and 6.01–6.07 μ. The ultraviolet spectrum (ethanol) had λ_{max} 228 mμ (log ε 4.45) and 292 mμ (log ε 4.02). The compound was soluble in dilute acid and did not give ferric chloride or Ehrlich tests.

Anal. Calcd. for $C_{16}H_{18}O_2N_4$: C, 64.41; H, 6.08; N, 18.78. Found: C, 64.25; H, 6.04; N, 18.72.

BETHESDA 14, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY, AND EIN SHAMS UNIVERSITY]

Photochemical Reactions in Sunlight. XVII.[1] Experiments with 4-Cyano-1,2-naphthoquinone

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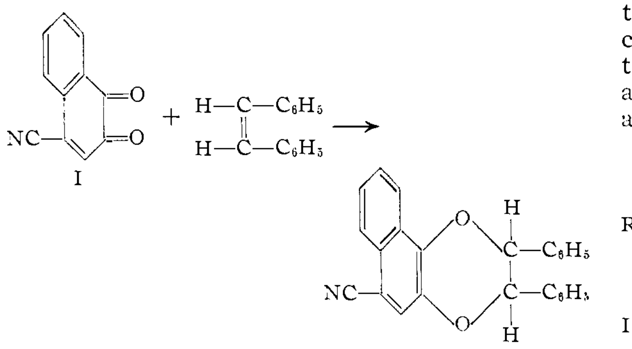
Photochemical reactions (sunlight) of 4-cyano-1,2-naphthoquinone are investigated. The addition of stilbene yields II; the addition of some derivatives of benzaldehyde and of cinnamaldehyde proceeds according to scheme B. The photoreaction with acetaldehyde leads to the formation of 1,2-dihydroxy-3-aceto-4-cyanonaphthalene (V) and with propionaldehyde, 1,2-dihydroxy-3-propiono-4-cyanonaphthalene is obtained. Blank, dark experiments in all cases proved to be negative.

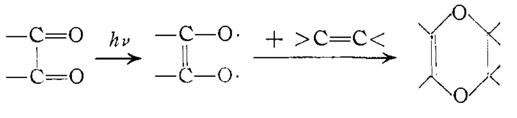
(a) We have investigated the action of stilbene on 4-cyano-1,2-naphthoquinone and found that whereas no action takes place in the dark, in sunlight 6-cyano-2,3-diphenyl-2,3-dihydronaphtho-(1,2)-*p*-dioxin (II) is formed. The reaction takes place as in the case of phenanthrenequinone[2] and similar quinones[3]; 4-cynano-1,2-naphthoquinone is therefore less reactive than certain derivatives of *o*-benzoquinone, *e.g.*, tetrachlorobenzoquinone which adds stilbene even in the dark.[4]



I

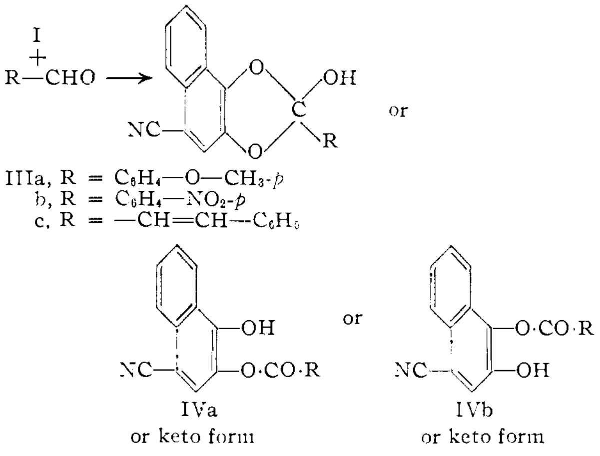
II Scheme A

On the Mechanism of the Photoaddition of Olefins to *o*-Quinones.—Though we have described a great number of such photoadditions,[3] (compare scheme A) we have not yet offered a mechanism. Recently Schenck[5a] and Schenck and Schmidt-Thomée[5b] have advanced the theory that the quinones are changed photochemically into diradicals followed by the addition of the olefins.



Some of these olefins polymerize in sunlight, *e.g.*, stilbene forms a photo dimer.[6] The monomer therefore can be activated by the action of sunlight, and the possibility that the photoaddition of *o*-quinones to the olefins may be due to the action of the photoactivated olefins on the non-activated quinones should not be overlooked. It also is possible that both mechanisms are operative.

(b) **Photochemical Action of 4-Cyano-1,2-naphthoquinone on Aldehydes.**—We have found that in the case of anisaldehyde, cinnamaldehyde, colorless addition products were obtained and in the case of *p*-nitrobenzaldehyde the reaction product was yellow. The products have either the constitution III, IVa or IVb. The possibility of ring chain tautomerism should be taken into consideration.[7,8] None of these photoaddition products in alcoholic solution gives a color reaction with aqueous ferric chloride.



IIIa, R = $C_6H_4—O—CH_3$-*p*
b, R = $C_6H_4—NO_2$-*p*
c, R = —CH=CH—C_6H_5

IVa or keto form

IVb or keto form

Scheme B

In contrast to anisaldehyde, cinnamaldehyde and *p*-nitrobenzaldehyde the addition of acetaldehyde and propionaldehyde leads to orange colored products giving in alcohol a green ferric chloride reaction.[9] It is believed that in these cases the reaction proceeds according to scheme C (acetaldehyde is taken as an example).

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[1] Part XVI, *J. Chem. Soc.*, 1346 (1951).

[2] A. Schönberg and A. Mustafa, *ibid.*, 387 (1944); 2126 (1948).

[3] A. Schönberg and A. Mustafa, *Chem. Revs.*, **40**, 190 (1948).

[4] A. Schönberg and N. Latif, THIS JOURNAL, **72**, 4828 (1950).

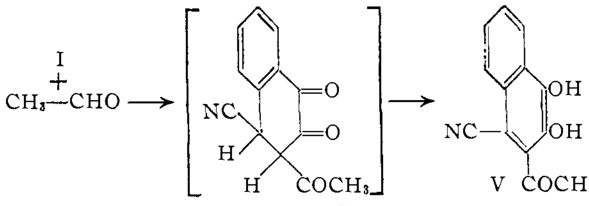
[5] (a) G. O. Schenck, *Naturwissenschaften*, **40**, 229 (1953); (b) G. O. Schenck and G. A. Schmidt-Thomée, *Ann.*, **584**, 199 (1953).

[6] G. Ciamician and P. Silber, *Ber.*, **35**, 4129 (1902).

[7] A. Schönberg and R. Moubasher, *J. Chem. Soc.*, 1430 (1939); A. Schönberg and co-workers, *J. Chem. Soc.*, 1364 (1951).

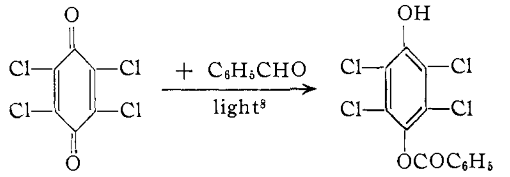
[8] R. F. Moore and W. A. Waters, *ibid.*, 238 (1953).

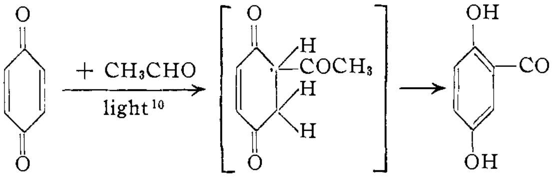
[9] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 239 (1949), observed differences in the free radical reactions of aryl or α,β-unsaturated aldehydes and aliphatic aldehydes with olefins.



Scheme C

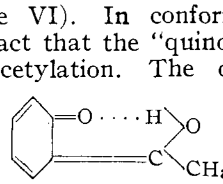
In the case of *p*-quinones also the photoaddition of aldehydes proceeds according to two different schemes and the relation between these schemes and the two schemes for *o*-quinones is evident.





The constitution of 1,2-dihydroxy-3-aceto-4-cyanonaphthalene (V) is based on the following: The substance is soluble in alkali and sodium carbonate and from the latter solution is recovered by acidification. The alcoholic solution gives a color test with titanic chloride and a green color[11] with ferric chloride; in the latter case the addition of small amounts of soda or ammonia changes the color into reddish-brown. Such changes are well known with benzcatechols.[12] The substance gives phthalic anhydride on oxidation (sulfuric acid and mercuric sulfate) and does not react with *o*-phenylenediamine under conditions (30°) under which 4-cyano-1,2-naphthoquinone yields the quinoxaline[13]; no reaction was observed at 60°. When V is heated with hydrochloric acid followed by the action of alkali, no ammonia is produced. V gives an almost colorless diacetyl derivative.

The orange color of 1,2-dihydroxy-3-aceto-4-cyanonaphthalene is not incompatible with the structure proposed, since 1,2-dihydroxy-3-acetobenzene forms dark yellow crystals[11] and 2-hydroxy-3-benzoylnaphthalene is yellowish-orange.[14] The color of these substances may be due to the contribution of structures of *o*-quinonoid character (compare VI). In conformity with this theory is the fact that the "quinonoid color" disappears on acetylation. The diacetyl derivative of 1,2-dihydroxy-3-acetobenzene is colorless[11] and the diacetyl derivative of V is also practically colorless.



VI

The value of the reactions according to scheme C lies in the fact that 1,2-dihydroxy-3-acylnaphthalenes now are easily accessible, which was not previously the case.

Experimental

General Considerations.—The benzene used for the photochemical experiments was thiophene free and dried over sodium. The photochemical reactions were carried out in a Schlenk tube[2,15] (Monax or Pyrex glass) in carbon dioxide atmosphere. The titanium trichloride solution was about 15% and free from iron.

The photo experiments were carried out in direct sunlight. Parallel dark experiments were made in all cases and were negative.

Photochemical Reaction between 4-Cyano-1,2-naphthoquinone and (a) Stilbene.—One gram of stilbene and 1 g. of the quinone in 20 ml. of benzene was exposed to sunlight for a fortnight (February–March). The solution was filtered off from a minute quantity of a dark brown product and the filtrate was concentrated under reduced pressure, when a sticky substance was obtained. This residue was triturated with benzine (40–60°) and left in ice overnight, when it solidified. II was recrystallized from absolute alcohol in colorless crystals m.p. 202° (brown melt) (yield 1.3 g.). It gave no color with concentrated sulfuric acid.

Anal. Calcd. for $C_{25}H_{17}O_2N$: C, 82.6; H, 4.7; N, 3.9. Found: C, 82.9; H, 4.7; N, 4.0.

(b) Anisaldehyde.—One and thirty-six hundredths grams of anisaldehyde and 0.6 g. of the quinone in 20 ml. of benzene were exposed to sunlight for a week (March). The formation of a deposit was observed; this was filtered off and recrystallized from benzene and then from absolute alcohol in colorless crystals, m.p. 206–208° (yield 0.42 g.). IIIa or the corresponding IVa or IVb gave no color with concentrated sulfuric acid. When treated with sodium hydroxide (10%) it went very slowly into solution (yellow color). The low solubility in alkali also was observed when sodium hydroxide solution of less concentration was used. The solution of the substance in alcohol gave no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{19}H_{13}O_4N$: C, 71.5; H, 4.1; N, 4.4. Found: C, 71.0; H, 4.1; N, 4.4.

(c) *p*-Nitrobenzaldehyde.—One and one-half grams of the aldehyde and 0.6 g. of the quinone were dissolved in 20 ml. of benzene and exposed to sunlight for one week (September). The brown deposit which appeared was filtered off and recrystallized from dilute acetone in bright yellow crystals, m.p. about 243° dec., yield 0.9 g. IIIb or the corresponding IVa or IVb gave a yellow color with concentrated sulfuric acid. It was insoluble in concentrated and dilute alkali but turned orange after some time when suspended in concentrated alkali.

Anal. Calcd. for $C_{18}H_{10}O_5N_2$: C, 64.7; H, 3.0; N, 8.4. Found: C, 65.0; H, 3.1; N, 8.4.

(d) Cinnamaldehyde.—Forty-four hundredths gram of the aldehyde and 0.6 g. of the quinone were dissolved in 20 ml. of benzene and exposed to sunlight for one week (March). The light brown crystalline deposit which appeared was filtered off and recrystallized from dilute ethyl alcohol in colorless crystals, m.p. 188° (brown melt), yield 0.4 g. IIIc or the corresponding IVa or IVb gave no color with concentrated sulfuric acid and was difficultly soluble in it. When a drop of concentrated nitric acid was added to the sulfuric acid suspension, the substance went into solution giving a strong orange-red color. The methyl alcoholic solution gave no color with titanic chloride. When treated with sodium hydroxide (10%), the substance went slowly into solution (deep yellow color).

Anal. Calcd. for $C_{20}H_{13}O_3N$: C, 76.2; H, 4.1; N, 4.4. Found: C, 76.3; H, 4.2; N, 4.6.

1,2-Dihydroxy-3-aceto-4-cyanonaphthalene (V).—Forty-four hundredths gram of acetaldehyde and 0.6 g. of 4-cyano-1,2-naphthoquinone (I) in 20 ml. of benzene were ex-

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[10] H. Klinger and W. Kolvenbach, *Ber.*, **31**, 1214 (1898).

[11] 1,2-Dihydroxy-3-acetobenzene in alcohol gives also a green color with ferric chloride (H. v. Krannichfeldt, *Ber.*, **46**, 4017, 4018 (1913)).

[12] Compare Paul Karrer, "Organic Chemistry," Fourth English Edition, Elsevier Publ. Co., Inc., New York, N. Y., p. 435.

[13] W. Bradley and R. Robinson, *J. Chem. Soc.*, 1484 (1934).

[14] R. Lesser, E. Kranepuhl and G. Gad, *Ber.*, **58**, 2122 (1925).

[15] Compare J. Houben, "Die Methoden der Organischen Chemie," second edition, Vol. 4, Georg Thieme, Leipzig, 1924, p. 960.

posed to sunlight for four days (March). The yellowish-brown deposit formed was filtered off and recrystallized from benzene in orange crystals, m.p. about 228° dec. (dark brown melt), yield 0.3 g. The compound gave green color with concentrated sulfuric acid. It was difficultly soluble in glacial acetic acid but went easily into sodium hydroxide solution (10%) and in sodium carbonate solution at room temperature (red color) and was recovered unchanged from the latter solution by acidification. V gave in alcoholic solution, a deep green color with ferric chloride, which on addition of small quantities of aqueous ammonia or aqueous sodium carbonate solution turned reddish-brown. V gave a deep red color with titanic chloride and V sublimes in vacuum.

Anal. Calcd. for $C_{13}H_9O_3N$: C, 68.7; H, 3.9; N, 6.2; active H, 0.9 (for 2 H). Found: C, 68.8; H, 3.9; N, 6.1; active H, 1.1.

Oxidation of V to Phthalic Anhydride.—Five-tenths gram of V, 0.3 g. of mercuric sulfate and 4 ml. of concentrated sulfuric acid were placed in a glass retort (100-ml. capacity). The mixture was then heated in a metal-bath for 10 minutes at 250° (bath temperature), then for 50 minutes at 300–310° (bath temperature), when colorless needles were observed on the colder part of the retort tube. The crystals were scratched out of the tube and sublimed to give the characteristic needles of phthalic anhydride (m.p. and mixed m.p. determination and positive fluorescein test).

Action of Hydrochloric Acid on V.—One-tenth gram of V and 10 ml. of dilute hydrochloric acid (1:1) were refluxed for 15 minutes. The mixture was allowed to cool and made alkaline with sodium hydroxide in presence of ice, when no evolution of ammonia was observed (HCl test).

Action of *o*-Phenylenediamine on V.—Fifteen-hundredths gram of V and 0.1 g. of *o*-phenylenediamine were dissolved in the necessary amount of glacial acetic acid at 30° and maintained at this temperature for a half-hour. The mixture then was poured into ice-cold water (600 ml.) and left to stand for one hour. The orange deposit formed was filtered off and proved to be V; the m.p. was undepressed on admixture with an authentic specimen; both samples gave the same ferric chloride reaction (green), the same titanic chloride reaction (deep red), the same color with aqueous sodium carbonate solution and the same shape and color of crystals (from benzene).

The same experiment was carried out at 60° and similar results were obtained.

1,2-Diacetoxy-3-aceto-4-cyanonaphthalene.—Two-tenths gram of V and 6 ml. of acetic anhydride were refluxed for one hour, poured on ice and left overnight. The deposit formed was filtered off and recrystallized from methyl alcohol in almost colorless crystals, m.p. 160° (deep reddish-brown melt), yield almost quantitative, not soluble in sodium hydroxide solution (10%) but soluble in alcohol giving a yellowish solution.

Anal. Calcd. for $C_{17}H_{13}O_5N$: C, 65.6; H, 4.2; N, 4.5. Found: C, 65.6; H, 4.3; N, 4.7.

1,2-Dihydroxy-3-propiono-4-cyanonaphthalene (V replace $COCH_3$ by COC_2H_5).—One gram of propionaldehyde and 1 g. of I in 30 ml. of benzene were exposed to sunlight for a fortnight (May–June). There was no deposit; the solution was concentrated under reduced pressure and cooled in ice. The orange deposit formed was filtered off and recrystallized from benzene in orange crystals, m.p. 168°, yield 0.22 g. The substance gave a green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_{11}O_3N$: C, 69.7; H, 4.6; N, 5.8; mol. wt., 241. Found: C, 69.6; H, 4.9; N, 5.6; mol. wt. (Rast), 229.

1,2-Dihydroxy-4-cyanonaphthalene from 4-Cyano-1,2-naphthoquinone.—Five-tenths gram of 4-cyano-1,2-naphthoquinone was powdered and suspended in 5 ml. of alcohol. A saturated solution of sodium hydrosulfite ($Na_2S_2O_4$) (room temperature) was added dropwise with shaking. Addition was continued till the color became very faint, when a pale brown deposit separated out. A small volume of water was added and the mixture warmed till the solid dissolved; it was filtered while hot and left to cool. The product that separated was filtered and recrystallized from dilute alcohol in colorless crystals, m.p. 208° (yield almost quantitative), undepressed on admixture with an authentic specimen.[13]

1,2-Diacetoxy-4-cyanonaphthalene.—Two-tenths gram of 1,2-dihydroxy-4-cyanonaphthalene and 3 ml. of acetic anhydride were refluxed for one hour, poured on ice and left for a few hours. The product obtained was triturated well, filtered off and recrystallized from methyl alcohol in colorless crystals, m.p. 152° (yield almost quantitative). It gave no color with concentrated sulfuric acid and was insoluble in sodium hydroxide solution (10%).

Anal Calcd. for $C_{15}H_{11}O_4N$: C, 66.9; H, 4.1; N, 5.2; acetyl group, 32.0 (for 2). Found: C, 67.0; H, 4.2; N, 5.4; acetyl group, 31.8.

Hydrolysis of 1,2-Diacetoxy-4-cyanonaphthalene.—One-tenth gram of 1,2-diacetoxy-4-cyanonaphthalene, 6 ml. of concentrated hydrochloric acid and 4 ml. of ethyl alcohol were refluxed for three hr. on a sand-bath, cooled and diluted with water. The colorless crystals formed (yield 0.05 g.) were filtered off and proved to be 1,2-dihydroxy-4-cyanonaphthalene by m.p. and mixed m.p. determinations. Both samples gave the same reaction with ferric chloride (green color).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Structure of Anthracene Photodimers

BY FREDERICK D. GREENE, S. LESLIE MISROCK AND JAMES R. WOLFE, JR.

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The products resulting from the irradiation by sunlight of several 9-substituted anthracene derivatives (formyl, carbomethoxy, hydroxymethyl) have been shown to be dimers composed of two anthracene units bonded together at the 9,9'- and 10,10'-positions. The head-to-head structure I for these products has been established by the unambiguous synthesis of a compound possessing structure I *via* the intramolecular cyclization of 9-anthroic anhydride.

Introduction

The conversion of anthracene and anthracene derivatives to higher melting compounds by the action of sunlight has been known since 1866 when Fritzsche isolated dianthracene from irradiation of a benzene solution of anthracene.[1] Many other photomerides have been reported, derived from anthracenes substituted at the 1-position (methyl,[2] chloro,[2] carboxy[3]), the 2-position (methyl,[4] carboxy[3]), the 1,4-positions (chloromethyl[2]), the 1,9-positions (chlorobromo[2]) and the 9-position (bromo,[2,5] carboxy,[3] methyl,[6] ethyl,[6] formyl[7] and

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(1) J. Fritzsche, *J. prakt. Chem.*, **101**, 333 (1867).

(2) O. Fischer and H. Ziegler, *ibid.*, [2] **86**, 289 (1912).

(3) F. Weigert and L. Kummerer, *Chem. Ber.*, **47**, 898 (1914).

(4) W. R. Orndorff and H. A. Megraw, *Am. Chem. J.*, **22**, 152 (1899).

(5) H. Meyer and A. Eckert, *Monatsh.*, **39**, 241 (1918).

(6) A. Willemart, *Compt. rend.*, **205**, 993 (1937).

(7) P. D. Bartlett and F. D. Greene, THIS JOURNAL, **76**, 1088 (1954).