minutes at room temperature the solution was refluxed for 1 hour, then treated with sodium hydroxide solution (50 ml., 2 *N*) and extracted with ether. Chromatography separated the residue (2.0 g.) from evaporation of the ether into three fractions. Each of these was again chromatographed into two fractions which were suitably combined to give VII (1.05 g., 49%), m.p. 117–118°, and XIII (0.75 g., 31%), m.p. 108–109°.

9,10-Dimethyl-10,9-borazarophenanthrene (VII).—*Anal.* Calcd. for $C_{14}H_{14}NB$: C, 81.16; H, 6.76; N, 6.76; B, 5.31; mol. wt., 207. Found: C, 81.13; H, 6.57; N, 6.59; B, 5.50; mol. wt., 189.

9,9,10,10-Tetramethyl-9,10-dihydro-10,9-borazarophenanthrene (XIII): *Anal.* Calcd. for $C_{16}H_{20}NB$: C, 81.01; H, 8.44; N, 5.90; B, 4.64; mol. wt., 237. Found: C, 80.84; H, 8.67; N, 5.66; B, 4.74; mol. wt., 206.

Experiment 9 was carried out exactly as described for experiment 11. Separation of the product by chromatography gave VIII, m.p. 122.5–123.5°, and XIV, m.p. 224–226°.

9-Methyl-10-phenyl-10,9-borazarophenanthrene (VIII): *Anal.* Calcd. for $C_{19}H_{16}NB$: C, 84.76; H, 5.95; N, 5.20; B, 4.09; mol. wt., 269. Found: C, 84.79; H, 5.85; N, 5.32; B, 4.40; mol. wt., 243.

9,9-Dimethyl-10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XIV): *Anal.* Calcd. for $C_{26}H_{24}NB$: C, 86.43; H, 6.65; N, 3.88; B, 3.05; mol. wt., 361. Found: C, 86.69; H, 6.81; N, 3.91; B, 3.23; mol. wt., 339.

The Conversion of 10,10-Dimethyl-9,10-dihydro-10,9-borazarophenanthrene (XII) into 10-Methyl-10,9-borazarophenanthrene (II). Experiment 18.—A solution of methyllithium (10.7 m*M*) in ether (20 ml.) was added to one of XI (0.3 g., 1.4 m*M*) in ether (15 ml.). Gas was evolved and the solution turned yellow-green. After stirring for a few minutes the solution was poured into hydrochloric acid (30 ml., 2 *N*) and extracted with ether. Chromatography of the residue from evaporation of the ether gave II (0.2 g., 71%), m.p. 99–101°, mixed m.p. 101–102°. Elution of the column with ether gave starting material (0.07 g., 23%).

The reactions of B-methyl- and B-phenyl-borazarophenanthrenes with Grignard reagents were carried out in similar fashion to that described for experiment 7a.

Deboronation of 10,10-Diphenyl-9,10-dihydro-10,9-borazarophenanthrene (XII).—The B-diphenyl compound (0.5 g.) was dissolved in cold concentrated sulfuric acid (15 ml.). After 7 hours at room temperature the solution was poured onto ice and neutralized with ammonia. Extraction with ether gave an oil which on chromatography yielded 2-aminobiphenyl (0.15 g., 58%), m.p. and mixed m.p. 50°.

The authors wish to thank the British Petroleum Co., Ltd., for the award of a fellowship to P. M. M. and Mr. P. Cook for the determination of the infrared spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

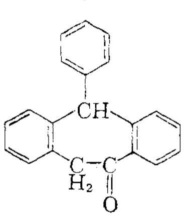
Synthesis of Pyranones and Benzofluorenones from Ketones and Carboxylic Acids[1]

BY ROBERT L. LETSINGER AND JOEL D. JAMISON[2]

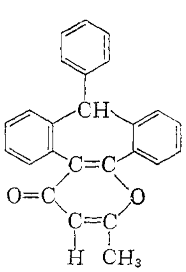
RECEIVED JUNE 27, 1960

Two new reactions of methylene ketones with carboxylic acids in polyphosphoric acid are discussed. One leads to substituted pyran-4-ones (*e.g.*, 1,3-diphenyl-2-propanone and acetic acid gave 2,6-dimethyl-3,5-diphenyl-4H-pyran-4-one) and the other to alkylated benzo[a] fluorenones (*e.g.*, deoxybenzoin and acetic acid yielded 5-methyl-11H-benzo[a]fluoren-11-one). The reactions provide simple synthetic routes to these ring systems.

It was reported recently that ketone I condensed with acetic acid in hot polyphosphoric acid to give (76% yield) a substituted 4H-pyran-4-one (II).[3] This novel reaction appeared particularly interesting since, if general for methylene ketones, it would provide an unusually simple and convenient route to the pyranones. No study of the reactions of methylene ketones with carboxylic acids in polyphosphoric acid seems previously to have been made, although condensations of great variety have been effected by polyphosphoric acid.[4] We therefore undertook an investigation of the scope of the reaction exemplified by the conversion of I to II. The present paper is concerned with the transformations involving 1,3-diphenyl-2-propanone, phenyl-2-propanone, 3-pentanone and deoxybenzoin.



I



II

A crystalline product was isolated in 76% yield after the treatment of 1,3-diphenyl-2-propanone with acetic acid in hot polyphosphoric acid. The analysis was consistent with the formula $C_{19}H_{16}O_2$; in agreement with a pyranone formulation the substance was soluble in 4 *M* hydrochloric acid, yielded a thio derivative (V) when heated with phosphorus pentasulfide, and exhibited a triplet of bands in the infrared between 6.0 and 6.3 μ, characteristic of 4H-pyran-4-ones.[3] Two structures appeared feasible: one (III) would have been produced by a condensation analogous to that by which II was formed from I; the other (IV) would have resulted if the ketone had undergone diacylation to give 3,5-diphenyl-2,4,6-heptanetrione as an intermediate. That IV is the correct structure was established by the n.m.r. spectrum, which showed a single band in the region for aliphatic hydrogen absorption. A more complicated spectrum would be predicted for III.

Phenyl-2-propanone reacted with acetic acid in polyphosphoric acid similarly to the diphenylpropanone; the product, 2,6-dimethyl-3-phenyl-4H-pyran-4-one (VI), was obtained in 48% yield. In support of the assigned structure, VI was converted in high yield *via* typical reactions for

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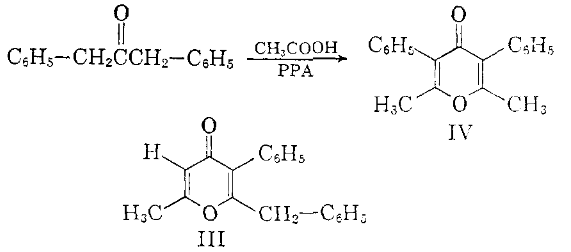
[1] Presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 14, 1960.

[2] Standard Oil Co. of Indiana Fellow, 1958.

[3] R. L. Letsinger, J. D. Jamison and A. S. Hussey, *J. Org. Chem.*, **48**, in press (1960).

[4] F. D. Popp and E. McEwen, *Chem. Revs.*, **58**, 321 (1958).

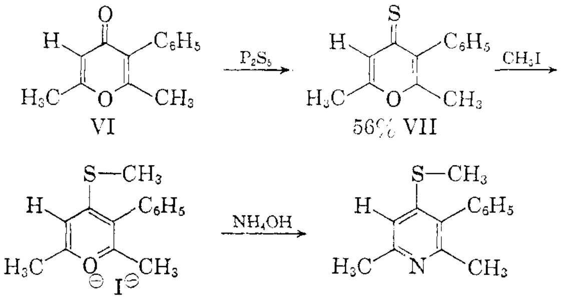


IV

III

pyranone compounds to a methylmercaptopyridine derivative (IX). The n.m.r. spectrum of VI (carbon tetrachloride solvent) exhibited four bands, attributable to the hydrogens of the phenyl group (chemical shift relative to tetramethylsilane, 288 c.p.s.), the hydrogen on the pyranone ring (239 c.p.s.), and the hydrogens of the two different methyl groups (89 and 85 c.p.s.).

CHART 1



VI

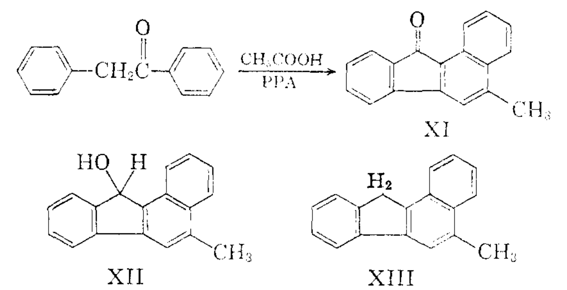
56% VII

97% VIII

95% IX

The reaction of 3-pentanone with acetic acid in polyphosphoric acid afforded the known tetramethyl-4H-pyran-4-one(X). Though the yield was relatively low (25%), this reaction demonstrates that the pyranone synthesis in not limited to use of methylene ketones activated by aryl groups. Furthermore, the synthesis is much simpler than the one previously employed for IX, which involved independent preparation of 2,4,6-heptanetrione and subsequent conversion (about 17% yield) to the pyranone in two steps.[5]

Of the ketones studied, deoxybenzoin is closest structurally to compound I. Yet only a trace of a pyranone type product was isolated from the reaction of deoxybenzoin with acetic acid in polyphosphoric acid. The reaction yielded a dark oil from which was isolated (15%) by chromatography an orange, crystalline compound, $C_{18}H_{12}O$ (XI). The infrared spectrum of this substance indicated the presence of a carbonyl group (5.9 μ) as well as aliphatic and aromatic C–H (3.26, 3.45 μ) and the absence of monosubstituted benzene (no bands between 14.1 and 14.5 μ).[6] A catalytic reduction of XI which was interrupted after consumption of one mole equivalent of hydrogen afforded an alcohol (XII) (93% yield), whereas prolonged hydrogenation gave a hydrocarbon, $C_{18}H_{14}$ (XIII) (89% yield). Alternatively, XI was converted to XII by reduction with lithium aluminum hydride and to XIII by a Wolff-Kishner reduction. Except for small bathochromic shifts, the ultraviolet spectra of XI and XIII were essentially the same as the spectra reported for 11H-benzo[a]fluoren-11-one and 11H-benzo[a]fluorene, respectively.[7] This fact, in conjunction with the analytical data and a consideration of the mode of formation of XI, indicated that XI was 5-methyl-11H-benzo[a]fluoren-11-one.[7]



XI

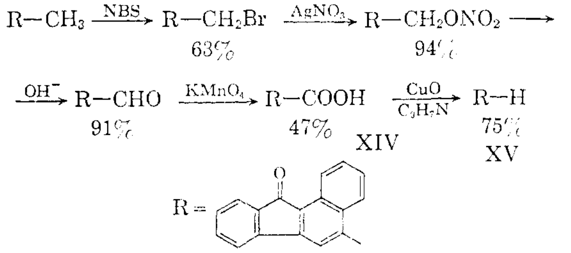
XII

XIII

Nuclear magnetic resonance data further supported this structural assignment. The spectrum of XIII (carbon tetrachloride solvent) exhibited a group of bands at low field attributable to aryl hydrogens, a band (149 c.p.s.)[8] due to the methylene hydrogens, and a band (104 c.p.s.)[8] characteristic for methyl hydrogens. The relative areas of these bands were 9.1:2.0:3.0, in excellent agreement with the theoretical values. Ketone XI exhibited only one band (88 c.p.s.; benzene solvent) in addition to the aromatic hydrogen resonance.

Conclusive evidence that XI was 5-methyl-11H-benzo[a]fluoren-11-one was provided by degradation to the known keto acid, 11H-benzo[a]fluoren-11-one-5-carboxylic acid (XIV), and ketone, 11H-benzo[a]fluoren-11-one (XV). The sequence of reactions employed is summarized in Chart 2. This stepwise procedure was adopted since attempts to oxidize XI directly to carboxylic acid XIV were unsuccessful. Compound XI either was not attacked or was converted to water-soluble products by alkaline permanganate and by chromic acid solutions. An oxidation with peracetic acid yielded o-phthalic acid as one of the products.

CHART 2



$$\underset{}{R{-}CH_3} \xrightarrow{NBS} \underset{63\%}{R{-}CH_2Br} \xrightarrow{AgNO_3} \underset{94\%}{R{-}CH_2ONO_2} \longrightarrow$$

$$\xrightarrow{OH^-} \underset{91\%}{R{-}CHO} \xrightarrow{KMnO_4} \underset{47\%\quad XIV}{R{-}COOH} \xrightarrow[C_5H_5N]{CuO} \underset{75\%\ XV}{R{-}H}$$

R =

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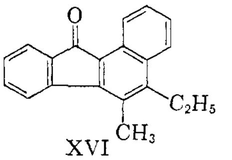
(5) J. N. Collie and B. D. Steel, *J. Chem. Soc.*, **77**, 961 (1900).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(7) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic compounds," John Wiley and Sons, Inc., New York, N. Y., 1951. The disparity in the spectra of XI and 11H-benzo[b]fluoren-11-one rendered highly unlikely an alternate structure, 10-methyl-11H-benzo[b]fluoren-11-one, which would be consistent with the chemistry leading to XI.

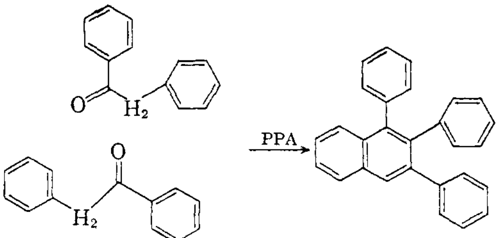
(8) These values refer to the chemical shifts with respect to tetramethylsilane. For comparison purposes it may be noted that the shifts for the methylene hydrogens of fluorene and the methyl hydrogens of toluene have been reported to be 152 and 95 c.p.s.; see G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance 'Shielding Values' for Hydrogen in Organic Structures," Minnesota Mining and Manufacturing Co., St. Paul, Minn., Table II.

Propionic acid reacted with deoxybenzoin in polyphosphoric acid much like acetic acid. An orange, crystalline ketone, $C_{20}H_{16}O$, was isolated in 14% yield. The ultraviolet and infrared spectra of this product were very similar to the spectra of compound XI. Therefore, in view of the mode of formation, this ketone may be regarded as 5-ethyl-6-methyl-11H-benzo[a]fluoren-11-one (XVI).



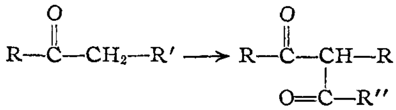
XVI

It is of interest that deoxybenzoin underwent condensation to 1,2,3-triphenylnaphthalene (XVII) when heated alone with polyphosphoric acid. The hydrocarbon could be isolated readily since it preceded ketonic material on a chromatography column; however, none of it could be found in the reactions involving the carboxylic acids. In somewhat analogous reactions, acetophenone and acetone have been converted to 1,3,5-triphenylbenzene[4] and mesitylene,[9] respectively, by polyphosphoric acid.



XVII

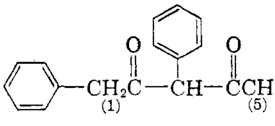
The formation of pyranones and benzofluorenones from ketones and carboxylic acids may be rationalized on the basis of a series of acylations and dehydrations proceeding by attack of an active acyl species (*e.g.*, an acylium ion or an acylphosphate) on an enol or enol acylate. Since a large number of acylate and phosphate intermediates are conceivable, only the gross aspects of the reactions are considered here. It may be assumed that the initial step in each case involves acylation at a position α to a carbonyl group and that products with three acyl groups joined to the same carbon are unstable or do not form. Diketone XVIII (or an enol acylate equivalent) would therefore be an intermediate in all reactions. Subsequent acylation of

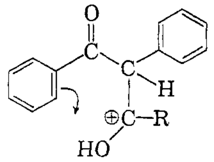


$$R-\overset{O}{\overset{\|}{C}}-CH_2-R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{O=\underset{}{C}-R''}{\underset{|}{CH}}-R'$$

XVIII, R″ = CH_3- or C_2H_5-

such an intermediate derived from ketone I would produce a 2,4,6-triketone which would dehydrate to pyranone II. In the case of 1,3-diphenyl-2-propanone the second acylation could occur at either carbon 1 or carbon 5. Preponderate attack would be expected at the carbon joined to the phenyl group, and, indeed, acylation occurs at carbon 1 as evidenced by formation of pyranone IV rather than III. The pathways to VI and X





XIX

are no doubt similar. On the other hand, the initial acylation product derived from deoxybenzoin may assume a conformation in which a carbonyl group (XIX, the carbonyl group is shown in the protonated form) is favorably oriented for interaction with a neighboring aromatic ring. Subsequent condensations would convert this intermediate to the benzofluorenone. It may be noted that geometrical restrictions imposed by the ring in compound I prohibit this course for compound I.

These reactions provide very simple methods for synthesis of the 4H-pyran-4-one and benzo(a)-fluorenone ring systems. Although a limited number of cases have been investigated, it seems likely that in general ketones of the type $RCH_2\overset{O}{\overset{\|}{C}}CH_2R'$ (R, R′ = aryl, alkyl or hydrogen) will yield pyranones when heated with aliphatic carboxylic acids in polyphosphoric acid and ketones of the type $RCH_2\overset{O}{\overset{\|}{C}}R'$ (R, R′ = aryl) will afford polynuclear compounds. The former reaction should make accessible a variety of 2,6-dialkylated-3,5-disubstituted pyran-4-ones for which no convenient preparative procedures have been available.[10]

Experimental Section

The infrared spectra were recorded with a Baird model AB-2 spectrophotometer with the sample in potassium bromide, the ultraviolet spectra were taken with a DK-2 Beckman ratio recording instrument with cyclohexane as a solvent, and the nuclear magnetic resonance spectra were obtained with a Varian 40 megacycle instrument. Combustion analyses were performed by Miss H. Beck; n.m.r. spectra were run by Mr. C. Creswell and Miss Mary Anderson. The polyphosphoric acid was kindly supplied by the Victor Chemical Co.

2,6-Dimethyl-3,5-diphenyl-4H-pyran-4-one (IV).—A solution containing 2.0 g. of 1,3-diphenyl-2-propanone in 40 g. of polyphosphoric acid and 25 ml. of acetic acid was refluxed at 140–150° for 1.5 hours. It was then cooled, hydrolyzed, and extracted with ether. The ether portion was washed with 10% aqueous potassium hydroxide, dried, and concentrated. The pyranone separated as a solid, m.p. 196–203°, weight 1.7 g. (76%). After several recrystallizations from ether it melted at 213–214°; λ_{max} (infrared), 3.26, 6.08, 6.15, 6.3, 6.7, 6.9, 7.1, 7.2, 7.3, 7.5, 7.6, 8.08, 8.45, 8.7, 9.25 μ; the n.m.r. spectrum (benzene solvent) showed one aliphatic hydrogen band separated from the benzene peak by 218 ± 2 c.p.s.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.80. Found: C, 82.88; H, 5.58.

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[9] H. R. Snyder and F. Y. Werber, THIS JOURNAL, **72**, 2965 (1950).

[10] The reaction should be particularly useful for preparation of pyranones with different alkyl or aryl groups in the 3- and 5-positions. Relatively few 3,5-dialkylated or arylated 4-pyranones have previously been made; those that have possessed the same groups in the 3- and 5-positions. See, for example, E. Banary and G. A. Bitter, *Ber.*, **61**, 1057 (1928); N. J. Leonard and D. Choudhury, THIS JOURNAL, **79**, 156 (1957); and ref. 5.

2,6-Dimethyl-3,5-diphenyl-4*H*-pyran-4-thione(V).—A mixture of phosphorus pentasulfide (3.0 g.) and 2,6-dimethyl-3,5-diphenylpyran-4-one (1.0 g.) was heated in refluxing benzene (20 ml.) for 12 hours. Benzene was then replaced by water and the aqueous suspension was warmed on a steam-bath for several hours to hydrolyze excess phosphorus pentasulfide. Filtration of the suspension and recrystallization of the crude product afforded 0.62 g. (55%) of fushia plates melting at 218–221°. Recrystallization from ether furnished an analytical sample melting at 220–221°; λ_{max} (infrared), 3.3, 6.15, 6.22, 6.45, 6.7, 6.92, 7.15, 7.52, 8.1, 8.45, 8.66, 9.3 μ. This material gave a positive test for sulfur (sodium fusion).

Anal. Calcd. for $C_{19}H_{16}SO$: C, 78.05; H, 5.48. Found: C, 77.83; H, 5.27.

2,6-Dimethyl-3-phenyl-4*H*-pyran-4-one (IV).—Phenyl-2-propanone (10.0 g.) was treated with acetic acid (55 ml.) and polyphosphoric acid (100 g.) as in the reaction involving 1,3-diphenyl-2-propanone, and the mixture was worked up similarly. Concentration of the ether solution afforded a dark, viscous oil which crystallized from carbon tetrachloride as colorless needles; 7.2 g. (48%), m.p. 78.0–78.5°; λ_{max} (infrared) 3.3, 6.02, 6.18, 6.27, 6.7, 6.9, 7.1, 7.3, 8.05, 9.2, 9.3 μ.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.00; H, 5.98. Found: C, 78.34; H, 5.68.

2,6-Dimethyl-4-methylmercapto-3-phenylpyrylium Iodide (VIII).—Phosphorus pentasulfide (6.0 g.) and 2,6-dimethyl-3-phenylpyran-4-one (2.0 g.) in 50 ml. of benzene was treated as in the preparation of 2,6-dimethyl-3,5-diphenyl-4-pyran-4-thione. The thiopyrone thus obtained (m.p. 99–101°, weight 1.22 g. (56%)) was treated with methyl iodide (1.25 g.) in refluxing acetone for 1 hour.[11]

Filtration afforded 1.45 g. of a yellow solid, m.p. 210–215° dec., which was insoluble in ether but was soluble in water and nitromethane. An analytical sample (m.p. 210–215° dec.) was prepared by precipitating the salt from nitromethane with ether.

Anal. Calcd. for $C_{14}H_{15}OSI$: C, 46.93; H, 4.20. Found: C, 46.80; H, 4.03.

4-Methylmercapto-3-phenyl-2,6-lutidene (IX).—A solution of ammonium carbonate (0.5 g.) and 2,6-dimethyl-4-methylmercapto-3-phenylpyrylium iodide (0.30 g.) in 5 ml. of water was warmed on a steam-bath for 10 minutes with 10 ml. of 15% aqueous ammonia. After cooling, the solution was extracted with ether. The ether portion was then extracted with 6 *M* hydrochloric acid and the aqueous layer was made alkaline with potassium hydroxide. Ether extraction of the alkaline solution afforded an oil which crystallized from hexane; m.p. 99–100°, weight 0.18 g. (95%). The product was colorless, soluble in dilute aqueous acid, and insoluble in water or dilute alkali.

Anal. Calcd. for $C_{14}H_{15}NS$: C, 73.33; H, 6.65; N, 6.12. Found: C, 73.44; H, 6.62; N, 6.29.

Tetramethyl-4*H*-pyran-4-one (X).—3-Pentanone (2.0 g.) was treated with acetic acid (25 ml.) and polyphosphoric acid (40 g.) as in the reaction involving 1,3-diphenyl-2-propanone. A similar work-up of the reaction mixture yielded a black oil that would not solidify. Extraction of the oil with several small portions of water and concentration of the aqueous extracts afforded 1.25 g. of a solid, which on recrystallization furnished 1.0 g. (26%) of colorless tetramethyl-4H-pyran-4-one hydrate, m.p. 63–64°, lit. m.p. 63–64°. Recrystallization of the hydrate from pentane furnished 0.87 g. (25% over-all yield) of tetramethyl-4H-pyran-4-one, m.p. 92–93°, lit.[5] m.p. 92°.

5-Methyl-11H-benzo[a]fluoren-11-one(XI).—A solution of 5.3 g. of deoxybenzoin, 50 ml. of glacial acetic acid and 40 g. of polyphosphoric acid was heated with constant swirling to 110°. Acetic acid was removed by distillation until the pot temperature was 150°, whereupon the mixture was refluxed 2 hours, cooled and poured into water. The aqueous suspension was extracted with five 100-ml. portions of ether and the ether solution washed with three 75-ml. portions of 10% aqueous potassium hydroxide, and two 100-ml. portions of ether. The ether was removed, leaving a black, viscous oil, which was chromatographed on 60 g. of activated silica gel, using a 50% solution of benzene in *n*-hexane as an eluent. From the red band, 1.26 g. of crude product was obtained. Recrystallization from methanol gave 1.00 g. (15% yield) of an orange crystalline solid melting at 150–152°. Successive recrystallization from methanol of a small portion of the product gave an analytical sample of yellow-orange, hair-like needles melting at 152–153°; major λ_{max} (infrared) 3.26(w), 3.45(w), 5.9, 6.3, 6.56, 6.8, 8.48, 8.68, 8.9, 9.4, 11.2, 11.6, 12.81, 13.4, 13.9 μ; λ_{max} (ultraviolet, cyclohexane) 270 mμ (log ϵ 4.78), 292 (shoulder, log ϵ 4.34), 372 (352), 393 (3.60); λ_{max} (ethanol) for 11H-benzo(a)-fluoren-11-one (taken from graph in Friedel and Orchin[7]) 268 (4.80), 295 (shoulder, 4.34), 370 (3.55).

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.92; mol. wt., 244. Found: C, 88.45; H, 4.83; mol. wt., 246 (by method of Signer[12]).

When 20 g. of deoxybenzion was treated as above the yield was 11.2%. In one experiment a few milligrams of a colorless solid, m.p. 142–144°, was isolated in addition to the orange ketone. It showed a triplet in the infrared spectrum characteristic of the 4-pyranones; therefore it was possibly a pyranone analogous to compound II.

Hydrazone of 5-Methyl-11H-benzo[a]fluoren-11-one.—A solution of 0.158 g. of XI and 5 ml. of 85% hydrazine hydrate in 10 ml. of 95% ethanol was refluxed for 12 hours. The ethanol was removed in a stream of air and water was added to precipitate the product. Filtration yielded 0.114 g. of yellow solid melting at 120–180°. Two recrystallizations from hexane gave yellow needles of the hydrazone melting at 186°[13]; λ_{max} (infrared) 2.95, 6.22, 6.28, 6.90, 6.95, 8.52, 8.61, 13.20 μ.

Anal. Calcd. for $C_{18}H_{14}N_2$: N, 10.85. Found: N, 10.81.

Oxime of 5-Methyl-11H-benzo[a]fluoren-11-one.—A solution of 1.07 g. of ketone XI, 2.0 g. of hydroxylamine hydrochloride and 5 ml. of pyridine in 15 ml. of absolute ethanol was refluxed for 5 hours. Water was then added and the aqueous suspension extracted with ether. The ether layer, after being washed with dilute hydrochloric acid to remove pyridine, was dried and concentrated. The yellow solid which remained weighed 1.08 g. (95%) and melted at 198–200°. Several recrystallizations of a portion gave yellow plates melting at 201–203°; λ_{max} (infrared) 3.15, 6.30, 6.97, 10.30, 11.30, 11.40 and 13.3 μ.

Anal. Calcd. for $C_{18}H_{13}NO$: N, 5.40. Found: N, 5.94.

5-Methyl-11H-benzo[a]fluorene(XIII). (a) **Wolff–Kishner Reduction.**—A solution of 0.7 g. of the hydrazone of ketone XI and 5 ml. of 85% hydrazine hydrate in 50 ml. of 10% ethanolic potassium hydroxide was refluxed for 24 hours. Removal of the ethanol by evaporation, addition of water, and filtration of the resulting suspension gave 0.61 g. (98% yield) of a white crystalline product melting at 123–125°. Recrystallization from ethanol afforded a pure product melting at 127–128°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.99; H, 6.01. Found: C, 93.99; H, 6.09.

(b) **Catalytic Reduction.**—A solution of 0.744 g. of the ketone in 150 ml. of absolute ethanol and 0.12 g. of 10% palladium-on-charcoal catalyst was shaken with hydrogen at a pressure of 45 lb./sq. in. in a Parr apparatus for 12 hours at 25°. After filtration and concentration a white solid (0.623 g.), m.p. 125–126°, separated. It showed no melting point depression when mixed with the hydrocarbon from the hydrazone decomposition.

This hydrocarbon decolorized rapidly a dilute solution of bromine in carbon tetrachloride and gave a positive Zimmerman test.[14] The principal bands in the infrared spectra occurred at 3.25, 3.42, 6.23, 6.82, 6.9, 7.1, 7.33, 8.6, 11.32, 12.8, 13.2 and 13.76 μ. A comparison of the ultraviolet spectrum of XIII with that of 11H-benzo[a]fluorene[7] is given in Table I.

5-Methyl-11H-benzo[a]fluoren-11-ol(XII). (a) **By Catalytic Reduction.**—A mixture of 0.099 g. of ketone XI and 0.02 g. of 10% palladium-on-charcoal catalyst in 10 ml.

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[11] Procedure of L. C. King, F. J. Ozog and J. Moffat, THIS JOURNAL, **73**, 300 (1951), for preparing mercaptopyrylium salts.

[12] E. P. Clark, *Anal. chem.*, **13**, 820 (1941).

[13] The compound slowly decomposed near the melting point. In order to obtain a sharp melting point it was necessary to bring the temperature of the block within a few degrees of the melting point before placing the sample on it.

[14] L. F. Fieser and M. Fieser, "Organic Chemistry," 1st ed., D. C. Heath and Co., Boston, Mass., 1944, p. 748.

Table I

Ultraviolet Spectra

Compound XIII		11H-Benzo[a]fluorene[7] (ethanol solvent)	
λmax, mμ	log ϵ	λmax, mμ	log ϵ
256	4.65	252	4.75
266	4.95	262	4.94
286	3.98		
295	4.12	291	4.16
309	4.06	303	4.12
323	4.00	314	4.05
331	3.34	328	3.27

of absolute ethanol was shaken at room temperature at one atmosphere of hydrogen until one equivalent of hydrogen had been taken up. Filtration and evaporation yielded 0.093 g. (93%) of pale yellow solid melting at 187–188°. Recrystallization from ethanol gave colorless crystals of the fluorenol, m.p. 188–189°; λ_{max} (infrared) 3.06, 6.2, 6.8, 7.56, 8.42, 9.02, 9.48, 9.7, 9.86, 11.3, 12.8, 13.25, 13.5 μ; λ_{max} (ultraviolet) 260 mμ (log ϵ 4.67), 269 mμ (log ϵ 4.75).

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.90; H, 5.69. Found: C, 87.75; H, 5.80.

(b) **By Reduction with Lithium Aluminum Hydride.**—A solution of 1.9 g. of ketone XI in 50 ml. of ether was added to a slurry of 0.4 g. of lithium aluminum hydride in 50 ml. of ether and refluxed for 1 hour. The mixture was hydrolyzed with 6 *M* hydrochloric acid and the ether layer was separated, dried, and evaporated. On addition of 200 ml. of ethanol the major portion (A) of the residue dissolved; however, 0.2 g. of a white precipitate remained (portion B). Concentration of the alcoholic solution to 50 ml. gave 1.5 g. (79%) of crystalline precipitate (compound XII), m.p. 180–186°. After recrystallization from ethanol it melted at 188–189° and did not depress the melting point of the alcohol prepared by catalytic reduction. Portion B melted at 295–297°; after recrystallization from dioxane it melted (with decomposition) at 330°. Combustion analysis gave 84.82, 84.27% carbon and 5.30, 5.56% hydrogen. This high melting product was not further characterized.

Oxidation of 5-Methyl-11H-benzo[a]fluoren-11-one.—A mixture of 2.00 g. of ketone XI and 200 ml. of 40% peracetic acid was allowed to stand at room temperature for 21 days. During this time the ketone slowly dissolved and gave a yellow solution. Excess peracetic acid was decomposed by the slow addition of ferrous sulfate; then the solution was extracted with ether. An alkaline extract of the ether portion yielded on acidification a mixture of organic acids (1.50 g.), from which was isolated by chromatography 0.61 g. of a solid product, m.p. 192–208°. Recrystallization from ether afforded 0.30 g. of *o*-phthalic acid.

5-Bromomethyl-11H-benzo[a]fluoren-11-one.—A suspension of 0.85 g. of N-bromosuccinimide in a carbon tetrachloride (50 ml.) solution containing 1.0 g. of 5-methyl-11H-benzo[a]fluoren-11-one and a small crystal of benzoyl peroxide was refluxed for 1.5 hours, whereupon a red solid was observed to precipitate from the solution. After refluxing an additional hour, the carbon tetrachloride was distilled from the reaction vessel and replaced with 100 ml. of water. The water suspension was warmed on a steam-bath with occasional stirring to dissolve the succinimide. The hot suspension was filtered and the product washed several times with hot water; 1.31 g. of red solid was obtained (99% yield) melting at 245–255°. Recrystallization from chloroform gave 0.84 g. of red needles melting at 259–260°; λ_{max} (cyclohexane) 277.5 mμ (log ϵ 4.80); λ_{max} (infrared) 5.90 μ.

Anal. Calcd. for $C_{18}H_{11}OBr$: C, 66.90; H, 3.40. Found: C, 67.12; H, 3.65.

5-Dibromomethyl-11H-benzo[a]fluoren-11-one.—A solution of 0.2 g. of 5-methyl-11H-benzo[a]fluoren-11-one and 0.5 g. of N-bromosuccinimide in 25 ml. of dry benzene (with a crystal of benzoyl peroxide) was refluxed 24 hours. The benzene was distilled out and 50 ml. of water was added. The precipitate, 0.174 g. (53%), melted at 216–221°; after two recrystallizations from ethanol–chloroform the dibromoketone melted at 225–228°, λ_{max} (infrared) 5.88 μ.

Anal. Calcd. for $C_{18}H_{10}OBr_2$: C, 53.60; H, 2.49. Found: C, 53.77; H, 2.39.

5-Nitratomethyl-11H-benzo[a]fluoren-11-one.—A solution of 2.0 g. of silver nitrate and 5 g. of water in 20 ml. of dioxane was added to a solution of 0.919 g. of 5-bromomethyl-11H-benzo[a]fluoren-11-one in 100 ml. of dioxane. Although silver bromide precipitated immediately, the mixture was allowed to stand for 2 hours at room temperature to assure complete reaction. Concentration of the solution to about 30 ml., addition of water to precipitate the product, and filtration led to 0.85 g. (94% yield) of a reddish-orange solid, m.p. 173–183°. Successive recrystallizations from ethyl acetate gave 0.5 g. (58% yield) of orange fluffy crystals that melted at 191–192°. Although the analysis was not very satisfactory this substance was clearly a nitrate ester since the infrared spectrum contained strong bands at 6.10 and 7.77 μ.[6]

Anal. Calcd. for $C_{18}H_{11}NO_4$: C, 70.81; H, 3.60; N, 4.59. Found: C, 70.34, H, 3.45; N, 3.92.

11H-Benzo[a]fluoren-11-one-5-carboxaldehyde.—A solution of 0.280 g. of 5-nitratomethyl-11H-benzo[a]fluoren-11-one, 0.75 g. of potassium hydroxide and 2.5 g. of water in 22.5 ml. of dioxane was refluxed for 2 hours, cooled, and poured into ice-water. Filtration of the suspension gave 0.217 g. (91.5% yield) of red solid melting at 223–227°. Recrystallization from ethyl acetate gave the fine red needles of the aldehyde, m.p. 226–227°. Good evidence for an aldehyde group was provided by an infrared band at 3.65 μ (formyl hydrogen). Also, in addition to the conjugated ketone band at 5.9 μ there was a shoulder at 5.85 μ attributable to the aldehyde carbonyl.

Anal. Calcd. for $C_{18}H_{10}O_2$: C, 83.72; H, 3.88. Found: C, 83.27; H, 3.82.

11H-Benzo[a]fluoren-11-one-5-carboxylic acid (XIV).—A solution of 0.10 g. of aldehyde and 0.20 g. of potassium permanganate in 20 ml. of acetone was refluxed for 45 minutes. The suspension was filtered to remove manganese dioxide and the acetone was removed by evaporation and replaced with 50 ml. of ether. Extraction of the ether solution with three 30-ml. portions of 10% aqueous potassium hyroxide and acidification of the base washes gave 0.09 g. of a dark solid. Recrystallization from ethanol gave 0.05 g. (47% yield) of acid XIV, m.p. 300–315°. Sublimation at 200° gave fine orange crystals melting at 318–320° with decomposition. The melting point reported for 11H-benzo[a]fluoren-11-one-5-carboxylic acid is 320°.[15]

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.85; H, 3.65. Found: 78.64; H, 3.82.

11H-Benzo[a]fluoren-11-one (XV).—A solution of 0.141 g. of the benzofluorenonocarboxylic acid in 5 ml. of quinoline was refluxed in the presence of 0.05 g. of cupric oxide for 30 minutes. It was then cooled, diluted with 30 ml. of ether, filtered, and extracted with three portions of 6 *M* hydrochloric acid and 2 portions of 10% aqueous potassium hydroxide. Drying and concentration of the ether solution afforded an orange viscous oil which crystallized as needles from hexane; weight 0.90 g. (75%), m.p. 130–132°. After recrystallization from methanol the ketone melted at 131–132°, λ_{max} 267 mμ (log ϵ 4.79); lit.[16] m.p. 132.5°; lit.[7] λ_{max} 268 mμ (log ϵ 4.80).

Preparation of 5-Ethyl-6-methyl-11H-benzo[a]fluoren-11-one (XVI).—A solution of 4.0 g. of deoxybenzoin and 30 g. of polyphosphoric acid in 25 ml. of propionic acid was heated at 145–150° for 45 minutes. When the reaction mixture was worked up as in the case of 5-methyl-11H-benzo[a]fluoren-11-one, 4.68 g. of black oil was obtained. Chromatography of 2.34 of this oil on 60 g. of activated silica gel gave 0.497 g. of crude product (from the red band) which melted at 47–105°. Recrystallization from methanol furnished 0.40 g. (14%) of orange needles melting at 118–121°. Two sublimations gave pure orange crystals melting at 123–124°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.23; H, 5.88. Found: C, 88.18; H, 5.88.

Reaction of Deoxybenzoin in Polyphosphoric Acid.—Deoxybenzoin (2.0 g.) was heated for 2 hours with 20 g. of polyphosphoric acid at 145–150° without stirring. The mixture was then poured into water and the organic products extracted with ether. The oil remaining after evaporation of the ether was crystallized from methanol, yielding 0.268

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(15) K. T. Potts, *J. Chem. Soc.*, 1269 (1956).

(16) C. Graebe, *Ann.*, **335**, 132 (1904).

(15%) of 1,2,3-triphenylnaphthalene, m.p. 151–152°, lit.[17] m.p. 152°. The residual material was largely deoxybenzoin, as shown by the infrared spectrum.

The mononitro derivative, prepared by nitration of 0.169 g. of the 1,2,3-triphenylnaphthalene with 0.1 ml. of concentrated nitric acid in 5 ml. of acetic acid (warmed 50 minutes on a steam-bath) melted at 210–203°, lit.[17] m.p. 200–201°. Reduction of this nitro compound by hydrogen (1 atm.) over palladium-on-charcoal yielded the monoamino derivative, m.p. 187–189°, lit.[17] m.p. 189–190°.

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(17) L. E. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

Stereospecific Angular Alkylation. A New Application of the Claisen Rearrangement[1]

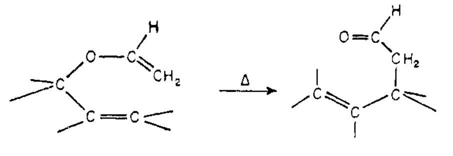
BY ALBERT W. BURGSTAHLER AND IVAN C. NORDIN

RECEIVED JULY 15, 1960

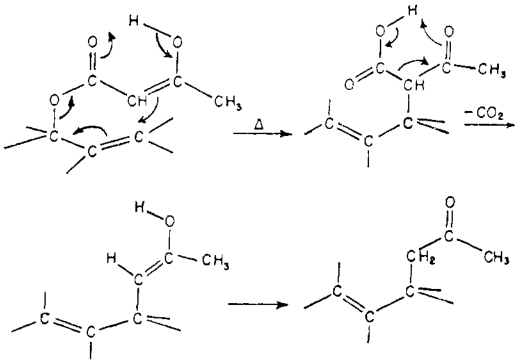
Claisen rearrangement of vinyl ethers of suitably constituted polycyclic allylic alcohols is shown to provide a new, stereospecific method for the introduction of an angular substituent into polycyclic systems. Model studies with Δ^2-cyclohexenol and 3-methyl-Δ^2-cyclohexenol are described, and applications of the sequence to $\Delta^{9(10)}$-1-octalol and the epimeric Δ^4-cholestene-3-ols are reported.

Despite the fact that various effective methods have been devised for the synthesis of angularly substituted polycyclic systems,[2] there is continued interest in the development of still other means for this purpose, especially ones which are completely or at least highly stereoselective. By virtue of its intramolecular character, the Claisen-type rearrangement of allyl vinyl ethers (A)[3] and of allyl acetoacetates (B)[4] appeared to us to offer the possibility of being applicable as a new and potentially useful method for the stereoselective introduction of an angular functional group into a suitably constituted ring structure. This stereospecificity is such that, if the allylic group is contained in a ring, the new carbon–carbon bond which is formed in the reaction will necessarily be *cis* to the carbon–oxygen bond that undergoes cleavage. In this report we present results of an exploratory investigation into such an extension of these rearrangements.

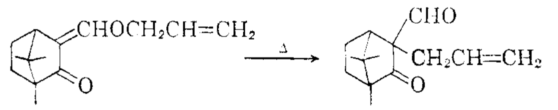
(A)



(B)



Model Studies.—Except for the phenyl ether of Δ^2-cyclohexenol,[5] substances in which the participating allylic group is incorporated into a ring apparently have not been examined previously in the Claisen or Cope rearrangement. Thus, although Claisen in his original memoir[6] disclosed the rearrangement of 3-allyloxymethylenecamphor (I) to the C-allyl derivative II,[7] and, more recently,



I II

Brannock[8] has reported three additional examples of a similar nature, vinyl ethers or acetoacetic esters of cyclic allylic alcohols do not appear to have been prepared or studied previously. Accordingly, as a basis for possible extensions to bicyclic and larger ring systems, preliminary investigations were undertaken with these derivatives of Δ^2-cyclohexenol and 3-methyl-Δ^2-cyclohexenol.

The Δ^2-cyclohexenol used in this work was prepared by hydrolysis of 3-bromocyclohexene, which, in turn, was obtained directly from cyclohexene by the Wohl–Ziegler method with N-bromosuccinimide.[9] 3-Methyl-Δ^2-cyclohexenol[10] was prepared by carefully controlled borohydride reduction of

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(1) From the Ph.D. Thesis of Ivan C. Nordin, The University of Kansas, 1960. A preliminary report of this work appeared as a Communication to the Editor, THIS JOURNAL, **81**, 3151 (1959). A portion of it was also presented before the Division of Organic Chemistry at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959.

(2) For leading references (in relation to the steroid field), see L. F. Fieser and M. Fieser, "Steroids," Reinhold Publ. Corp., New York, N. Y., 1959, particularly Chapters 15, 16 and 19.

(3) Reviewed by D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. 1.

(4) W. Kimel and A. C. Cope, THIS JOURNAL, **65**, 1992 (1943), and later papers.

(5) J. W. Cornforth, C. K. Hughes and F. Lions, *J. Proc. Royal Soc. N. S. Wales*, **71**, 323 (1938) [*C. A.*, **33**, 148 (1939)].

(6) L. Claisen, *Ber.*, **45**, 3157 (1912).

(7) Experimental details of this work do not appear ever to have been published. Out of interest in the degree to which this particular rearrangement is stereospecific, we have prepared the *dl*-form of I and have found that its rearrangement at 220° leads, in excellent yield, to a mixture of the two possible stereoisomers of II. One of these, formed to a slightly greater extent than the other, is crystalline (m.p. 51–53°) and is readily separated from the second, which is a liquid. The fact that both possible stereoisomers of II are formed, and in comparable amounts, indicates that in a system of this type steric requirements for the rearrangement are practically non-selective.

(8) K. C. Brannock, THIS JOURNAL, **81**, 3379 (1959).

(9) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942); *cf.* H. J. Dauben, Jr., and L. L. McCoy, THIS JOURNAL, **81**, 4863 (1959).

(10) M. I. Bowman, C. C. Ketterer and G. Dinga, *J. Org. Chem.*, **17**, 563 (1952).