layer chromatography eluting with chloroform–methanol yielded 31.7 mg (12%) of **2** which when recrystallized from benzene had mp 136.8–137.2 °; ir (KBr) 3150–3400 cm⁻¹; nmr (CDCl₃) 1.67 (m, 13 H), 2.70 (m, 1 H), 3.90 (m, 1 H), 6.10 (s, 1 H), 6.95 (A₂B₂, 4 H, *J* = 8 Hz); mass spectrum *m/e* 220 (M⁺).

Anal. Calcd for C₁₄H₂₀O₂: C, 76.36; H, 9.09. Found: C, 76.15; H, 9.07.

Acid-Catalyzed Photoaddition of *p*-Benzoquinone to Cyclooctatetraene. A solution of 0.8455 g (8.12 mmol) of cyclooctatetraene and 0.112 g (1.03 mmol) of *p*-benzoquinone in 350 ml of glacial acetic acid was irradiated open to the air with an argon laser for 1.5 hr. The solvent was evaporated and the oily residue was dissolved in 25 ml of ether. The ether solution was washed with 2 × 20 ml of dilute sodium bicarbonate and 20 ml of saturated sodium chloride solution. The aqueous layers were combined and extracted with 10 ml of ether. The organic phases were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness to yield 0.256 g of an oily mixture of **6** and **7**. Preparative thick-layer chromatography of the mixture eluting with chloroform–methanol yielded 57.4 mg (26%) of the less polar product **7** which when recrystallized from benzene–ligroin had mp 81.5–82.5 °; ir (KBr) 3370 cm⁻¹; nmr (CDCl₃) 4.82 (s, 1 H), 5.57 (d, 1 H, *J* = 7 Hz), 6.54 (d, 1 H, *J* = 7 Hz), 6.72–7.52 (m, 7 H), 7.71 (m, 2 H); uv (absolute MeOH) λ_{max} 213 sh nm (ε 14,200) and 266 (22,600); mass spectrum *m/e* 212 (M⁺). *Anal.* Calcd for C₁₄H₁₂O₂: C, 79.23; H, 5.70. Found: C, 78.99; H, 5.76. The major product (162.4 mg, 58%) **6** was isolated as a very unstable viscous oil: ir (CHCl₃) 3350 and 1730 cm⁻¹; nmr (CDCl₃) 2.05 (s, 3 H), 2.41 (q, 1 H, *J* = 6 Hz), 5.45 (m, 2 H), 6.35 (m, 2 H), 6.83 (m, 8 H); uv (absolute MeOH) λ_{max} 223 nm (ε 10,600) and 267 (6300).

Acid-Catalyzed Rearrangement of **5.** A solution of 0.1228 g (0.58 mmol) of **5** in 10 ml of glacial acetic acid was stirred under nitrogen 4 hr and then heated to 50 ° for 9.25 hr. Removal of the solvent and preparative thick-layer chromatography eluting with chloroform yielded 90.7 mg (74%) of **7** and a trace of **6**.

Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene Using an Argon Laser. A solution of 4.9762 g (47.8 mmol) of cyclooctatetraene and 1.005 g (9.31 mmol) of *p*-benzoquinone in 1700 ml of CCl₄ was stirred for 0.5 hr. The solution was irradiated open to the air with an argon laser for 2.75 hr. The photolysis mixture was concentrated to ca. 30 ml, filtered through Celite to remove insoluble polymer, evaporated to dryness, and evacuated under high vacuum for several hours. Crystallization of the residue from methanol yielded four crops totaling 0.852 g (39%) of 4'a,10'a-dihydrospiro[2,5-cyclohexadiene-1,3'-cycloocta-*as*-trioxin]-4-one (**11**); mp 111.7–111.9 °; positive starch–iodine test for peroxide; nmr (90 MHz, CCl₄) 4.88 (m, 2 H), 5.70 (bt, 2 H), 6.13 (m, 4 H), 6.25 (dd, 1 H, *J* = 10.8 and 2 Hz), 6.30 (dd, 1 H, *J* = 10.4 and 2 Hz), 6.58 (dd, 1 H, *J* = 10.4 and 3.1 Hz), 7.62 (dd, 1 H, *J* = 10.8 and 3.2 Hz); ir (KBr) 1670 and 1635 cm⁻¹; uv (absolute MeOH) λ_{max} 207 nm (ε 20,800), 213 sh (19,700), 249 sh (7610); mass spectrum *m/e* 244 (M⁺).

Anal. Calcd for C₁₄H₁₂O₄: C, 68.85; H, 4.95. Found: C, 68.80; H, 4.94.

The mother liquors were collected and chromatographed on thick-layer plates. Elution with chloroform yielded an additional 0.253 g (10%) of **11** and 0.603 g (31%) of spiro[2,5-cyclohexadiene-1,8'-[7']oxabicyclo[4.2.2]deca[2',4',9']trien]-4-one (**5**).

Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene at 3500 Å. A solution of 0.6638 g (6.38 mmol) of cyclooctatetraene and 0.212 g (1.96 mmol) of *p*-benzoquinone in 400 ml of carbon tetrachloride was irradiated open to the air in a Rayonet photochemical reactor with 3500-Å lamps for 19.25 hr. The reaction mixture was highly polymeric and displayed ill-defined product spots on tlc. Removal of the solvent and preparative thick-layer chromatography eluting with chloroform yielded 19.6 mg (4.1%) of **11** and a small quantity of **5**.

Preparation of 3-Bromo-4'a,10'a-dihydrospiro[2,5-cyclohexadiene-1,3'-cycloocta-*as*-trioxin]-4-one (13**).** A solution of 0.2734 g

(1.12 mmol) of **11** and 0.3637 g (1.135 mmol) of pyridinium hydrobromide perbromide in 25 ml of methylene chloride was stirred for 12 hr under argon. The solution was concentrated, filtered to remove insoluble salts, and chromatographed on a preparative thick-layer plate. Elution with chloroform yielded 42.9 mg (15.7%) of recovered **11**, and based on recovered starting material 269.8 mg (89%) of **13** which was crystallized from 2-propanol: mp 138.8–139.1 °; ir (KBr) 1675, 1645, and 1605 cm⁻¹; nmr (90 MHz, CDCl₃) 4.87 (m, 2 H), 5.70 (m, 2 H), 6.13 (m, 4 H), 6.38 (d, 1 H, *J* = 10 Hz), 6.59 (dd, 1 H, *J* = 10 and 3 Hz), 8.04 (d, 1 H, *J* = 3 Hz); uv (absolute MeOH) λ_{max} 202 nm (ε 19,700), 221 sh (14,500), 253 sh (7410); mass spectrum *m/e* 322 and 324 (M⁺).

Anal. Calcd for C₁₄H₁₁O₄Br: C, 52.04; H, 3.43; Br, 24.73. Found: C, 52.12; H, 3.44; Br, 24.76.

Even though **13** gave a good analysis, exhibited a sharp melting point, and gave one spot by thin-layer chromatography, an X-ray analysis of **13** indicates the presence of a small amount of the 5-bromo isomer (*vide infra*).

Collection and Reduction of X-Ray Intensity Data. A colorless crystal of the bromo peroxide **13** was mounted along its *b* axis with epoxy resin on a glass fiber and precession photographs of the *h*0*l*, 0*kl*, *h*1*l*, and 1*kl* zones were taken. The monoclinic space group *P*2₁/*c* (No 14, *C*₂^{5h}),³² was indicated by systematic absences of *h*0*l* for *l* odd and 0*k*0 for *k* odd.

After the crystal was optically centered on a Syntex P $\bar{1}$ diffractometer for intensity data collection, a full rotation photograph was taken and 15 intense reflections were chosen and centered using manufacturer-supplied software. The auto-indexing program gave three axial choices in agreement with those previously determined from precession photographs. The orientation of the crystal (determined by least squares) is given by the following orientation matrix described by Busing and Levy³³ except that the incident and

$$\mathbf{A} = \begin{bmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ a_z^* & b_z^* & c_z^* \end{bmatrix} = \begin{bmatrix} -0.08306 & -0.01401 & -0.01789 \\ 0.02380 & -0.02338 & -0.05290 \\ -0.01129 & -0.15309 & 0.00633 \end{bmatrix}$$

diffracted beams have been interchanged. The corresponding lattice constants are *a* = 11.485 (4) Å, *b* = 6.417 (2) Å, *c* = 17.821 (7) Å, and β = 91.81 (3) °. With four molecules per unit cell the calculated density is 1.02 g cm⁻³; the experimental is 1.04 (3) g cm⁻³.

Intensity data were collected using Mo Kα radiation (λ 0.7107 Å) with a graphite single crystal as the monochromator. This crystal was considered to be 50% mosaic. The sample crystal was positioned 45 mm from the collimator (diameter = 1 mm) and 90 mm from the counter (aperture diameter = 2 mm). The take-off angle was 3.6 °. A θ–2θ scan mode was used with a 2θ range below Kα₁ and above Kα₂ of 1 °. The scan rate was varied from 1.5 to 12 °/min depending on the intensity of the reflection. The background to scan ratio was 1.0. Four intense reflections, chosen to span the angular variations of the diffractometer, were used as standards and remeasured every 40 reflections to check on machine and crystal stability.

The 96 step peak profiles³⁴ were checked for uneven backgrounds and off-center peaks. If the backgrounds are uneven, automatic checks are made to see if (1) a neighboring reflection is intruding into one end of the scan; if so, the off-center one of the two is subtracted out, or (2) the peak itself has considerable intensity at one end of the scan, which presumably occurs because the peak is too broad and/or too badly centered for the scan; if so, the intensity is computed using twice the lower background. The position of the peak center (PC) in the 96 step scan is approximated using the expression

$$PC = \frac{\sum_{i=1}^n iC_i}{\sum_{i=1}^n C_i}$$

(32) "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 99.

(33) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967).

(34) The manufacturer supplied software for data collection accumulates counts for each of 96 equal steps throughout the 2θ scan. These are then corrected for coincidence and a normalized intensity calculated. This and other pertinent information is then written on magnetic tape for processing by our SYNTX link of XRAY 67.

where C_i is the number of counts for the i th step.³⁵ Those reflections whose centers are outside desired limits are rejected (this crystal: the 010 reflection was rejected).

The data were preprocessed by a program SYNTAX which has been inserted into our version of the program package XRAY 67.³⁶ The integrated intensity (I) was calculated according to the expression $I = [SC - (B_1 + B_2)/B_R]T_R$ where SC is the scan counts, B_1 and B_2 are the background counts, B_R is the background time to scan time ratio, and T_R is the 2θ scan rate in $^\circ/\text{min}$. The standard deviation of I was calculated: $\sigma(I) = T_R[SC + (B_1 + B_2)/B_R^2 + (pI)^2]^{1/2}$ where p in this case was equal to 0.02.³⁷

The standard reflections are used to automatically rescale the data in the following manner: the normalized integrated intensities of each of the standards in the group are summed; the ratio of any standard group sum to the first sum then gives a relative scale factor.

A total of 4059 reflections was measured, approximately half of which was unique (h, k , and l varied from -12 to 12 , 7 to 0 , and 19 to 0 , respectively). These were then averaged in SYNTAX and 1672 unique reflections were processed. The scale factor monotonically increased from 1.000 to 1.231, apparently due to crystal decomposition during the course of data collection. However, since the reflections are symmetric about 000 in terms of the order in which they were measured (the first reflection is equivalent to the last, the second to the next to last, etc.), the otherwise substantial error in the intensities of the various reflections due to decomposition is reduced.

The linear absorption coefficient μ of the compound for Mo K α radiation is 20.8 cm^{-1} . Minimum and maximum values of μR are 0.713 and 0.152. Since the maximum relative error in F_o due to absorption would be approximately 50%, it was decided to perform absorption corrections on the data set.

The crystal shape was measured with a microscope equipped with filar micrometer eyepiece. This crystal had dimensions of 0.686 mm, 0.343 mm, and 0.073 mm corresponding respectively to the length, width, and height of a regular parallelepiped.

The coordinates necessary to describe the plane faces bounding the crystal were entered into a version of the SYNTAX link which has been modified to calculate absorption corrections.³⁸ Experimental observation of several reflections measured stepping through values of ψ (the rotation angle about the diffraction vector) in 5° increments agreed with the transmission coefficients calculated for these conditions. A transmission coefficient was calculated for each reflection.

This set of unique, normalized, integrated, absorption corrected intensities was processed by the DATRDN link to give relative values of $[F]$ and $[E]$.³⁹ Of the 1672 unique reflections, 1107 were treated as observed [$F_o^2 \geq 3\sigma(F_o^2)$].

(35) J. E. Oberholtzer and L. B. Rogers, *Anal. Chem.*, **41**, 1234 (1969).

(36) XRAY 67, J. M. Stewart, University of Maryland, Crystallographic Computer Program System (locally modified).

(37) P. W. P. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(38) This calculation uses a modified version of the code of D. J. Wehe, W. R. Busing, and H. A. Levy, "A FORTRAN Program for Calculating Single Crystal Absorption Corrections," ORABS, Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1952.

(39) Scattering factors were obtained from "International Tables

Structure Solution and Refinement. A sharpened Patterson function was computed using the observed reflections, and it indicated the position of the bromine atom. An electron density map computed using the signs derived from the heavy atom location showed the position of 12 carbon and 3 oxygen atoms. A density map with these atoms inserted into the calculations revealed the remaining atom positions. The data set was full-matrix least-squares refined with anisotropic temperature parameters until each parameter shift divided by its estimated error indicated convergence ($R = \sum |F_o| - |F_c| / \sum F_o = 0.086$).

A difference density map revealed as the major disagreement a small peak (approximately one-third the height of the carbon atoms on the regular density map) presumably due to bromination at C(5) for some of the molecules in the crystal. A model with partial bromination at both positions was adopted for further refinement. The last cycle of refinement of all variables including the population parameters of the bromine atoms with no constraint on their sum resulted in an 8.7 (6)% population in the new position and a 92.4 (8)% population in the original, which appears to indicate an exclusively monobrominated compound. The R factor had significantly decreased to 0.073. This treatment which assumed that the molecules brominated at C(5) were positioned in exactly the same manner in the crystal as those brominated at C(3) is certainly overly simplistic, since one expects the entire molecule to be positioned in a slightly different fashion. Thus the C(3)-Br distance was a reasonable 1.89 Å whereas the C(5)-Br distance is found to be 1.56 Å with this model. Since only the peak due to the bromine atom on C(5) was distinct in the difference map, we were forced to assume that the remainder of the atoms in the C(5) brominated molecules are crudely described by small modifications of the temperature parameters and possibly the positions for the atoms of the predominant isomer.

Interestingly, reexamination of the nmr spectrum of **13** reveals trace signals in the dienone region (7.00–8.00 ppm) which reasonably may be ascribed to the presence of the C(5) bromine isomer.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-2955.

for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1952, pp 202–205.