Anal. Calcd. for $C_{16}H_{13}N_3O_2$: N, 15.0. Found: N, 14.85.

XXIV was comparatively stable to 2% sodium hydroxide. Under the conditions described for the hydrolysis of XXa, the m. p. was only lowered to 190–195° dec.

1-Benzoyl-3-anilino-5-benzoyloxypyrazole, XXV.—A mixture of 5 g. of 3-anilino-5-pyrazolone, XVI,[1,4] and 4 g. of benzoyl chloride in 50 ml. of dioxane was stirred on the steam-bath overnight. After cooling, the solution was decanted from an oil, diluted with water (5 ml.) until cloudy, cooled, filtered, and the product recrystallized from 15 ml. of dioxane. 1 g. (13%) of short ivory needles; m. p. 132–134°.

Anal. Calcd. for $C_{23}H_{17}N_3O_3$: N, 10.97. Found: N, 10.94.

The oil formed in the reaction mixture, on trituration first with water and then methanol, gave 0.5 g. of unchanged 3-anilino-5-pyrazolone XVI.[17]

Film-strip Test.—A sample (about 0.005 g.) of the compound to be tested and an approximately equal weight of *p*-aminodimethylaniline hydrochloride are dissolved in 5 ml. of 3% sodium carbonate in a test-tube. A strip of exposed photographic film (*e. g.*, Kodalith) is immersed in the solution and the test-tube shaken occasionally until, within one to five minutes, a high density of silver is developed. The strip is then rinsed with running water for about one minute, and silver and silver halide are removed by shaking the strip in a mixture (5 ml. total) of equal parts of solutions 1 and 2, until the film is translucent. It is then washed in running water and inspected.

Solution 1: 25 g. of potassium ferricyanide, 5 g. of potassium bromide, 5 g. of sodium carbonate, water to make 1 liter. Solution 2: 200 g. of sodium thiosulfate, 5 g. of sodium carbonate, water to make 1 liter.

Summary

The acetylation and benzoylation of 3-phenyl-5-pyrazolone, I, and of 3-anilino-5-pyrazolone, XVI, were studied.

3-Phenyl-5-acetoxypyrazole, VI, 1-acetyl-3-acetoxy-5-phenylpyrazole, IX, 1-acetyl-3-hydroxy-5-phenylpyrazole, IV, 3-phenyl-5-benzoyloxypyrazole, X, 1-acetyl-3-phenyl-5-benzoyloxypyrazole, XI, 1-benzoyl-3-phenyl-5-benzoyloxypyrazole, XIV, 1-benzoyl-3-benzoyloxy-5-phenylpyrazole, XV, 1-acetyl-3-hydroxy-5-anilinopyrazole, XVII, 1-acetyl-3-anilino-5-pyrazolone, XXa, 1-acetyl-3-anilino-5-acetoxypyrazole, XXIa, 1-acetyl-3-acetoxy-5-anilinopyrazole, XXII, 3-anilino-5-benzoyloxypyrazole, XX, 1-benzoyl-3-anilino-5-pyrazolone, XXIV, and 1-benzoyl-3-anilino-5-benzoyloxypyrazole, XXV, were prepared as new compounds and their structures established.

Pure 1-acetyl-3-phenyl-5-pyrazolone, II, melts at 127°. The compound reported in the literature as melting at 121° is contaminated with VI. The diacetyl derivative of 3-phenyl-5-pyrazolone melting at 84° is not 1,2-diacetyl-3-phenyl-5-pyrazolone, VII, but 1-acetyl-3-phenyl-5-acetoxypyrazole, VIII.

A migration of acetyl from nitrogen to oxygen was found to occur when 1-acetyl-3-phenyl-5-pyrazolone, II, was treated with pyridine, yielding 3-phenyl-5-acetoxypyrazole, VI.

A migration of acyl from position 1 to position 2 was observed with several of the above-named pyrazoles.

The formation of dyes by color development of a photographic film is described as a test.

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[COMMUNICATION NO. 932 FROM THE KODAK RESEARCH LABORATORIES]

A New Synthesis of the Pentacene Ring System

BY C. F. H. ALLEN AND J. W. GATES, JR.

During the last decade an increasing interest has been shown in the chemistry of the linear polynuclear hydrocarbons. The substances are colored and show an unusual activity toward reagents, whereas their quinones are the starting materials for the preparation of many derivatives. The pentacene ring system has always been formed by essentially the same type of reaction, *i. e.*, a phthalic anhydride has been condensed with an aromatic ring system, followed by ring closure. Most of the syntheses are the work of Marschalk, although the one known longest is that of Mills,[1] who started with pyromellitic anhydride and benzene. Marschalk[2] devised improvements of a patent procedure[3] in which phthalic anhydride and leucoquinizarin were employed, so that this became an easier method for obtaining pentacene. He also described a less useful synthesis[4] from anthracene-2,3-dicarboxylic anhydride and hydroquinone.

During the course of our work with arylated

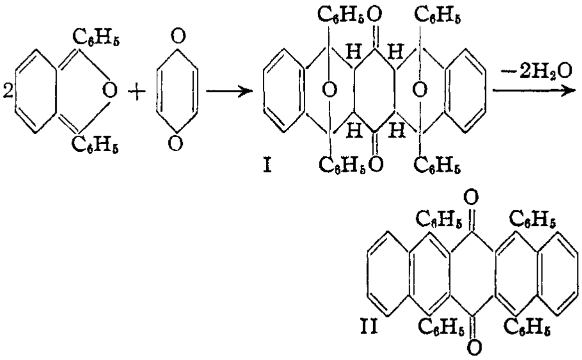
(1) Mills and Mills, *J. Chem. Soc.*, **101**, 2194 (1912).

(2) Marschalk, *Bull. soc. chim.*, [5] **4**, 1535 (1937); **5**, 156 (1938).

(3) German Patent 298,345 [*Frdl.*, **13**, 390 (1923)], ex. 6.

(4) Marschalk, *Bull. soc. chim.*, [5] **5**, 306 (1938); **6**, 1112 (1939).

isobenzofurans[5] it was found that two molecules of 1,3-diphenylisobenzofuran very easily added to one molecule of benzoquinone, giving the partially reduced, polyphenylated pentacenequinone I. The presence of the ring system was shown by its conversion to the known tetraphenylpentacenequinone II[6] by the action of concentrated sulfuric acid at room temperature. A similar addition was observed with 1,3-diphenyl-5,6-dimethylisobenzofuran. No attempt was made to isolate any of the 1,1-addition product (if present) described by Barnett.[7]



This new synthesis makes it possible to obtain symmetrical or unsymmetrical polyarylated pentacenes, which are only difficultly or not at all accessible in other ways. It also confirms the structure previously[6] assigned to II, which had been arrived at by an examination of the products of degradation. It is limited only by the nature of isobenzofurans available, but these are now relatively accessible substances.[8,9,10]

Experimental

5,7,12,14-Tetraphenyl-7,12,5,14-dioxido-5,5a,6a,7,12,12a,13a,14-octahydro-6,13-pentacenequinone I: A suspension of 5.4 g. of 1,3-diphenylisobenzofuran in 200 cc. of alcohol containing 1 g. of benzoquinone was refluxed for two hours, cooled, and the addition product filtered. It was recrystallized from chlorobenzene, from which it separates in rods, m. p. 197–198°.

Anal. Calcd. for $C_{46}H_{32}O_4$: C, 85.2; H, 4.9. Found: C, 84.9; H, 5.1.

The 2,3,9,10-tetramethyl derivative (rods) was obtained in a similar manner.

Anal. Calcd. for $C_{50}H_{40}O_4$: C, 85.2; H, 5.7. Found: C, 84.8; H, 6.0.

5,7,12,14-Tetraphenyl-6,13-pentacenequinone II resulted when 0.5 g. of the octahydroquinone I was dissolved in 5 cc. of concentrated sulfuric acid at −10° and allowed to stand for one hour at room temperature; after it had been decomposed by ice and after subsequent appropriate manipulation, the already known quinone was isolated in a yield of 0.2 g. after crystallization from pyridine. The melting point alone and on admixture with the known specimen on hand[6] was 397–398°.

Summary

A new synthesis of the pentacene ring system has been described. It consists in adding two molecules of an isobenzofuran to one molecule of benzoquinone.

A tetraphenylpentacenequinone, whose structure had been deduced by degradation, has been synthesized.

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(5) Allen and Gates, THIS JOURNAL, **65**, 1283 (1943).

(6) Allen and Bell, *ibid.*, **64**, 1253 (1942).

(7) Barnett, *J. Chem. Soc.*, 1326 (1935).

(8) Adams and Gold, THIS JOURNAL, **62**, 56 (1940).

(9) Allen and Gates, *ibid.*, **65**, 1230 (1943).

(10) Norton, "Diels-Alder Synthesis," *Chem. Rev.*, **31**, 474 (1942).

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[CONTRIBUTION FROM THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH, DIVISION OF ORGANIC CHEMISTRY]

The Preparation and Properties of the 7-Epimeric Cholestanediols-3(β),7

BY O. WINTERSTEINER AND MILDRED MOORE

The preparation of the 7-epimeric cholestanediols-3(β),7 and their esters was undertaken with two objectives in mind First, it seemed of interest to establish by comparison of the specific rotations their stereochemical relationship with other 7-epimeric steroids, especially with the corresponding unsaturated diols, the 7-hydroxycholesterols, which cannot be directly converted into the saturated diols.[1] Second, we needed 3-mono-esters of the saturated diols for the dehydration experiments which are described in the following paper.

The only previous reference to the preparation of a cholestanediol-3,7 we could find is in a paper by Marker and Rohrmann.[2] These authors obtained a diol melting at 166° by hydrogenation of 7-keto-cholesteryl acetate with platinum oxide in acetic acid and subsequent hydrolysis, or alternatively by reduction of 7-ketocholestanyl acetate with aluminum isopropylate. The product

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(1) Wintersteiner and Ruigh, THIS JOURNAL, **64**, 2453 (1942).

(2) Marker and Rohrmann, *ibid.*, **61**, 3022 (1939).