Alkyne–Quinone Photoaddition. Formation and Solvolytic Rearrangement of 1-Methoxybicyclo[4.2.0]octa-3,7-diene-2,5-diones[1]

S. Peter Pappas,[2] Betty C. Pappas, and Norman A. Portnoy

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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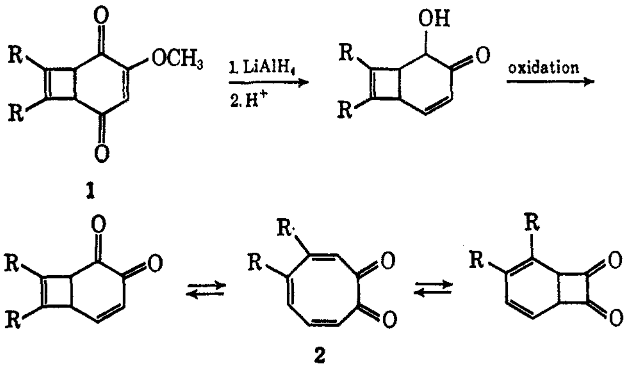
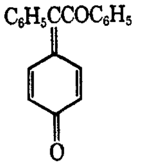
Photoaddition of dimethyl-, diphenyl-, and methylphenylacetylene to methoxy-*p*-benzoquinone and 2-methoxy-1,4-naphthoquinone yields 1-methoxybicyclo[4.2.0]octa-3,7-diene-2,5-dione adducts of structure **5** and **7**, respectively. With each quinone and methylphenylacetylene, a single orientational isomer was obtained and fully characterized. When heated in hydroxylic solvents, the photoadducts undergo facile, skeletal rearrangement to a bicyclo[3.3.0]octadiene ring system. The mechanism of this process is discussed.

Recently, we became interested in the photoaddition of alkynes to methoxy-*p*-benzoquinone as a possible route to adducts of structure **1**. Such compounds were desirable as precursors of the cycloocta-3,5,7-triene-1,2-dione[3] ring system **2** and valence bond tautomers thereof, as outlined in Scheme I. Since there was ample precedent for the steps involved in converting **1** into the desired products,[4] the critical feature of the scheme was considered to be the photoaddition.

Scheme I



Cyclobutenes had been obtained from the photoaddition of 2-butyne to cycloalkenones,[5–7] maleic acid derivatives,[8,9] as well as chromone.[10] Photoaddition of olefins and dienes to quinones had been investigated.[11] However, only one example of alkyne addition to a *p*-quinone had been recorded.[12] This was the addition of diphenylacetylene to *p*-benzoquinone which yielded a 1:1 adduct of structure **3**, indicating that reaction had occurred at the carbonyl group. The oxetene adduct **4** was postulated as an intermediate in this process.[12] Thus, while there was no precedent for cyclobutene formation in alkynequinone photoaddition, there was cause for optimism and clearly a need for further studies.



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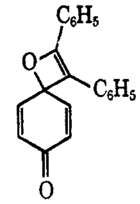

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In fact, photoaddition of both aromatic and aliphatic alkynes to methoxy-*p*-benzoquinone, which might have occurred at either of the carbonyl groups and/or the carbon–carbon double bonds, provided cyclobutene adducts of structure **5** in good yield to the apparent exclusion of other isomers.[1a] Furthermore, a single orientational isomer was obtained in the addition of an unsymmetrical alkyne. For these reasons, despite the inapplicability to our original plan, both the photoaddition and the chemistry of the adducts were considered to be attractive subjects for further studies.

Results

Photoaddition of dimethyl-, diphenyl-, and methylphenylacetylene to methoxy-*p*-benzoquinone was carried out in acetonitrile solution with light filtered through a Pyrex reaction vessel. In each case, only one product was isolated in significant quantity which was shown to be a 1:1 adduct of quinone and alkyne on the basis of elemental analysis and molecular weight determination (mass spectral).

The adduct from diphenylacetylene exhibited a single carbonyl band at 5.93 μ, suggestive of a 2-ene-1,3-dione part structure. The presence of a methoxyl group on this chromophore was clearly excluded from a consideration of model compounds, such as **6** ($R = OCH_3$), which displays two distinct carbonyl bands at 5.88 and 6.04 μ.[13] The ultraviolet spectrum of the adduct

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[1] (a) A portion of this work has appeared in a preliminary report: S. P. Pappas and B. C. Pappas, *Tetrahedron Letters*, 1597 (1967). (b) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health for partial support of this research.

[2] College of Chemistry and Physics, North Dakota State University, Fargo, N. D. 58102.

[3] The synthesis of a dibenzo derivative has recently been reported: V. I. Bendall and J. F. Neumer, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract 088.

[4] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

[5] P. E. Eaton, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 4Q; *Tetrahedron Letters*, 3695 (1964).

[6] R. L. Cargill, J. Dorn, and A. E. Siebert, Abstracts, 148th National Meeting of the American Society, Chicago, Ill., Aug 1964, p 25S; R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

[7] R. Criegee and H. Furrer, *Ber.*, **97**, 2949 (1964).

[8] R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freund, *ibid.*, **97**, 2942 (1964).

[9] D. Seebach, *ibid.*, **97**, 2953 (1964).

[10] J. W. Hanifin and E. Cohen, *Tetrahedron Letters*, 5421 (1966), which appeared during the course of our preliminary investigations.

[11] For a current review, see J. M. Bruce, *Quart. Rev.* (London), **21**, 405 (1968).

[12] H. E. Zimmerman and L. Craft, *Tetrahedron Letters*, 2131 (1964); D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, 2137 (1964).

[13] G. I. Birnbaum, *J. Org. Chem.*, **25**, 1660 (1960).

TABLE I

NMR SPECTRA OF THE PRODUCTS[a–c]

	τ (multiplicity) (J, Hz)				
Compd	O–CH_3	Methine H	C–CH_3	Vinyl H	OH
5a	6.62	5.75		3.32, 3.52 (AB q) (10)	
5b	6.68	6.42 (m)	8.30 (m)	3.38, 3.47 (AB q) (10)	
5c	6.64	6.25 (m)	7.90 (d) (1.5)	3.35, 3.47 (AB q) (10)	
7a	6.50	5.50			
7b	6.60	6.20 (m)	8.32 (m)		
7c	6.55	6.02 (q) (1.7)	7.92 (d) (1.7)		
5a-CH_3OH	6.50, 6.80	6.35		2.46 (d) (6) 3.95 (d) (6)	5.96
7a-CH_3OH	6.50, 7.00	6.12			5.98
11a		5.55 (5.40)[d]			6.98[d]
11b		6.40 (m)	7.95 (qn) (1) 8.35 (h) (1)		5.92
11c		6.18 (q) (1.2)	7.60 (d) (1.2)		5.84
11a-OAc		5.36	7.84		

[a] Spectra were obtained in deuteriochloroform solution on a Varian A-60 spectrometer. [b] Multiplicities are expressed as follows: d = doublet, q = quartet, qn = quintet, h = sextet, m = multiplet. [c] Aromatic hydrogen resonances are not included. [d] Obtained in hexadeuteriodimethyl sulfoxide.

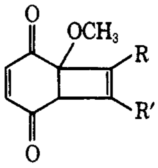
TABLE II

ABSORPTION SPECTRA OF THE PRODUCTS

Compd	Ir bands, μ[a]	Uv bands, mμ (log ε)[b]
5a	5.93	382 (2.89),[c] 292 (4.03), 223 (4.49)
5b	5.94	387 (2.19), 283 (2.48),[c] 223 (4.11)
5c	5.93	385 (2.46), 311 (2.74),[c] 258 (4.18), 232 (4.30)
7a	5.92	355 (3.37),[c] 288 (4.10),[c] 255 (4.25), 225 (4.55)
7b	5.93	350 (2.37), 301 (3.18), 227 (4.37)
7c	5.92	350 (2.84), 250 (4.47), 230 (4.57)
5a-CH_3OH	2.86, 5.81	255 (3.89)[c], 220 (4.30)
7a-CH_3OH	2.84, 5.78	275 (3.96),[c] 230 (4.43)
11a	2.82, 3.02,[d] 5.81[d]	320 (3.96), 300 (3.96), 231 (4.47)
11b	2.82, 2.92,[d] 5.83	370 (2.47),[c] 354 (2.64), 339 (2.62), 325 (2.52),[c] 297 (2.87), 245 (4.10), 225 (4.14)
11c	2.82, 2.92,[d] 5.81	355 (2.19), 340 (2.91), 324 (2.83) 278 (3.74), 227 (4.44)
11a-OAc	5.71,[c] 5.81	317 (3.92), 298 (3.89), 247 (4.32),[c] 230 (4.42)

[a] Obtained in chloroform solution on a Perkin-Elmer 257 spectrophotometer. [b] Obtained in 95% ethanol solution on a Cary 14 spectrophotometer. [c] Shoulder. [d] Broad

exhibited maxima (in 95% ethanol) at 382 mμ (ε 774), 292 (10,800), and 223 (30,700), a pattern which approximates the combination of *cis*-stilbene [$\lambda_{\max}^{\mathrm{EtOH}}$ 280 mμ (ε 10,500) and 224 (24,400)] and 2-ene-1,3-dione chromophores [for compound **6** (R = H), $\lambda_{\max}^{\mathrm{EtOH}}$ 360 mμ (ε 60) and 223 (11,900)]. Thus, infrared and ultraviolet spectra indicated that the adduct is 7,8-diphenyl-1-methoxybicyclo[4.2.0]octa-3,7-diene-2,5-dione (**5a**), with which the nmr spectrum (Table I) is in complete agreement.



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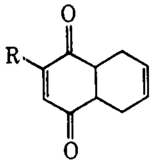

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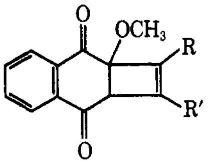

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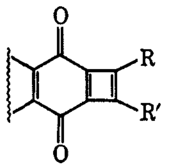
5, **7a**, R = R′ = C_6H_5 **c**, R = C_6H_5; R′ = CH_3
b, R = R′ = CH_3 **d**, R = CH_3; R′ = C_6H_5

On the basis of similar considerations of spectra, which are presented in Tables I and II, the dimethyl adduct is assigned structure **5b**, whereas the methyl phenyl adduct may be represented by either structure **5c** or **d**. However, tentative support for **5c** is obtained from a comparison of the methine hydrogen resonances in the nmr spectra of the adducts. The extent to which this proton is deshielded by the phenyl ring in the methylphenyl adduct is only 25% of that observed in the diphenyl case. Since this effect is expected to be most pronounced for a phenyl ring on the adjacent carbon atom in this system, the relative chemical shift of the methine hydrogen appears to be inconsistent with assignment **5d**.

Several preliminary attempts to obtain further evidence for the structural assignments of the adducts, including catalytic hydrogenation, were complicated by the presence of the 3,4 carbon–carbon double bond. Consequently, analogous photoadditions with 2-methoxy-1,4-naphthoquinone were undertaken, primarily for the purpose of incorporating this unsaturation into an aromatic system. A single adduct was obtained, in each case, which possessed the corresponding 3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione skeleton, represented by structure **7**, as clearly indicated by the spectral properties, presented in Tables I and II.

A comparison of the nmr spectra of adducts derived from the same alkyne in each series is particularly informative. First, there is the obvious correspondence between the C-methyl hydrogen resonances. Second, the chemical shifts of the methine and O-methyl hydrogens are at lower field by 14 ± 1 and 6 ± 1 Hz, respectively, in the naphthoquinone series. Thus, after correction for the apparent deshielding effect of the fused benzene ring in the naphthoquinone adducts, there is a remarkable correlation between the corresponding resonances. These relationships also establish that the orientation of addition of methylphenylacetylene is the same in both series.

One of our major synthetic objectives has been the conversion of these and related adducts[14] into cyclobutadiene derivatives of structure **8**. Our first attempt in this direction involved heating the diphenyl adduct **5a** in ethanol solution containing pyridine. It was expected that, if base-catalyzed elimination of methanol occurred, the resulting cyclobutadiene would be highly reactive toward nucleophiles and would, therefore, add ethanol to yield **9**.



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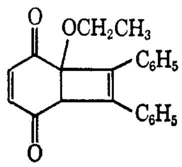

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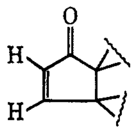

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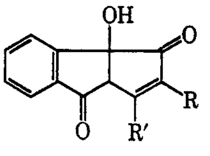
Although compound **9** was not obtained, reaction did occur and proceeded, as well, in the absence of pyridine. The product was a mixture of isomers resulting from the net addition of ethanol, as determined by elemental analysis and nmr spectra. A single adduct, **5a**-CH_3OH, mp 154° dec, was obtained on heating **5a** in methanol. Its spectral properties are presented in Tables I and II. The presence of a cyclopentenone part structure **10** is apparent from the nmr (α- and β-vinyl hydrogens at τ 3.95 and 2.46, respectively) and infrared (carbonyl band at $5.81\,\mu$) spectra, indicating that a skeletal rearrangement had occurred. The compound slowly decomposed on standing.

The diphenyl adduct in the naphthoquinone series was similarly transformed into **7a**-CH_3OH, mp 170–171°, which appears to be the benzo analog of **5a**-CH_3OH, as indicated by the spectral properties presented in the tables. On standing for several days, a solution of **7a**-CH_3OH in deuteriochloroform containing D_2O, the nmr sample, deposited crystals of a new compound, mp 125–126°. The same product was obtained from a solution of the methanol adduct in concentrated sulfuric acid after dilution with ice water, as well as directly from the photoadduct **7a** when heated in aqueous acetonitrile. The dimethyl and methylphenyl adducts, **7b** and **c** (or **d**), also rearranged on heating in aqueous acetonitrile, although at a considerably slower rate than **7a**, as determined by monitoring carbonyl absorptions in the infrared region. The products are assigned the previously unreported 3,3a,8,8a-tetrahydrocyclopent[*a*]indene-3,8-dione ring system, represented by structure **11**, on the basis of elemental analysis, molecular weight determination (mass spectral), and spectral properties (Tables I and II).

A comparison of the methine and C-methyl hydrogen resonances in the nmr spectra of the photoadducts **7** and rearranged products **11** is particularly informative. This comparison indicates that the R and R′ groups of the adducts have been transformed into α and β components of a conjugated carbonyl chromophore, and remain similarly disposed to a bridgehead proton. The presence of conjugated carbonyl groups is supported by the ultraviolet spectra; their placement in five-membered rings follows from the position of carbonyl absorption in the infrared region. The presence of a hydroxyl group is clearly in evidence from both infrared and nmr spectra.



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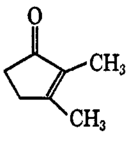

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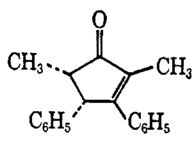

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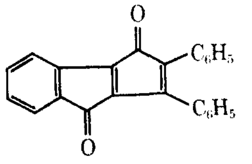
a, R = R′ = C_6H_5 **c**, R = C_6H_5; R′ = CH_3
b, R = R′ = CH_3 **d**, R = CH_3; R′ = C_6H_5

These general conclusions are fully supported by nmr spectral comparisons with related compounds of known structure. Thus, the C-methyl hydrogen resonances of the dimethyldione **11b**, at τ 7.95 and 8.37, correspond remarkably well with those of cyclopentenone **12**, at 7.97 and 8.39.[15] Since the low-field resonances undoubtedly represent the β-methyls, it is seen that the α-methyl of **11b** exhibits about the same chemical shift as the C-methyls of the precursor **7b**, whereas the β-methyl appears 22 Hz downfield. This relationship is noteworthy because the chemical shift exhibited by the C-methyl of the methylphenyldione (τ 7.60) is 19 Hz downfield from that of the precursor (τ 7.92), indicating that this dione possesses structure **11c**, in which the methyl group is β. In support of this assignment, the chemical shift of the α-methyl group on the conjugated chromophore of compound **13** appears at τ 7.92.[16]

The presence of a hydroxyl group was confirmed by the ready conversion of the diphenyldione **11a** into an acetate, **11a**-OAc, which undoubtedly possesses an unrearranged structure as indicated by a comparison of its spectral properties (Table I and II) with those of the precursor **11a**. The acetate was also prepared as a potential precursor of 1,2-diphenyl-3,8-dihydrocyclopent[*a*]indene-3,8-dione (**14**), which represents an unknown ring system of theoretical interest.[17] Significantly, an (M − CH_3COOH)$^+$ fragment is the base peak in its mass spectrum.



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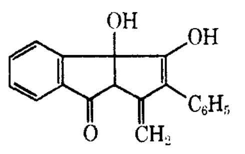

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[14] S. P. Pappas and N. A. Portnoy, *J. Org. Chem.*, **33**, 2200 (1968).

[15] H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc.*, *B*, 73 (1966).

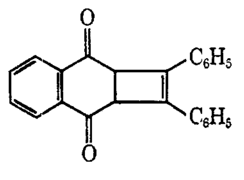
[16] P. Bladon, S. McVey, P. L. Pauson, G. D. Broadhead, and W. M. Horspool, *ibid.*, *C*, 306 (1966).

[17] With reference to the concept of antiaromaticity, see R. Breslow, *Chem. Eng. News*, **43**, 90 (June 28, 1965).

In view of the import of the methylphenyldione assignment, (**11c** or **d**), both with regard to the orientation of photoaddition and substituent effects on the rearrangement of the photoadducts, chemical confirmation was desirable. It was found that the methyl and methine hydrogens were exchanged for deuterium atoms when this dione was heated in a dioxane–heavy water solution for several days, followed by aqueous treatment in the work-up.[18] This was established by infrared, mass, and nmr spectral comparisons between the proteo and deuterio analogs. The change was visually most dramatic in nmr spectra which were identical except for the absence of methine and methyl hydrogen resonances in that of the deuterio compound. Addition of D_2O to the latter sample resulted in exchange of the hydroxyl hydrogen as well, and only aromatic hydrogens remained in evidence.

Facile exchange of the methyl hydrogens is readily explicable in terms of structure **11c**, *via* the intermediate enol **15**, but cannot be reasonably accommodated by the alternative formulation **11d.** This result confirms the conclusions based on nmr data. The precursor of **11c** and the corresponding adduct in the benzoquinone series are now confidently assigned structures **7c** and **5c**, respectively.

Having established these structures, it was of interest to reinvestigate the course of solvolytic rearrangement of the photoadducts, since qualitative observations had indicated that the dimethyl and methylphenyl analogs **7b** and **c** reacted considerably slower than **7a.** In agreement with these observations, relative rates of the hydrolytic rearrangement 7 → 11, obtained from the corresponding half-lives of reaction, were found to be 9.2:1.5:1.0 for **7a, b,** and **c,** respectively. Furthermore it was determined that the presence of the bridgehead methoxy group was a necessary requirement for facile rearrangement since the desmethoxy analog **16**, prepared by the photoaddition of diphenylacetylene to 1,4-naphthoquinone,[14] was quantitatively recovered after extended hydrolytic treatment, conditions which resulted in the complete conversion of **7c** to **11c.**



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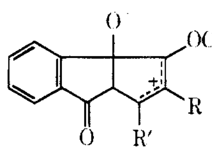
Discussion

These studies have provided convenient, efficient routes to new and interesting bicyclo[4.2.0]- and [3.3.0]octadienedione ring systems, which are otherwise quite inaccessible. A high degree of orientational specificity has been observed in the photoaddition of unsymmetrical alkynes to methoxy-*p*-quinones. The present study indicates that the favored product is derived from the most stable biradical intermediate, which has also been observed recently in a similar system.[19]

The results also provide insight on the course of the solvolytic rearrangements. It appears likely that these reactions proceed by rate-limiting formation of the solvated zwitterionic species **17,** which may arise directly from **7** in a 1,6 to 2,6 bond migration or *via* the valence-bond tautomer **18.** The requirement of the methoxy group, which resides at one end of the allyl cationic system, and sensitivity of the rate to substituent R′, which occupies the other, are consistent with this interpretation. Furthermore, the solvolysis products are readily derivable from species **17.** The methanol adduct, derived from **7a,** undoubtedly possesses structure **19** or **20** on the basis of its ready conversion to **11a** and spectral properties (Tables I and II). The corresponding "methanolysis" product in the benzoquinone series is tentatively formulated as structure **21,** since the alternative assignment **22** is inconsistent with the finding that rearrangement in methanol yields a single adduct, whereas two isomeric adducts, clearly in evidence from nmr spectra, are produced in ethanol. Consequently, in view of the spectral similarities, **7a**-CH_3OH is tentatively assigned structure **19.**



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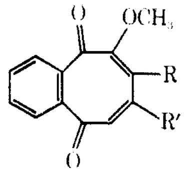

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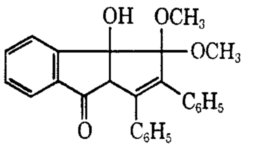

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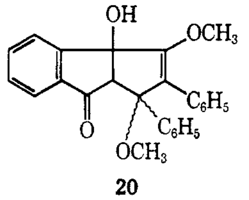

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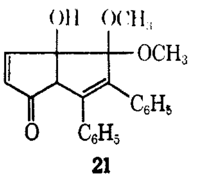

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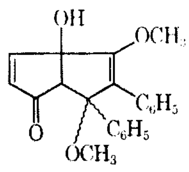

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A possible alternative route in the hydrolytic rearrangement of 7 → 11, which proceeds by vinyl bond migration[20] *via* species **23** and dione **24,** is presented in eq 1. However, this scheme suffers from the disadvantage of not providing an appropriate methanol adduct. The anticipated product, structure **25,** would not be expected to exhibit carbonyl absorption at 5.78 μ, as observed for **7a**-CH_3OH.

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(18) Base-catalyzed exchange experiments have been unsuccessful to date, due to extensive decomposition, which is undoubtedly related to the presence of labile β-hydroxy ketone and vinylogous β-diketone groupings in the diones.

(19) S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Letters,* 4147 (1968).

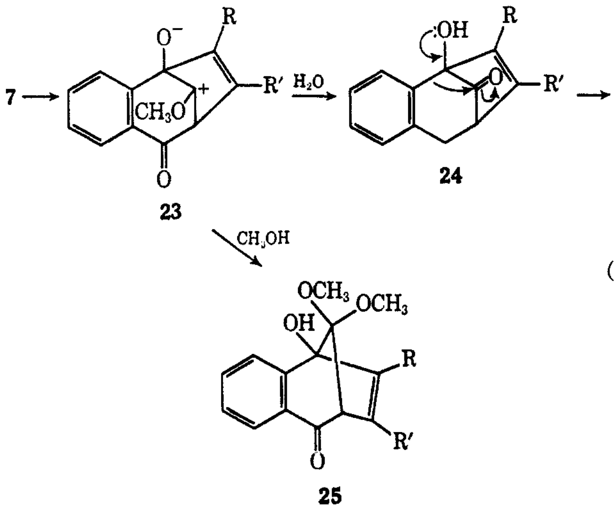
(20) R. D. Cargill and J. W. Crawford, *ibid.,* 169 (1967).

TABLE III

CHARACTERIZATION PROPERTIES OF THE PRODUCTS

Compd	Color	Mp, °C	Recrystn solvent	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
5a	Orange	130–131	Ether–hexane	50	79.7	5.1	79.8	5.2
5b	Yellow	50–51	Ether–hexane	30	68.7	6.3	68.8	6.4
5c	Yellow	135–136	Ether–hexane	70	75.6	5.6	75.7	5.6
7a	Yellow	128–129	Benzene–hexane	60	82.0	5.0	81.8	4.8
7b	Yellow	91–92	Hexane	40	74.4	5.8	74.2	5.9
7c	Yellow	120–121	Ether–hexane	70	78.9	5.3	79.1	5.3
5a-CH_3OH	Colorless	156 dec	Ether–hexane	90	75.8	5.8	75.9	5.9
7a-CH_3OH	Colorless	170–171	Ether–hexane	95	78.4	5.6	78.2	5.5
11a	Pale yellow	225–226	Acetone–hexane	85	81.8	4.6	81.7	4.5
11b	Colorless	165–166	Acetone–hexane	85	73.7	5.3	74.0	5.4
11c	Colorless	176–177	Acetone–hexane	85	78.6	4.9	78.5	4.8
11a-OAc	Colorless	173–174	Acetone–hexane	85	79.2	4.6	79.4	4.7

The observed trend in the rates of hydrolytic rearrangement **7** → **11** in this series, although limited, suggests that such information may be extremely useful in determining the orientation of photoaddition of unsymmetrical alkynes. The results indicate that the rate will be enhanced by electron-releasing R′ substituents and relatively insensitive to the nature of group R. We have found this to be the case with adducts of diarylacetylenes, which has prompted a kinetic investigation of polar effects[21,22] on the photoaddition.



(1)

Experimental Section[23]

Photoaddition of Methylphenylacetylene to Methoxy-*p*-benzoquinone.—A "Black Light" source (G.E. H100P5P38-4) was utilized and placed about 10 cm from the reaction vessel (a Pyrex jacketed beaker), which contained an acetonitrile solution (80 ml) of methylphenylacetylene (8.05 g, 0.069 mol) and methoxy-*p*-benzoquinone[24] (1.03 g, 0.0075 mol). Nitrogen was passed through the solution for 20 min prior to and during illumination. The solution was cooled by circulating tap water. The reaction was over after 100 min, as conveniently determined by monitoring the disappearance of the low-frequency carbonyl band of starting quinone in the infrared region. The crude product was absorbed on a small amount of Mallinckrodt SilicAr (100–200 mesh), which was applied to a SilicAr column, 2.5 × 6 cm, with hexane, whereupon the unreacted alkyne was eluted with hexane. The adduct (1.53 g) was obtained crystalline on elution with benzene and a 3:1 benzene–ether mixture and further purified by recrystallization from ether–hexane, which provided 1.32 g (70% yield) of 1-methoxy-7-methyl-8-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (**5c**), mp 135–136°.

The same general irradiation and work-up procedure was followed in all of the photoadditions in this series as well as with 2-methoxy-1,4-naphthoquinone,[14] with minor modification in experiments with 2-butyne because of its high volatility. In these cases, the solutions were cooled by circulating ice water and were not purged by nitrogen during the course of irradiation. Pertinent information on the photoadducts and other products, reported herein, is presented in Table III.

"Alcoholysis" of 1-Methoxy-7,8-diphenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (5a).—The yellow solution of photoadduct **5a** (122 mg) in ethanol (12 ml) and pyridine (1 ml) was refluxed for 3 hr in a nitrogen atmosphere, after which time the color had faded, and then evaporated to dryness. A colorless crystalline residue was obtained, which, after recrystallization from ether–hexane solution, provided 121 mg of a substance, mp 119–126°, resulting from the net uptake of the elements of ethanol.

Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.3; H, 6.1. Found: C, 76.7; H, 6.1.

The same product was obtained when the reaction was carried out in the absence of pyridine. Reaction in methanol provided a similar product as indicated by infrared and ultraviolet spectra. However, whereas the methanol adduct, **5a**-CH_3OH, is a single isomer, it was clear from its behavior on recrystallization and nmr spectrum, which exhibits two methoxyl and two sets of ethoxyl resonances, that the "ethanolysis" product represents a mixture of isomers. The "methanolysis" product is tentatively formulated as 6,6-dimethoxy-7,8-diphenylbicyclo[3.3.0]octa-3,7-dien-2-one (**21**).

"Methanolysis" of 1-Methoxy-7,8-diphenyl-3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione (7a).—A methanolic solution (12 ml) of the photoadduct **7a** (436 mg) was refluxed for 6 hr and then evaporated to dryness. After recrystallization from ether–hexane solution, 453 mg (95% yield) of a methanol adduct, **7a**-CH_3OH, was obtained and is tentatively assigned the structure 1,2-diphenyl-3,3-dimethoxy-3a-hydroxy-3,3a,8,8a-tetrahydrocyclopent[*a*]inden-8-one (**19**).

Hydrolysis of 7a-CH_3OH.—This adduct (200 mg) was dissolved in concentrated sulfuric acid (5 ml), which was then poured onto ice. The resulting precipitate was filtered, washed thoroughly with water, and recrystallized from acetone–hexane solution to afford 60 mg of 1,2-diphenyl-3a-hydroxy-3,3a,8,8a-tetrahydrocyclopent[*a*]indene-3,8-dione (**11a**), mp 124–126°. The same product crystallized from an nmr sample of **7a**-CH_3OH in deuteriochloroform, which also contained 1 drop of D_2O, after standing at room temperature for about 1 week.

Hydrolytic Rearrangement of 7a.—A solution of photoadduct **7a** (263 mg) in acetonitrile (6.5 ml) and water (1.5 ml) was refluxed for 5 hr in a nitrogen atmosphere, after which the addition of water provided 222 mg (88% yield) of the diphenyldione **11a**, mp 225–226°, identical with that obtained on hydrolysis of **7a**-CH_3OH.

Similarly, the photoadducts **7b** and **c** were converted into the

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[21] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

[22] J. A. Barltrop and B. Hesp, *J. Chem. Soc., C*, 1625 (1967).

[23] Acetonitrile was distilled from phosphorus pentoxide prior to use. Commercially available alkynes were utilized without further purification. The melting points are corrected and elemental analyses were determined by Spang, Ann Arbor, Mich.

[24] C. D. Logan, R. M. Husband, and C. B. Purves, *Can. J. Chem.*, **33**, 82 (1955).

corresponding diones **11b** and **c**, after the solution was refluxed about 20 and 30 hr, respectively. In each case, infrared spectra of the crystalline crude product, obtained after evaporation to dryness, were identical with those of the pure diones, indicating that the conversions are essentially quantitative.

When the progress of hydrolysis was carefully monitored in the infrared region, plots of A_1/A_2 were found to be linear with time in the range of 30–70% reaction, as determined by comparison with spectra of standard mixtures of reactant and product, where A_1 and A_2 are the carbonyl absorbancies of product (at $\sim$5.82 μ) and reactant (at $\sim$5.92 μ), respectively. This finding simplified the conversion of absorbancy ratios of known 1:1 mixtures into half-lives of reaction. The experiments were carried out on approximately 20 mg of photoadduct in a solution of acetonitrile (4 ml) and water (2 ml) heated at reflux in an oil bath held at 105°. Under these conditions, the half-lives of reaction were found to be 27.5, 168, and 252 min for **7a**, **b**, and **c**, respectively.

1,2-Diphenyl-3a-acetoxy-3,3a,8,8a-tetrahydrocyclopent[*a*]-indene-3,8-dione (11a-OAc).—A solution of the diphenyldione **11a** (220 mg) in pyridine (1.5 ml) and acetic anhydride (0.1 ml) was stirred at room temperature for 2 days and then poured into an ice–water mixture. The resulting precipitate (250 mg) was collected and recrystallized from acetone–hexane solution to provide 206 mg (84% yield) of **11a-OAc**, mp 173–174°.

Deuterium Exchange Experiment with 1-Methyl-2-phenyl-3a-hydroxy-3,3a,8,8a-tetrahydrocyclopent[*a*]indene-3,8-dione (11c).—A solution of the methylphenyldione **11c** (111 mg) in dioxane (5.5 ml) and D_2O (1.5 ml) was refluxed for 90 hr and then evaporated to dryness. The resulting solid was taken up in benzene, which was washed with water and dried. After removal of the benzene and recrystallization from benzene–hexane solution, 108 mg of colorless crystals, mp 176–177°, were isolated and shown to be the tetradeuterio analog of **11c**, in which the methyl and methine hydrogens had been replaced by deuterium atoms, on the basis of infrared, ultraviolet, nmr, and mass spectra. The mass spectrum exhibited molecular ions for only tri- (*m/e* 294) and tetradeuterated (*m/e* 295, base peak) material in the ratio of 1:7 indicating that more than 85% of the material was tetradeuterated.

Registry No.—**5a**, 16343-59-2; **5a** (ethanolysis product), 18945-02-3; **5b**, 16343-60-5; **5c**, 18926-54-0; **7a**, 16526-86-6; **7b**, 18926-56-2; **7c**, 18926-57-3; **11a**, 18926-58-4; **11a** (acetylated), 18926-59-5; **11b**, 18926-60-8; **11c**, 18926-61-9; **19**, 18926-62-0; **21**, 18926-30-2.

Synthesis and Deamination of 1-Amino-4-bromo-7,7-dimethylbicyclo[2.2.1]heptan-2-ol

H. O. Larson, Thean-Chit Ooi,[1] Walter K. H. Luke,[2] and Kikuye Ebisu[3]

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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Deamination of the amino alcohol **9** leads to the formation of the bicyclo[2.1.1]hexane derivative **10**. The amine **9** is available from the degradation of **2**. Lead tetraacetate oxidation of the semicarbazone **6** yields the novel heterocycle **7** that hydrolyzes remarkably easily to the amine.

Interest in the chemistry of small cyclic systems remains at a high level.[4] The synthesis of bicyclo[2.1.1]hexane and its derivatives employs photochemical reactions almost exclusively. The photochemical cyclization of 1,5-hexadiene[5] and related 1,5-hexadienes[6–8] is an expeditious route which has been exploited recently. Photosensitized internal cycloaddition reactions of suitably constituted dienes may provide the best method for the synthesis of the bicyclo[2.1.1]hexane ring system.[9,10] The observation, "there is considerable need for additional synthetic methods to the bicyclo[2.1.1]hexane system from commercial starting materials and by procedures which can be operated on a reasonable scale,"[8] is relevant. The rearrangement of the amino alcohol **1** to 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde on treatment with nitrous acid may have been due to a fortunate choice for the migrating group.[11] The deamination of a similarly constituted amino alcohol unsubstituted at C-3 would determine the scope of the reaction.

The amide **2** appeared to be useful for our objective,[12] and oxidation of the corresponding nitrile with alkaline hydrogen peroxide furnished the requisite amide; usual hydrolytic procedures fail to produce the amide.[13] Treatment of **2** with alkaline sodium hypobromite resulted in the heterocycle **3**. Formation of the cyclic compound in the Hofmann reaction from the intermediary isocyanate is similar to the formation of cyclic urethans in the Curtius degradation of β-hydroxy acid azides.[14] The conversion of **3** into an amino alcohol proved to be arduous.

The cyclic urethan **3** was converted to a neutral compound, $C_9H_{13}BrO$, which was devoid of nitrogen, by the action of hot sulfuric acid. Absorption bands in the infrared (ir) spectrum at 7.22 and 7.33 μ indicated that the *gem*-dimethyl group had been retained. The characteristic absorption of a carbonyl group in a five-membered ring was observed at 5.70 μ. The nuclear magnetic resonance (nmr) spectrum required that the bromine atom be attached to a tertiary carbon atom. Structure **4** was tentatively assigned to the product. Cleavage of a C–N bond at the bridgehead position is surprising. The reaction appears to be a

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[1] East-West Center Grantee, 1965 to present.

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[3] N.D.E.A. Fellow, 1962 to 1965.

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