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Photochemical Reactions of Diketones. The 1,4-Addition of Ethers to 9,10-Phenanthrenequinone

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A new photochemical reaction of phenanthrenequinone (PQ), the reversible 1,4-addition of ethers, is described. In the resulting 1:1 adducts the original ether function is converted to an acetal group. Attempts to apply the photoreaction for cleavage of ethers by hydrolysis of the adducts have met with limited success; 3β-methoxycholestane was converted to a mixture of cholestanone plus cholestanol in 50% yield while 3β-methoxycholestene was not cleaved.

Since the first report of a light-catalyzed reaction of 9,10-phenanthrenequinone (PQ) in 1886,[1] many investigators, notably Schönberg and his collaborators, have described studies of four photochemical addition reactions of PQ and related *o*-quinones.[2a,b] These are the addition of sulfur dioxide to form a cyclic sulfate,[3] of olefins to form dioxenes,[4] of aldehydes to give monoesters of 9,10-dihydroxyphenanthrene,[5] and of substituted methylbenzenes to form 9,10-dihydro-9-keto-10-hydroxy-10(X-benzyl)phenanthrenes.[6] The extent of these investigations may be illustrated by the fact that olefin addition reactions involving at least thirteen *o*-quinones and forty-five olefins have been documented.[4] This report describes the photochemical addition of ethers to PQ,[8] representing the fifth example of what promises to be a very general class of reactions.

Irradiation of a suspension of PQ in dioxane resulted in isolation, after removal of excess dioxane, of a crystalline 1:1 adduct (Ia) in 90% yield. The conversion of the ether to an acetal was confirmed by facile hydrolysis in the present of dilute mineral acid to give PQ in high yield.[9] Further evidence on this point was provided by the results obtained with 3β-methoxycholestane (II) (visible-infrared).

The ultraviolet spectrum of Ia was rich in detail (six maxima) and corresponded closely to that of the adduct (Id) of benzaldehyde and PQ.[10] This spectrum underwent marked change in alkaline solution as expected of a phenol. Further confirmation that 1,4-addition across the dione moiety had occurred was provided by infrared and n.m.r. spectra. The infrared spectrum exhibited a strong hydroxyl band at 3.0 μ and no significant absorption in the 5.5–6.05-μ region. In addition to the expected complex absorption at low field characteristic of phenanthrenes and the phenolic hydroxyl group in the n.m.r., a quartet centered at 4.96 τ (O–CH–O) and a complex group of lines at 5.7–6.3 τ (O–CH–OH–O) were observed. The ratio of the integrated areas of these three groups of lines was 9:1:6 in agreement with the structure assigned.

The photochemical reversibility of the addition was demonstrated by irradiation of Ia in refluxing benzene.[11] Analysis by chromatography on Florisil after irradiation for seventy-two hours indicated 69% Ia, 22% PQ, and 9% phenanthrenequinhydrone.[12] This appears to approximate the photostationary state since a mixture of essentially the same composition was obtained from irradiation of an equimolar solution of PQ and dioxane under similar conditions. The amount of quinhydrone formed increased slowly on more prolonged irradiation.

Adducts similar to Ia were also obtained from tetrahydrofuran (97% yield) and anisole (86% yield). As expected, the tetrahydrofuran adduct (Ib) resulted from attack at the α- rather than the β-position of tetrahydrofuran. This was clearly established by the n.m.r. spec-

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(1) H. Klinger, *Ber.*, **19**, 1862 (1886).

(2) (a) An excellent general summary is to be found in "Präparative Organische Photochemie," A. Schönberg, Springer-Verlag, Berlin, 1958; (b) *cf.* also "Ultraviolet Photochemistry," P. de Mayo, in "Advances in Organic Chemistry," Vol. II, Interscience Publishers, New York, N. Y., 1960, pp. 367–425.

(3) G. O. Schenck and G. A. Schmidt-Thomee, *Ann.*, **584**, 199 (1953).

(4) Ref. 2a, p. 89 ff.

(5) Ref. 2a, p. 101.

(6) The earlier assignment[7a,b] of the 9-hydroxy-10(X-benzyloxy)phenanthrene structure to these adducts has been shown to be incorrect; M. B. Rubin and P. Zwitkowits, to be published.

(7) (a) A. Benrath and A. Von Meyer, *J. prakt. Chem.*, **89**, 258 (1914); (b) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 3405 (1953).

(8) Klinger[1] reported the formation of a crystalline product on exposure of a diethyl ether solution of PQ to sunlight. This product was converted to the diacetate of 9,10-dihydroxyphenanthrene by hot acetic acid, but was not otherwise characterized.

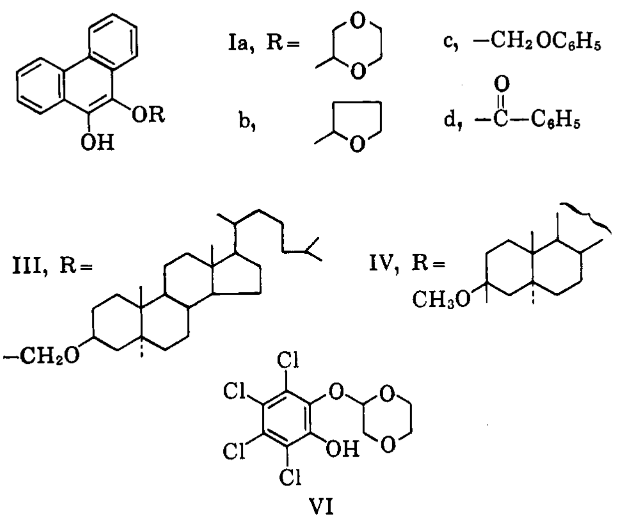
(9) The anticipated hydrolysis product, 9,10-dihydroxyphenanthrene, undergoes rapid air oxidation to PQ.

(10) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953).

(11) In the absence of light Ia was recovered quantitatively after 72 hr. reflux in benzene solution.

(12) Phenanthrenequinhydrone presumably is formed by dimerization of intermediate semiquinone radicals.[7b]

trum which showed a poorly resolved triplet centered at 4.96 τ (O–CH–O), and multiplets centered at 6.34 τ ($C–CH_2–O$) and 8.49 τ ($C–CH_2–C$) with areas in the ratio of 1:2:4 in addition to the expected complex lower field absorption. Both Ib and the anisole adduct (Ic) had ultraviolet spectra essentially identical with that of Ia.



An intriguing aspect of this new addition reaction is the conversion of the normally unreactive ether function to the readily hydrolyzable acetal or ketal group, suggesting the possibility of a convenient, two-step procedure for cleavage of ethers. As a model compound for investigation of this attractive possibility we selected 3β-methoxycholestane (II). A further point of interest in this choice lay in the fact that two adducts, III and IV, are possible, resulting from reaction either at the primary or tertiary carbon atoms adjacent to the ether oxygen. Since acid hydrolysis of III would lead to cholestanol and of IV to cholestanone, this experiment also was expected to provide information on the behavior of unsymmetrical ethers.

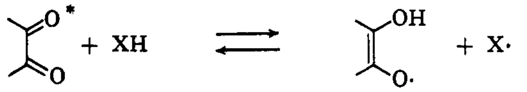
In the event, irradiation of a benzene solution of PQ and II did lead to formation of adduct(s) as shown by spectroscopic examination of fractions separated by chromatography. The best fractions obtained, however, were contaminated with II and contained about 50% of adduct (based on ultraviolet spectra). Since no crystalline material could be obtained, the crude irradiation product was hydrolyzed directly in aqueous acidic dioxane. Chromatographic separation of the resulting mixture afforded recovered PQ, II (24%), cholestanol (15%), and cholestanone (4.2%). It is noteworthy that the 3.6:1 ratio of cholestanol to cholestanone which reflects a corresponding ratio of adducts III and IV is close to the 3:1 ratio would be predicted on purely statistical grounds.

Results previously presented represent the best yield of ether cleavage products obtained by varying time, temperature, and concentration of reactants. In an effort to improve these results we investigated the photochemical reaction of PQ and II in benzene–acetic acid and benzene–acetic acid–water solutions. It was anticipated that the presence of acetic acid would lead to hydrolysis of the adducts to cholestanol and cholestanone (*cf.* reference 9) with concomitant shifting of the photochemical equilibrium and thus provide in higher yield a one-step ether cleavage. This expectation was realized to a limited extent. Irradiation of PQ and II for seventy-one hours in benzene containing 15% of acetic acid afforded recovered II (30%), cholestanol (15%), and cholestanone (35%), representing a two and one-half fold improvement in total cleavage product. Similar results were obtained in benzene–acetic acid–water solution. The change in cholestanol cholestanone ratio from 3.6:1 to 0.43:1 probably does not reflect a change in the ratio of adducts III and IV, since it was demonstrated that cholestanol undergoes oxidation under the conditions of the photochemical reaction.

A further limitation on any practical value of the ether cleavage reaction was revealed by irradiation of PQ and 3β-methoxy-5-cholestene (V) in benzene or benzene–acetic acid solution. In addition to considerable recovered ether there could be isolated by chromatography noncrystalline fractions with complex ultraviolet spectra. These apparently contained adducts formed by addition of the olefinic bond of V to PQ since they exhibited characteristic methoxyl absorption at 9.1 μ and afforded unchanged spectra after attempted acid-catalyzed hydrolysis.

The photochemical behavior of a number of other quinones was also investigated in dioxane solution (or suspension). Tetrachloro-*o*-benzoquinone gave a 1:1 adduct (VI) in 20% yield.[13] Benzil and acenaphthenequinone underwent photochemical change as shown by infrared analysis of crude reaction product but no pure substances have been isolated from these reactions. *p*-Benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone were recovered substantially unchanged after prolonged irradiation.

The mechanism of photochemical addition and dehydrogenation reactions of PQ is generally accepted[3,7b,10,14a,b] as being of a free radical nature. Moore and Waters have proposed that the benzaldehyde and *p*-xylene addition reactions involve abstraction of a hydrogen atom by an excited PQ molecule to give a semiquinone radical and a benzoyl or *p*-methylbenzyl radical. For the reactions described in this work, a sequence involving initial abstraction of hydrogen atom from the carbon adjacent to oxygen seems eminently reasonable. Both radical recombination and radical chain mechanisms have been suggested for the subsequent steps in the earlier additions although no experimental evidence is available. We currently are investigating this question particularly with regard to providing an explanation for the occurrence of 1,2-addition with substituted toluenes and of 1,4-addition with aldehydes and ethers.



Experimental[15]

Photoirradiations.—Except where noted otherwise, the photoirradiations were performed in an atmosphere of nitrogen using a

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[13] The low yield is presumably due to competing photoreactions of tetrachloro-*o*-quinone itself since irradiation of the quinone alone in benzene solution resulted in pronounced alteration of its ultraviolet spectrum.

[14] (a) H. L. J. Bäckström, *Z. Physik. Chem.*, **25**, 99 (1934); *Naturwissenschaften*, **22**, 170 (1934). (b) G. O. Schenck, *Z. Elektrochemie*, **64**, 997 (1960).

General Electric 1000-w., water-cooled, high pressure mercury lamp (AH-6) with Corning 7-51 glass filter to eliminate radiation below 3000 Å.

Photoadduct of Phenanthrenequinone and Dioxane (Ia).—A suspension of 1.00 g. of quinone in 20 ml. of dioxane[16] was irradiated for 20 hr. The solid had completely dissolved and the characteristic orange color of the quinone faded to a pale yellow. The solution fluoresced strongly. Removal of excess dioxane under reduced pressure left 1.37 g. of tan solid which was washed through a column of 50 g. of Florisil with 500 ml. of benzene to give 1.21 g. (90%) of nearly colorless crystals of Ia, m.p. 105–106°. The analytical sample was obtained by recrystallization from isopropyl ether, m.p. 105–105.5°; λ_{max} (CH_3OH) 249 mμ (sh) (44,000), 255 (51,000), 273 (14,000), 295 (9000), 307 (9000), 327 (sh) (800), 343 (1200), 360 (1300); (0.1 *M* NaOH, 40% dioxane) 256 mμ (37,000), 335 (6000), 385 (sh) (2000); (KBr) 3.0 μ.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C 72.93; H, 5.59.

Ia gave a negative ferric chloride test in alcohol solution.

Refluxing 331 mg. of Ia in benzene under nitrogen for 72 hr. in the absence of light gave 327 mg. of recovered starting material, m.p. 104.5–106°.

Extraction of a chloroform solution of Ia with five portions of 5% aqueous sodium hydroxide afforded after acidification, etc., 30% of Ia. The remaining 70% was recovered by evaporation of the neutral fraction.

Hydrolysis of Ia.—A solution of 29 mg. of Ia in 2 ml. of methanol containing 1 drop of concentrated hydrochloric acid was kept at 50° for 10 min. Sodium bicarbonate and water were added and the mixture concentrated under reduced pressure to remove methanol. The aqueous residue was extracted with ethyl acetate and these extracts, after drying and concentration under reduced pressure, yielded 26 mg. of orange solid. Recrystallization from ethyl acetate–petroleum ether gave 16 mg. (80%) of orange needles, m.p. 208–210°, identical with PQ.

Photoadduct of PQ and Benzaldehyde (Id).—This compound, m.p. 186–187°, was prepared by the procedure of Moore and Waters[10,17] in order to determine the ultraviolet spectrum for comparison purposes; λ_{max} (dioxane) 249 mμ (sh) (51,000), 254 (56,000), 274 (18,000), 295 (10,000), 306 (9000), 325 (1500), 341 (1800), 359 (1900). The spectrum underwent rapid change in alkaline solution.

Photochemical Reversibility of PQ–Dioxane Addition.[18]—Two experiments were performed in Pyrex flasks fitted with reflux condensers. One flask (forward reaction) contained 0.50 ml. (0.0117 mole) of dioxane and 1.207 g. (0.0117 mole) of PQ in 75 ml. of benzene and the second (reverse reaction) contained 1.732 g. (0.0117 mole) of Ia in 75 ml. of benzene, both in nitrogen atmospheres. Each flask was irradiated with a General Electric S-4 mercury vapor lamp placed about 2 in. below the bottom of the flask so that reflux was maintained by the heat of the lamp. Aliquots of each were withdrawn after 24 and 72 hr. and analyzed by chromatography on Florisil. Elution with 50% benzene–petroleum ether, 90% benzene–petroleum ether, and pure benzene gave the adduct Ia; ethyl acetate eluted PQ; and methanol eluted phenanthrenequinhydrone (characterized by color reactions and by oxidation to PQ). The composition of the mixtures was as follows: after 24 hr., forward reaction, 63% Ia, 27% PQ, 7% quinhydrone; reverse reaction, 76% Ia, 15% PQ, 8% quinhydrone; after 72 hr., forward reaction, 72% Ia, 21% PQ, 6% quinhydrone; reverse reaction, 69% Ia, 22% PQ, 9% quinhydrone.

Photoadduct of PQ and Tetrahydrofuran (Ib).—The experiment was performed as described for the dioxane reaction. From 1.00 g. of quinone and 20 ml. of tetrahydrofuran (distilled over lithium aluminum hydride) there was obtained after chromatography on Florisil 1.10 g. (82%, 97% based on recovered starting material) of nearly colorless adduct (Ib), m.p. 94–96°, and 0.16 g. of PQ (eluted with ethyl acetate). The analytical sample of Ib was obtained by crystallization from isopropyl ether, m.p. 96.5–97.5°; λ_{max} (CH_3OH) 249 mμ (sh) (48,000), 256 (54,000), 272 (15,000), 295 (9000), 308 (9000), 326 (sh) (900), 345 (1300), 362 (1400); (KBr) 3.0 μ.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.21; H, 5.98.

Photoadduct of PQ and Anisole (Ic).—Irradiation of a suspension of 1.00 g. of quinone in 20 ml. of distilled anisole was continued for 130 hr., when all the quinone had dissolved. Removal of excess anisole under reduced pressure left 1.50 g. of red-orange solid which was washed through a column of 50 g. of Florisil with 500 ml. of benzene to give 1.30 g. (86%) of nearly colorless crystals, m.p. 93.5–96.5°. The analytical sample was obtained by recrystallization from isopropyl ether, m.p. 115–115.5°; λ_{max} (CH_3OH) 249 mμ (sh) (45,000), 254 (51,000), 270 (sh) (14,000), 295 (9000), 307 (9000), 328 (sh) (800), 343 (1200), 361 (1200); (KBr) 3.0 μ. N.m.r., singlet at 4.25 τ ($O\text{–}CH_2\text{–}O$) in addition to aromatic and phenolic protons.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.09. Found: C, 79.43; H, 5.40.

Photoaddition of PQ and 3β-Methoxycholestane (II) in Benzene.—A solution of 0.50 g. of quinone and 1.00 g. of II[19] in 50 ml. of dry benzene was irradiated for 92 hr. A 5-ml. aliquot was chromatographed on 10 g. of Florisil. Elution with 350 ml. of benzene and 100 ml. of 1% ethyl acetate–benzene afforded 113 mg. of nearly colorless oil which could not be induced to crystallize; λ_{max} (dioxane) 251 mμ (sh) (22,800), 257 (25,500), 271 (sh) (9000), 298 (4600), 310 (4600), 334 (1100), 364 (700); (CH_2Cl_2) 3.0 μ, 6.1, 6.2. Elution with 100 ml. of ethyl acetate gave 33 mg. of PQ and with 100 ml. of methanol gave 22 mg. of quinhydrone.

Hydrolysis of Adduct(s) of PQ and 3β-Methoxycholestane (II).—The crude reaction mixture from irradiation of 0.50 g. of PQ and 0.50 g. of II in 50 ml. of benzene for 72 hr. was dissolved (after removal of benzene) in 25 ml. of dioxane, and 5 ml. of water containing 0.5 ml. of concentrated sulfuric acid was added. Clear solution was heated on the steam bath for 1.5 hr., cooled, and excess solid sodium carbonate added. The mixture was concentrated to *ca.* 5 ml. under reduced pressure and the residue taken up in ethyl acetate. The layers were separated, the organic layer washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated to dryness on the steam bath under reduced pressure. The benzene-soluble portion (545 mg.) of the yellow residue was chromatographed on 20 g. of Florisil collecting 200-ml. fractions. Elution with 20% benzene in petroleum ether gave 120 mg. (24%) of crystalline II.

Further elution with 90% benzene in petroleum ether and pure benzene gave 135 mg. of light orange solid. This was rechromatographed on 4 g. of alumina collecting 40-ml. fractions. With 20% benzene in petroleum ether there was obtained 20 mg. (4.2%) of cholestanone, white crystals, m.p. 114–121°, identical by infrared spectral comparison with an authentic sample.[20] One recrystallization from methanol gave 11 mg., m.p. 127–129° (reported[20] m.p. 129–129.5°).

Elution with 50% benzene in petroleum ether and pure benzene gave 72 mg. (15%) of cholestanol, m.p. 139–142° (reported[21] m.p. 140–141°), identical by infrared spectra with an authentic sample.

Irradiation of PQ and II in Benzene–Acetic Acid.—A suspension of 1.00 g. of PQ and 0.91 g. of II in 50 ml. of 15% acetic acid in benzene (v./v.) was irradiated for 71 hr. The quinone dissolved slowly and the solution became dark, wine red in color. The solvents were removed under reduced pressure on the steam bath and the dark residue was treated with three 5-ml. portions of hot benzene.

Chromatographic separation of the benzene-soluble portion on Florisil and alumina as described earlier afforded 274 mg. (30%) of II, 303 mg. (35%) of cholestanone, and 130 mg. (15%) of cholestanol.

Photooxidation of Cholestanol with PQ.—A suspension of 1.0 g. of PQ and 1.0 g. of cholestanol in 50 ml. of 15% acetic acid in benzene was irradiated for 24 hr. The clear, wine red solution was concentrated under reduced pressure and the residue treated

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[15] Melting points are corrected. N.m.r. spectra were determined in deuteriochloroform at 60 Mc. using tetramethylsilane as internal standard. Microanalyses were performed by Weiler and Strauss and by Galbraith Laboratories. Petroleum ether was a fraction of b.p. 66–75°.

[16] Purified over alumina; W. Dosler and C. D. Bauer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 52 (1946).

[17] The authors revised the earlier proposal of a cyclic pseudo-ester structure on the basis of a strong band at 5.82 μ in Nujol. We observed this band in potassium bromide and in methylene chloride solution.

[18] Experiments performed by J. Yevich.

[19] L. Dunn, I. M. Heilbron, R. J. Pnipers, K. M. Samant, and F. S. Spring, *J. Chem. Soc.*, 1576 (1934); *cf.* also J. C. Babcock and L. F. Fieser, *J. Am. Chem. Soc.*, **74**, 5472 (1952). In order to eliminate the possibility of contamination by cholestanol the recrystallized ether was washed through alumina with petroleum ether.

[20] W. F. Bruce, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 139.

[21] W. F. Bruce and J. O. Ralls, *ibid.*, p. 191.

with three portions of benzene. The benzene-soluble material was washed through 50 g. of Florisil with 1.5 l. of benzene to give 0.98 g. of faintly yellow, oily solid. This was chromatographed on 30 g. of alumina collecting 300-ml. fractions. Elution with petroleum ether and two fractions of 20% benzene in petroleum ether gave 0.275 g. (28%) of cholestanone, m.p. 125.5–128°, identical with an authentic sample.[20] Elution with 50% benzene in petroleum ether and pure benzene gave 0.497 g. (50%) of recovered cholestanol, m.p. 141.5–142.5°.

Photoirradiation of PQ and 3β-Methoxy-5-cholestene (V).—A suspension of 2 g. of PQ and 0.91 g. of V[19] in 70 ml. of benzene was irradiated for 94 hr. The dark, wine red solution was concentrated on the steam bath to 10 ml., the 0.44-g. sample of unchanged PQ was filtered, and the filtrate washed through 50 g. of Florisil to give 1.19 g. of faintly yellow oil. This was dissolved in petroleum ether and chromatographed on 50 g. of Florisil, collecting 250-ml. fractions. Elution with four fractions of 10% benzene–petroleum ether, two of 20%, and one of 30% afforded 0.29 g. of nearly colorless oil, identical by infrared spectra with V.

Further elution with one fraction each of 30%, 50%, and 90% benzene–petroleum ether and one of pure benzene yielded 0.66 g. of faintly yellow oil; λ_{max} (dioxane) 251 mμ (sh) (39,000), 256 (47,500), 272 (sh) (18,800), 305 (7500), 318 (9100), 335 (6000), 373 (1500), 395 (770) (extinctions based on molecular weight of a 1:1 adduct); (CH_2Cl_2) 6.1 μ, 6.2, 9.1, no absorption at 2.5–3.1. Treatment of 287 mg. of the oil with aqueous acidic dioxane as described for the adducts of PQ and II afforded 262 mg. of crude product with essentially unchanged ultraviolet and infrared spectra. Repeated chromatography on Florisil failed to give any crystalline products.

Photoadduct (VI) of Tetrachloro-*o*-quinone and Dioxane.—A solution of 3 g. of quinone in 90 ml. of dioxane was irradiated for 14 hr. when the deep red color had faded to light orange. The excess dioxane was removed under reduced pressure without heating to give a tan solid which after one recrystallization from ethyl acetate gave 946 mg. (20%) of V as white needles, m.p. 159–161°. The analytical sample was obtained by crystallization from ethyl acetate, m.p. 167–168°; λ_{max} (dioxane) 291 mμ (sh) (2000), 298 (2400); (KBr) 3.05 μ, no strong maxima at 5.5–6.05.

Anal. Calcd. for $C_{10}H_8O_4Cl_4$: C, 35.96; H, 2.41; Cl, 42.46. Found: C, 35.78; H, 2.23; Cl, 42.28.

Attempted isolation of additional product yielded only solids with broad melting ranges.

Acknowledgment.—The author wishes to acknowledge the generous cooperation of Professor G. J. Mains and Dr. R. Doepker in the photoirradiation experiments and of Professor R. J. Kurland in the determination and interpretation of n.m.r. spectra.

Allene Chemistry. I. Free Radical Addition of Thiols to Allene

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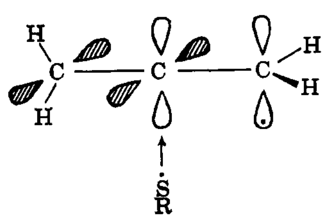
Methanethiol, benzenethiol, and thiolacetic acid added readily to allene under homolytic conditions. The initial attack of the corresponding thiyl radicals occurred quite selectively at the terminal positions of allene, to yield 1:1 and 2:1 adducts. The methanethiol–allene reaction has been studied in greater detail with the help of capillary gas chromatography, n.m.r., and infrared analysis. Allyl methyl sulfide, 1,3-bis(methylthio)propane, and 1,2-bis(methylthio)propane were the reaction products. The yield of the 1:1 adduct (allyl methyl sulfide) varied between 40 and 75 mole % when the reaction temperature was changed from −75 to +17°. 1,3-Bis(methylthio)propane was derived from allyl methyl sulfide, whereas 1,2-bis(methylthio)propane was mainly (>93%) derived from 2-methylthiopropene, the product of a center attack to allene. The selectivity of the initial attack of the thiyl radicals at the terminal positions of allene increased with decreasing reaction temperature. It was found to be 88% at 17° and 95% at −75°. In the addition of thiolacetic acid to allene terminal attack by the thiyl radical occurs with about 91% selectivity, whereas the benzenethiol–allene reaction is less selective. At 17° only about 80% terminal attack was observed.

Free radical reactions of diolefins containing isolated[3] and conjugated[4–6] double bonds have been examined previously in this laboratory. This paper reports about the consequent extension of these studies to the cumulative double bond system of allene.

The over-all course of free radical addition reactions to allene is obviously dependent on the point of initial attack of the radical species which starts the chain. In the case of unsymmetrically substituted mono-[7a] and diolefins,[5] it has been generally demonstrated that the reaction path involving the more stable of the possible radical intermediates is preferred. On this basis it might at first glance seem that initial attack at the center carbon of allene should be favored, since one can write a resonance-stabilized allylic radical intermediate (I), whereas terminal attack leads to a vinylic radical (II). However, in view of the special geometry of the allene molecule, such a representation of the initial attack is certainly oversimplified. The incipient radical from a center attack resembles a primary radical rather than an allylic one, since the orbital of the odd electron does not overlap with the π-orbitals of the remaining double bond.



This complication, though it might cause an increase of the activation energy for the center attack and possibly favor terminal addition, has never been discussed in previous publications on this subject.

The question of terminal and center attack in free radical additions to allene has been answered differently by previous workers. Szwarc and co-workers[8] have

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[3] A. A. Oswald and F. Noel, *J. Org. Chem.*, **26**, 3948 (1961).

[4] A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *ibid.*, **27**, 2439 (1962).

[5] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).

[6] A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 1262 (1963).

[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) p. 314; (b) pp. 321–323.

[8] A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).