and the solid (2 g.) filtered off and washed successively with pyridine, benzene and ether. Crystallization from 1-methylnaphthalene gave light orange plates of heptaphene, m.p. 473–474°. In organic solvents it had a green fluorescence and dissolved to give a violet-red solution in concentrated sulfuric acid. When the pyridine mother liquor from the above filtration was added to water, a precipitate formed which after being washed and sublimed *in vacuo* gave additional heptaphene (1.5 g.).

Anal. Calcd. for $C_{30}H_{18}$: C, 95.20; H, 4.80. Found: C, 95.04; H, 4.98.

Maleic Anhydride Adduct (IV).—Heptaphene (0.1 g.) and excess maleic anhyride were heated under reflux in xylene (20 ml.) until the solution became colorless. Concentration of the xylene gave colorless crystals, m.p. 292–296° dec., of the dianhydride (IV).

Anal. Calcd. for $C_{38}H_{22}O_6$: C, 79.44; H, 3.86. Found: C, 78.71; H, 3.77.

Ring Closure and Reduction of the Isomeric Acids (B).—Treatment of the mixed acids (B) with sulfuric acid, as above, gave a dark greenish-yellow product which was reduced with zinc dust, pyridine and acetic acid. When the pyridine solution was poured into water, a precipitate formed which was sublimed to give a reddish-orange mixture of hydrocarbons. No separation of the mixture could be achieved by crystallization and the very low solubility of the hydrocarbons made complete chromatographic separation difficult. Elution with benzene from alumina, gave an initially colorless band, fluorescing blue in ultraviolet light, which yielded a small quantity of yellow plates, m.p. 485–487°; these showed no depression of the melting point when mixed with a sample of 2,3,8,9-dibenzopicene (V) obtained as below. All other fractions taken from the column were mixtures of the three hydrocarbons. The anthracenotetracene tended to oxidize during the long period required to develop the chromatogram.

Dibenzoylphenanthrene.—Powdered aluminum chloride (22 g.) was added to a paste of benzoyl chloride (23 g.) and phenanthrene (10 g.) at room temperature. The mixture was heated on a steam-bath for 30 minutes. After decomposition, the product was washed with hot dilute acetic acid, hot ammonia solution and water. A small quantity of ether caused the plastic solid material to crystallize. Crystallization from alcohol gave colorless silky needles, m.p. 183–184°, of a dibenzoylphenanthrene.

Anal. Calcd. for $C_{28}H_{18}O_2$: C, 87.02; H, 4.70. Found: C, 86.91; H, 5.07.

2,3,8,9-Dibenzopicene.—A mixture of di-*o*-toluoylphenanthrenes was prepared in a similar manner to dibenzoylphenanthrene. The solid product from the decomposition of the reaction mixture was dissolved in xylene. The xylene solution was extracted with hot dilute hydrochloric acid, hot ammonia solution and water. The xylene was distilled off and the residue of crude diketones pyrolyzed at 400–420° until the evolution of water ceased. Sublimation *in vacuo* of the reaction product yielded a mixture of hydrocarbons which were identified as heptaphene, dibenzopicene and anthracenotetracene by visual spectroscopic examination. The mixture was dissolved in 1-methylnaphthalene, and small portions of maleic anhydride were added to the hot solution until the bands of heptaphene and anthracenotetracene disappeared. Crystallization from the solution yielded pale yellow plates, m.p. 489–490°, of 2,3,8,9-dibenzopicene (V). The crystals dissolved, on being heated, in concentrated sulfuric acid to give a yellowish-green color which changed to olive green. In organic solvents the hydrocarbon showed a strong blue fluorescence.

Anal. Calcd. for $C_{30}H_{18}$: C, 95.20; H, 4.80. Found: C, 95.02; H, 4.99.

2,3,8,9-Dibenzopicene-1,4,7,10-diquinone.—Finely powdered dibenzopicene was boiled with excess chromium trioxide in acetic acid. Addition of water yielded a precipitate which was sublimed *in vacuo* and crystallized from nitrobenzene to give yellow prisms, m.p. 416–417°, of the diquinone. It gave a brown solution in concentrated sulfuric acid and formed a red vat with alkaline sodium dithionite solution. It did not form a phenazine derivative with *o*-phenylenediamine.

Anal. Calcd. for $C_{30}H_{14}O_4$: C, 82.18; H, 3.22. Found: C, 82.47; H, 3.44.

Acknowledgment.—Microanalyses were performed by Mr. J. M. L. Cameron and Miss M. W. Christie of this Department.

GLASGOW, SCOTLAND

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW]

Aromatic Hydrocarbons. LXVIII. Triangulene Derivatives. Part II[1]

BY E. CLAR AND D. G. STEWART

RECEIVED OCTOBER 29, 1953

The syntheses of triangulenequinone and dodecahydrotriangulene from di-*p*-xylylphthalide and di-*m*-xylylphthalide are described.

Weiss, Spitzer and Melzer[2] have shown that dixylylphthalides can be prepared by adding powdered aluminum chloride to *sym*-phthaloyl chloride and a xylene in carbon disulfide. As this method gives a considerable amount of *o*-diaroylbenzene as by-product the yield of phthalide is low, 50 and 25% from *p*- and *m*-xylene, respectively. Fuson, Speck and Hatchard[3] who demonstrated that *o*-diaroylbenzenes are readily formed under such conditions obtained an 81% yield of this compound from mesitylene. We have found that the dixylylphthalides can be prepared free from these by-products by treating a xylene with a preformed complex of *as*-phthaloyl chloride and aluminum chloride.

Two stage oxidation of the phthalides (I, R = H, R = CH_3 and R′ = CH_3 R′ = H), first with boiling dilute nitric acid and then with either alkaline potassium permanganate solution or dilute nitric acid, resulted in a rearrangement which is analogous to that which occurs when di-*o*-tolylphthalide (I, R = R′ = H) is oxidized.[4] The resulting dispirans (II, R = R′ = H; R = H, R′ = CO_2H and R = CO_2H, R′ = H) on heating with copper powder at 350° gave a compound which was identical with the lactone III prepared by Scholl and Donat.[5]

To avoid the above rearrangement the phthalides I were reduced with zinc dust and ethanolic potassium hydroxide solution to the acids IV which on heating in a sodium chloride–zinc chloride melt condensed to the arylanthrones V. Two-stage

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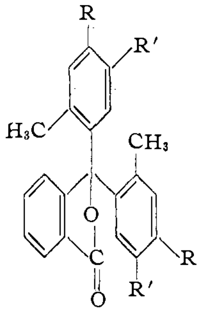
[1] Part I, THIS JOURNAL, **75**, 2667 (1953).

[2] R. Weiss, A. Spitzer and J. L. Melzer, *Monatsh.*, **47**, 306 (1926).

[3] R. C. Fuson, S. B. Speck and W. R. Hatchard, *J. Org. Chem.*, **10**, 55 (1945).

[4] E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951).

[5] R. Scholl and J. Donat, *Ann.*, **512**, 1 (1934).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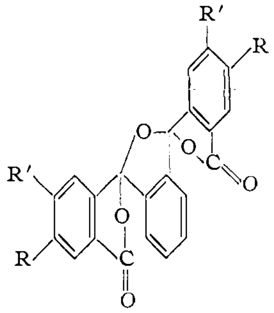
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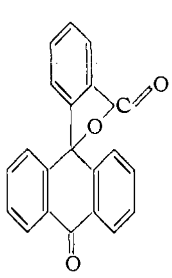
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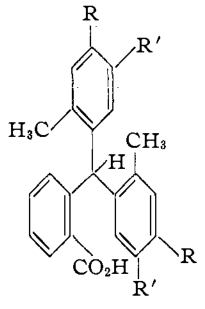
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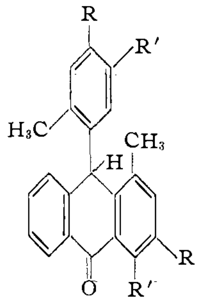
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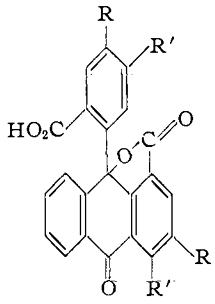
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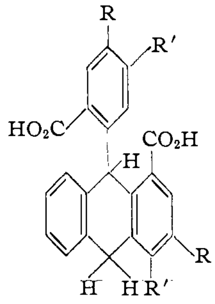
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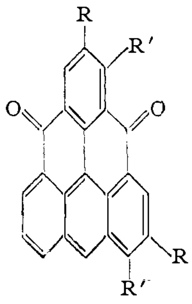
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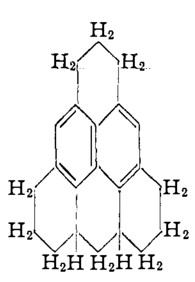
IX

oxidation of V gave the tetracarboxylic acid lactones VI which were reduced with zinc dust and sodium hydroxide solution to the dihydroanthracene derivatives VII. The latter gave, on heating with concentrated sulfuric acid, the triangulenequinone dicarboxylic acids VIII from which triangulene-4,8-quinone (VIII, R = R′ = H) was obtained by decarboxylation with copper powder.

Reduction of the dicarboxylic acids VIII with hydriodic acid and red phosphorus and decarboxylation of the hydrogenated product with soda lime gave a hydrocarbon which was identical with dodecahydrotriangulene (IX) prepared by Clar and Stewart.[1]

Experimental[6]

Di-*p*-xylylphthalide (I, R = H, R′ = CH_3).—Powdered aluminum chloride (93 g.) and *sym*-phthaloyl chloride (93 g.) were heated at 100° for 10 hours with intermittent shaking. The resulting complex was cooled and powdered, and then slowly added to *p*-xylene (200 g.); the reaction mixture was cooled to keep the temperature below 20°. After 2.5 hours, the dark red product was heated to 60° for 5 minutes and when cold, was decomposed with dilute hydrochloric acid and crushed ice. The organic layer was separated, washed with hot water and the excess xylene removed by steam distillation. Extraction of the solid residue with dilute sodium hydroxide solution and acidification of the alkaline filtrate with hydrochloric acid yielded 26 g. of 2-(2′,5′-dimethylbenzoyl)-benzoic acid. The phthalide was crystallized from ethyl alcohol or acetic acid in colorless prisms (116 g., 74%), m.p. 178–179° (lit.[2] m.p. 180–184°), which gave a red solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 84.33; H, 6.53.

Di-*m*-xylylphthalide (I, R = CH_3, R′ = H).—The complex, formed as above from *sym*-phthaloyl chloride (101 g.) and aluminum chloride (101 g.), was added to *m*-xylene (200 g.) and the mixture kept at room temperature for 30 minutes; 2-(2′,4′-dimethylbenzoyl)-benzoic acid (28 g.) and di-*m*-xylylphthalide were isolated according to the above procedure. The phthalide, crystallized from ethyl alcohol or acetic acid in colorless prisms (123 g., 72%), m.p. 167–168° (lit.[2] m.p. 159–162°), gave a red solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 84.10; H, 6.30.

1,3-Dihydroisobenzofuran-1,3-bis-spiro-(3-phthalide-5-carboxylic Acid) (II, R = H, R′ = CO_2H).—Di-*p*-xylylphthalide (50 g.) mixed with nitrobenzene (10 cc.) was boiled in 20% nitric acid (800 cc.) for 3 days. When the nitrobenzene was distilled off, a yellow solid was obtained which was extracted with dilute sodium hydroxide solution from unoxidized material (1 g.). Acidification of the alkaline filtrate gave a precipitate (50 g.) which was isolated and washed; portions were further oxidized by the following two methods: (a) powdered potassium permanganate was added to a boiling sodium carbonate solution of the partially oxidized material (25 g.) until the permanganate color was stable for seven minutes. After the excess permanganate had been destroyed with ethyl alcohol, and the manganese dioxide filtered off, acidification with hydrochloric acid gave a white precipitate (25 g.); (b) the partially oxidized material (3 g.) was heated under pressure at 200° in 20% nitric acid; after 9 hours the precipitate (3 g.) was filtered off and washed with water. Crystallization of these oxidized products from acetic acid gave colorless crystals (6 and 1 g.) of the dispiran (II) which softened at 270° and gave a clear melt at 300°. The compound dissolved in concentrated sulfuric acid to give a colorless solution which turned green on warming.

Anal. Calcd. for $C_{24}H_{12}O_9$: C, 64.87; H, 2.72. Found: C, 64.59; H, 2.78.

Dilution of the acetic acid mother liquors with water gave a viscous oil (18 and 1.8 g.) which could not be crystallized. In concentrated sulfuric acid it gave a colorless solution which turned deep blue on heating to 150° with copper powder.

1,3-Dihydroisobenzofuran-1,3-bis-spiro-(3-phthalide-6-carboxylic Acid) (II, R = CO_2H, R′ = H).—Di-*m*-xylylphthalide (50 g.) was treated as described above. The partially oxidized material (42 and 6 g.) was oxidized by methods (a) and (b) and then crystallized from acetic acid to yield colorless crystals (10 and 2 g., respectively). Recrystallization from nitrobenzene gave colorless needles, m.p. 357–358°, of the dispiran which gave a colorless solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{12}O_9$: C, 64.87; H, 2.72. Found: C, 64.61; H, 2.87.

Dilution of the mother liquors with water gave an oil (30 and 4 g.) which could not be crystallized. It gave a deep blue solution when heated to 150° in concentrated sulfuric acid with copper powder.

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[6] All melting points are uncorrected and were taken in evacuated capillaries.

9-*o*-Carboxyphenyloxanthranol Lactone (III).—Each of the three dispirans (II, R = R' = H; R = H, R' = CO_2H; R = CO_2H, R' = H) (1 g.) was ground with copper powder and the mixtures heated at 350° until a quiet melt was obtained. Sublimation under reduced pressure yielded large prisms, which crystallized from ethyl alcohol in colorless prisms, m.p. 232–233°. The compound was identified as the lactone (III) (lit.[5] m.p. 232–234°); it gave a yellow-green solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{21}H_{12}O_3$: C, 80.75; H, 3.88. Found: C, 80.64; H, 4.20.

2-(Di-*p*-xylylmethyl)-benzoic Acid (IV, R = H, R' = CH_3).—A solution of di-*p*-xylylphthalide (50 g.) in 20% ethanolic potassium hydroxide (450 cc.) was refluxed for 48 hours, while zinc dust (100 g.) was added in portions at regular intervals. After dilution with water (500 ml.), the hot solution was filtered, boiled to remove ethyl alcohol and acidified with concentrated hydrochloric acid. A precipitate was obtained which crystallized from acetic acid or ethyl alcohol to give colorless needles (48 g.), m.p. 233–234° (lit.[2] m.p. 235–236°), of the acid IV. The colorless solution of the compound in concentrated sulfuric acid turned green on heating.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.68; H, 7.02. Found: C, 83.56; H, 7.03.

2-(Di-*m*-xylylmethyl)-benzoic Acid (IV, R = CH_3, R' = H).—Following the above procedure, di-*m*-xylylphthalide (50 g.) was reduced to the corresponding acid IV, which crystallized from acetic acid or benzene in clusters of colorless needles (45 g.), m.p. 230–232° (lit.[2] m.p. 234–240°). The acid gave a colorless solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.68; H, 7.02. Found: C, 83.15; H, 7.13.

1,4-Dimethyl-9-*p*-xylylanthrone (V, R = H; R' = CH_3).—The acid IV (45 g.) from di-*p*-xylylphthalide, zinc chloride (45 g.) and sodium chloride (9 g.) were ground together and heated at 220° for 15 minutes with constant stirring. When cold, the dark green melt was decomposed with dilute hydrochloric acid, washed and extracted with dilute ammonia. Crystallization of the yellow-orange product from acetic acid gave colorless leaflets (41 g.), m.p. 190–191°, of the anthrone which gave a yellow solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.30; H, 6.80. Found: C, 88.53; H, 7.09.

1,3-Dimethyl-9-*m*-xylylanthrone (V, R = CH_3, R' = H).—Condensation of the acid IV (43 g.) as described above gave a product which crystallized from acetic acid to give prisms (40 g.), m.p. 166–168°, of the anthrone (V). The compound dissolved in concentrated sulfuric acid to give a yellow solution which changed to green on heating.

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.30; H, 6.80. Found: C, 87.96; H, 6.59.

9-Phenyloxanthranol-1,4,2',5'-tetracarboxylic Acid Lactone (VI, R = H, R' = CO_2H).—The anthrone (V, R = H, R' = CH_3) (40 g.) and nitrobenzene (8 ml.) were boiled with 20% nitric acid (450 ml.) for 48 hours. After removal of the nitrobenzene by steam distillation, the product was filtered off, dissolved in dilute sodium hydroxide solution and treated with powdered potassium permanganate until the permanganate color was stable to 10 minutes' boiling. Acidification of the hot filtrate (from the separated manganese dioxide) gave an oily precipitate which solidified after boiling for several minutes. The product crystallized from nitrobenzene containing a little ethyl alcohol to yield the lactone (VI) as colorless crystals (38 g.) which decomposed giving a violet-blue sublimate at 330–340°. The compound dissolved in concentrated sulfuric acid to give a pale yellow solution which did not change on heating, but turned deep blue on the addition of copper powder at 150°

Anal. Calcd. for $C_{24}H_{12}O_9$: C, 64.87; H, 2.72. Found C, 64.54; H, 2.91.

9-Phenyloxanthranol-1,3,2',4'-tetracarboxylic Acid Lactone (VI, R = CO_2H, R' = H).—The anthrone (V, R = CH_3, R' = H) (35 g.) was oxidized as above. The product crystallized from nitrobenzene containing a little acetic acid to yield the lactone IV as colorless needles (34 g.) which decomposed giving a violet-blue sublimate at 335–340°. The compound gave a deep blue solution when heated to 150° in concentrated sulfuric acid with copper powder.

Anal. Calcd. for $C_{24}H_{12}O_9$: C, 64.87; H, 2.72. Found: C, 64.74; H, 2.98.

9,10-Dihydro-9-phenylanthracene-1,4,2',5'-tetracarboxylic Acid (VII, R = H, R' = CO_2H).—The lactone (VI, R = H, R' = CO_2H) (35 g.) was dissolved in boiling 15% sodium hydroxide solution, covered with a thin layer of octyl alcohol, and zinc dust was added in portions at regular intervals. After the mixture had been refluxed for 24 hours, the octyl alcohol was distilled off, and the non-fluorescent solution was filtered from excess zinc. Acidification of the filtrate with hydrochloric acid gave an oily precipitate which solidified after boiling for some time; crystallization from nitrobenzene containing a little ethyl alcohol gave colorless leaflets (34 g.) of the tetracarboxylic acid (VII) which decomposed giving a red melt and sublimate at 340–345°.

Anal. Calcd. for $C_{24}H_{16}O_8$: C, 66.66; H, 3.73. Found: C, 66.62; H, 3.41.

9,10-Dihydro-9-phenylanthracene-1,3,2',4'-tetracarboxylic Acid (VII, R = CO_2H, R' = H).—The lactone (VI, R = CO_2H, R' = H) (30 g.) was reduced as described above. The product (30 g.) crystallized from concentrated hydrochloric acid in colorless crystals, which were found to contain water of crystallization; all attempts to find another solvent were unsuccessful. The hydrated acid softened at 240°, and decomposed giving a red melt and sublimate at 310°.

Anal. Calcd. for $C_{24}H_{16}O_8 \cdot 3H_2O$: C, 59.26; H, 4.56. Found: C, 60.05; H, 4.83.

Triangulene-4,8-quinone-7,11-dicarboxylic Acid (VIII, R = H, R' = CO_2H).—A solution of the tetracarboxylic acid (VII, R = H, R' = CO_2H) (32 g.) and *m*-nitrobenzenesulfonic acid (sodium salt) (20 g.) in concentrated sulfuric acid (300 ml.) was heated at 110–120° for 15 minutes; the initially pale yellow solution changed rapidly to red-violet; an intermediate green stage was observed. The hot solution was diluted slowly with ice and the temperature maintained at 110°, until a dark red solid began to crystallize. After cooling and further dilution with cold water, the crystalline precipitate was filtered off and washed with hot water until free from sulfuric acid and sulfonated material. After extraction with hot acetic acid, the product was crystallized from *o*-toluidine (prolonged heating of the solution being avoided) to give dark red crystals (20 g.) of the acid VII which did not melt below 400°. The violet-red solution of the compound in alkali changed to green on the addition of sodium dithionite.

Anal. Calcd. for $C_{24}H_{10}O_6$: C, 73.10; H, 2.56. Found: C, 72.75; H, 2.75.

Triangulene-4,8-quinone-6,10-dicarboxylic Acid (VII, R = CO_2H, R' = H).—The tetracarboxylic acid (VII, R = CO_2H, R' = H) (25 g.) was condensed with sulfuric acid as above. Due to its insolubility in organic solvents, the product (17 g.) could not be crystallized; therefore, it was extracted with nitrobenzene, acetic acid and acetone, dissolved in dilute ammonia, filtered and precipitated with concentrated hydrochloric acid. After it was filtered and washed, the compound was dried in a vacuum at 200°, but it could not be freed from water. The acid VIII, which did not melt below 400°, gave a green solution in alkaline sodium dithionite.

Anal. Calcd. for $C_{24}H_{10}O_6 \cdot 2H_2O$: C, 66.98; H, 3.28. Found: C, 66.87; H, 3.08.

7,11-Dicarbomethoxytriangulene-4,8-quinone (VIII, R = H, R' = CO_2Me).—The dark red silver salt of the dicarboxylic acid (VIII, R = H, R' = CO_2H) (1 g.), which was prepared by the addition of silver nitrate solution to a hot neutral solution of the ammonium salt, was finely powdered and refluxed with methyl iodide for 48 hours. After cooling, the solid was filtered off and extracted with dilute sodium carbonate solution to remove unesterified material. The ester crystallized from trichlorobenzene in dark red needles (0.6 g.), m.p. 289–290°, which gave a violet-red solution in concentrated sulfuric acid and a green solution in boiling alkaline sodium dithionite.

Anal. Calcd. for $C_{26}H_{14}O_6$: C, 73.93; H, 3.34. Found: C, 73.61; H, 3.53.

6,10-Dicarbomethoxytriangulene-4,8-quinone (VIII, R = CO_2Me, R' = H).—This compound was prepared from the dicarboxylic acid (VIII, R = CO_2H, R' = H) (1 g.) by the above method. Crystallization from trichlorobenzene gave dark red needles (0.55 g.) of the ester, which did not melt below 360°.

Anal. Calcd. for $C_{26}H_{14}O_6$: C, 73.93; H, 3.34. Found: C, 73.82; H, 3.47.

Triangulene-4,8-quinone (VIII, R = R′ = H).—The dicarboxylic acids (VIII) (1 g.) were ground separately with copper powder (3 g.), and the mixtures heated under reduced pressure (10^{-4} mm.) at 260–270° for 10 hours. In both cases, a sublimate of dark red needles was obtained, which on crystallization from nitrobenzene yielded needles (0.3 and 0.25 g., respectively), whose properties were identical with those of a sample of triangulene-4,8-quinone prepared as described by Clar and Stewart.[1]

Dodecahydrotriangulene (IX).—Each of the dicarboxylic acids (VIII) (2 g.) mixed with red phosphorus (2 g.), potassium iodide (1 g.) and 55% hydriodic acid (20 ml.) was heated under pressure at 210° for 10 hours. When cold, the reaction mixtures were diluted with water and the precipitates filtered off, dried and ground with soda lime (4 g.). On heating under reduced pressure a clear, greenish fluorescent oil distilled which gave a white solid on cooling. Chromatographic purification (alumina) with petroleum ether (b.p. 40–60°) as eluant gave a colorless, non-fluorescent solution, which on concentration and recrystallization from methyl alcohol yielded clusters of colorless silky needles, (0.6 and 0.5 g., respectively), m.p. 162–163°. When this compound was admixed with an authentic sample of dodecahydrotriangulene, no depression in melting point was obtained.

GLASGOW, SCOTLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

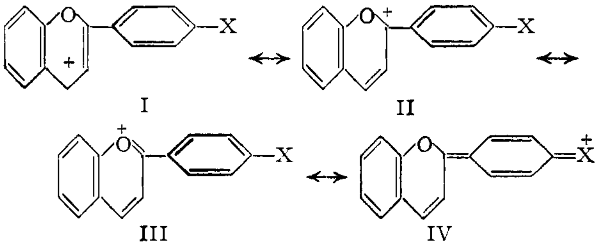
Basic Dissociation Constants of Some Substituted Flavones[1]

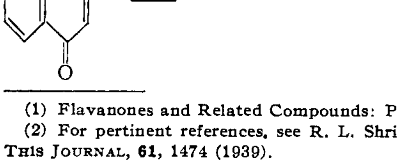
BY CHARLOTTE T. DAVIS AND T. A. GEISSMAN

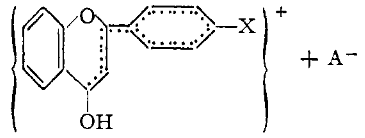
RECEIVED FEBRUARY 16, 1954

The pK_a values for five selected flavones have been determined by analyzing their absorption spectra in sulfuric acid solutions. Flavones are moderately strong oxygen bases, having pK_a values ranging from −0.8 for 4′-methoxyflavone to −2.45 for 2′,3,4′,6′-tetramethylflavone; these can be compared with the pK_a −6.0 for acetophenone. The importance of the chromone ring and the contribution of the 2-aryl group in stabilizing the protonated forms of these bases are shown by these data.

Early discussions of the structure of pyrilium and flavylium salts, centering about the question of the location of the positive charge,[2] can be resolved today into questions of the relative contribution to a resonance hybrid of such forms as the following (I–IV),[3] and the effects of substituents upon such a system. The importance of contributions corresponding to IV when the substituent X is methoxyl or hydroxyl is qualitatively evident from the pronounced bathochromic effects of such substituents upon the absorption maxima of flavones.[4] It is, however, difficult to interpret absorption spectra quantitatively in terms of the role of substituents in increasing the relative importance of quinonoid contributions in the 2-aryl group. A measure of the stabilizing effect of substituents (such as X in IV) upon forms such as IV is to be found in the equilibrium constant of the reaction







Effective participation of the 4′-substituent in distribution of the positive charge should affect the equilibrium constant measurably. Since such participation of a 4′-substituent requires a degree of coplanarity of the 2-aryl group with the benzopyrilium ring system, the introduction of 2′- and 6′-substituents represents another means of altering this equilibrium constant. In the present study five flavones have been examined with respect to the dependence of their basic strength upon their structures.

It has long been known that many pyrones, chromones and flavones form isolable salts with mineral acids,[5–7] but only in the cases of a limited number of substituted γ-pyrones[8,9] have the dissociation constants of bases of these classes been measured. Weak bases of other kinds have been extensively studied, chiefly by Hammett and his collaborators,[10] and their data on the acidity, expressed as the acidity function H_0, of sulfuric acid solutions have been used in the present work.

The use of absorption spectra in sulfuric and other strong acids in the determination of the basic dissociation constants of very weak bases has been

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[1] Flavanones and Related Compounds: Paper IX.

[2] For pertinent references, see R. L. Shriner and R. B. Moffett, THIS JOURNAL, **61**, 1474 (1939).

[3] These structures are selected as illustrative; when other substituents are present (*e.g.*, a carbonyl group at position 4), other structures may be equally important.

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[6] H. Simonis, *Ber.*, **50**, 790 (1917).

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[10] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.