

were placed in a vial containing a few crystals of hydroquinone. The vial was tightly sealed and allowed to stand for several weeks in the dark with intermittent shaking. A white crystalline solid (0.6 g.) was formed. After recrystallization from high petroleum ether and sublimation at 65° (0.2 mm.), this compound melted at 80–80.5°. This compound is 1,4,10,11-tetrahydro-2,3-dimethylfluorenone.

Anal. Calcd. for C₁₅H₁₆O: C, 84.86; H, 7.60. Found: C, 84.58; H, 7.60.

2,3-Dimethylfluorenone (III).—Approximately 0.5 g. of the above 1,4,10,11-tetrahydrofluorenone was mixed with a 5% palladium-on-charcoal and heated to 150–175°. Hydrogen was evolved readily and in only about 30 minutes the reaction was complete. The product of this reaction was the yellow crystalline compound, 2,3-dimethylfluorenone, which melted at 109–110°, as reported in the literature.⁷

Anal. Calcd. for C₁₅H₁₂O: C, 86.50; H, 5.81. Found: C, 86.80; H, 6.43.

3-Bromoindanone (IV).—Twenty grams of indanone was placed in a quartz flask and dissolved in 150 ml. of carbon tetrachloride. The flask was irradiated by ultraviolet light for five hours. During the first four hours of irradiation 26.8 g. of *N*-bromosuccinimide was added in three portions. At the end of the full reaction time the carbon tetrachloride solution was filtered to remove the succinimide formed during the reaction, and the filtrate washed with water and dried over anhydrous magnesium sulfate. The carbon tetrachloride was removed under diminished pressure and the residue (reddish oil) dissolved in boiling commercial hexane (Skelly-Solve B). Upon cooling reddish colored crystals of 3-bromoindanone formed. These after repeated recrystallization and treatment with carbon-black were light yellow and melted at 54.5–55°. The yield of pure 3-bromoindanone was 9 g., or 28% of the theoretical amount.

Anal. Calcd. for C₉H₇OBr: C, 51.19; H, 3.34; Br, 37.88. Found: C, 51.53; H, 3.45; Br, 37.55.

(7) S. Huzise, *Ber.*, **71**, 2461 (1938).

In addition to 3-bromoindanone, this reaction mixture yielded small amounts of 2-bromoindanone, 2,3-dibromoindanone, 2,2-dibromoindanone and some unchanged indanone.

Oxidation of 3-Bromoindanone with Potassium Permanganate.—One gram of 3-bromoindanone was refluxed overnight with 76 ml. of 0.5 *N* aqueous potassium permanganate solution. The solid material formed during the reaction was removed by filtration and the filtrate made acid with hydrochloric acid. The water solution was extracted with ether in a continuous extraction apparatus for ten hours. The ethereal solution was evaporated to dryness and the residue recrystallized from water. The water solution was chilled rapidly until frozen in order to obtain good crystals. The free phthalic acid which separated and a mixture of it with authentic phthalic acid both melted at 232.5–233°.

Dehydrobromination of 3-Bromoindanone.—A solution of 4 g. of 3-bromoindanone in 50 ml. of anhydrous ether was placed in a 200-ml. round-bottomed flask. A few crystals of trinitrobenzene and 50 ml. of *sym*-collidine were added. The stirrer was started and the reaction mixture stirred for 3.5 hours. Heat was then applied and the reaction allowed to continue for an additional one-half hour at the temperature of refluxing ether. The solution was cooled and the collidine hydrobromide collected on a filter. The filtrate was cooled in an ice-bath and cold hydrochloric acid–water solution (one part water, one part concentrated hydrochloric acid) was added until the solution was strongly acid to congo red paper. The addition had to be made very slowly to keep the solution from overheating. The water layer was then drawn off and washed with ether. The combined ether layers were washed once with water, then 5% sodium bicarbonate and finally with water again. The ethereal solution was dried over anhydrous magnesium sulfate, filtered and the ether removed under vacuum. The residue was distilled under reduced pressure. The yield of indone was 60% of the theoretical calculated from the bromide. The boiling point was 61–63° at 0.9 mm., *n*_D²⁰ 1.5982.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF COLUMBIA UNIVERSITY AND THE UNIVERSITY OF MICHIGAN]

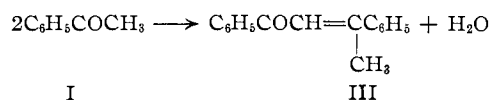
The Condensation of Acetophenone with Itself in the Presence of Lewis Acids¹

BY ROBERT C. ELDERFIELD² AND TE PIAO KING³

RECEIVED DECEMBER 23, 1953

The reaction by which acetophenone condenses with itself in the presence of boron trifluoride has been reinvestigated. From a study of the by-products of the reaction, a revised reaction sequence which accounts for the formation of 2,4,6-triphenylpyrylium fluoborate has been suggested.

Dovey and Robinson⁴ noted that when acetophenone (I) was heated with boron trifluoride at 120°, condensation to 2,4,6-triphenylpyrylium fluoborate (II) occurred. By analogy to the formation of 2,4,6-triphenylpyridine from acetophenone and ammonia as noted by Reihm⁵ they suggested that the formation of II occurred by a similar mechanism although no methane or other one-carbon fragment was reported among the products of the reaction



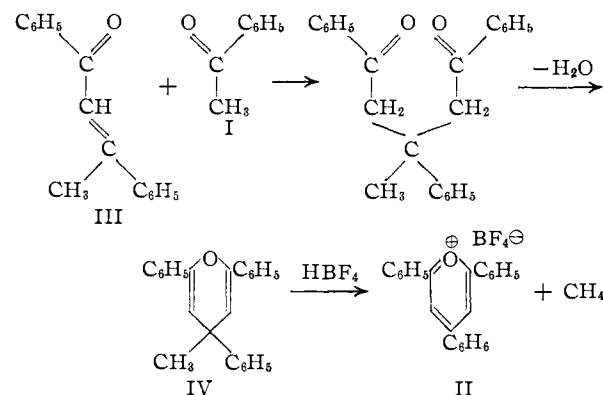
(1) The material here reported is taken from a dissertation presented by Te Piao King in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Department of Chemistry, University of Michigan, Ann Arbor, Mich.

(3) Parke, Davis and Company Fellow 1952–1953.

(4) W. C. Dovey and R. Robinson, *J. Chem. Soc.*, 1389 (1935).

(5) P. Reihm, *Ann.*, **238**, 16 (1887); C. Engler and H. Heine, *Ber.*, **6**, 638 (1873).



The condensation of acetophenone to a 2,4,6-triphenylpyrylium salt in the presence of potassium pyrosulfate and sulfuric acid at room temperature has been reported by Davis and Armstrong⁶ and

(6) T. L. Davis and C. B. Armstrong, *THIS JOURNAL*, **57**, 1583 (1935).

at 150° by LeFevre.⁷ Davis and Armstrong also stated that no gas or volatile material was formed in the reaction. However, this condensation reaction differs from that described by Dovey and Robinson⁴ in that a strong oxidizing agent is present. Oxidation of I to benzoic acid by pyrosulfuric acid has been reported.⁸

In view of the uncertainties regarding the exact course of the above reaction, a reinvestigation of it seemed desirable. Reactions involving facile elimination of hydrocarbons from partially reduced nitrogen heterocycles such as dihydroquinolines,⁹ 2,2-disubstituted benzimidazoles,^{10,11} 2,2-disubstituted benzoxazolines and benzothiazolines¹² are known and have been studied intensively in these laboratories. At least a portion of the energy required for the rupture of a carbon-carbon bond in these reactions appears to arise from the increased resonance stabilization of the "aromatic" product of the reaction compared to its reduced precursor. If Dovey and Robinson's suggested mechanism⁴ for the formation of II is correct, a similar gain in resonance stabilization by II conceivably can supply the requisite driving force.

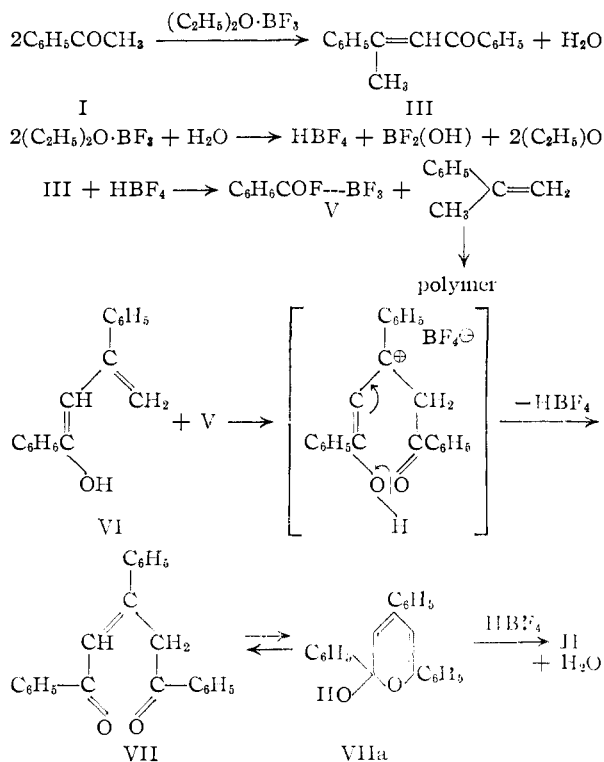
However, it should be noted that a fundamental difference exists between the reactions involving formation of a triphenylpyrylium salt from I and those involving formation of triphenylpyridine from I and ammonia. Formation of II requires interaction of the pyran IV with the acid. Thus the acid serves also as a reactant rather than merely as a catalyst.

Condensation of I in the presence of boron trifluoride was repeated under conditions similar to those of Dovey and Robinson⁴ except that boron fluoride etherate was used rather than the gaseous reagent. In conformity with their observation, no gas evolution was noted and II, isolated in 9% yield, was characterized by conversion to the ferrichloride and to 2,4,6-triphenylpyridine. From the reaction mixture, benzoic acid, 1,3,5-triphenylbenzene and dypnone (III) also were isolated.

The presence of benzoic acid among the reaction products is interesting and provided the clue necessary to explain the course of the reaction. Since no strong oxidizing agent was present, it must have resulted from a cleavage reaction, presumably from cleavage of dypnone. Dypnone is known to give benzoic acid in 34% yield and polymeric material on treatment with hydrogen fluoride at 50° followed by decomposition of the reaction mixture by water.¹³ III is cleaved also to benzoic acid by hydrochloric acid at 150°. These facts together with the observation of Hopf and LeFevre¹⁵ that dypnone condenses with benzoyl chloride in the presence of ferric chloride to give 2,4,6-triphenylpyrylium ferrichloride form the basis for a reaction sequence which takes into account the absence of

methane in the products during the passage from I to II.

The first step is the formation of dypnone (III) from I by an aldol condensation as suggested by Dovey and Robinson. Under the influence of fluoroboric acid (formed by hydrolysis of boron trifluoride), III is cleaved to benzoyl fluoborate (V). Addition of a positive benzoyl fragment to the enolic form of III (VI) followed by ejection of a proton would lead to the unsaturated 1,5-diketone VII which is a tautomer of the pseudo base VIIa of the triphenylpyrylium salt II to which it is converted in the presence of fluoboric acid. These reactions may be represented as



The above representation is supported by two observations. When dypnone is heated in the presence of boron fluoride etherate at 120°, II is formed in 11% yield. Therefore, the condensation of I to II does not require a third mole of I. Further, dypnone condenses with benzoyl fluoride in the presence of boron fluoride etherate at room temperature to give II in 12.6% yield.

The formation of triphenylpyrylium acid sulfate from I and potassium pyrosulfate and sulfuric acid probably proceeds in an analogous fashion.

Experimental¹⁶

Condensation of Acetophenone in the Presence of Boron Trifluoride Etherate.—Purified acetophenone (120 g., 1 mole) and freshly distilled boron trifluoride etherate (142 g., 1 mole) were heated at 115–120° for 30 minutes under a carbon dioxide atmosphere in a sealed system connected to a gas buret. After heating, the system was swept with carbon dioxide. The collected gas was displaced into a Hempel gas bulb with 40% potassium hydroxide solution. After standing, the gas was completely absorbed.

(16) All melting points are corrected for stem exposure and boiling points are uncorrected.

(7) R. J. W. LeFevre, *J. Chem. Soc.*, 1467 (1938).

(8) K. Krekler, *Ber.*, **19**, 2623 (1886).

(9) C. Engler and P. Reihm, *ibid.*, **18**, 2245 (1885); D. Craig, *THIS JOURNAL*, **60**, 1458 (1938).

(10) R. C. Elderfield and J. R. McCarthy, *ibid.*, **73**, 975 (1951).

(11) R. C. Elderfield and V. B. Meyer, *ibid.*, **76**, 1883 (1954).

(12) F. J. Kreysa, *et al.*, *ibid.*, **73**, 1155 (1951).

(13) J. H. Simons and E. O. Ramler, *ibid.*, **65**, 1390 (1943).

(14) F. Henrich and A. Wirth, *Monatsh.*, **25**, 442 (1904).

(15) P. P. Hopf and R. J. W. LeFevre, *J. Chem. Soc.*, 1989 (1939).

After addition of 100 ml. of benzene and 100 ml. of water, the reaction mixture was shaken thoroughly. After standing for 15 minutes, the yellow triphenylpyrylium salt (8.8 g.), m.p. 210–215°, was collected. The yield was 9% calculated on the basis that four moles of acetophenone was required to form one mole of pyrylium salt. After four recrystallizations from 95% ethanol, the salt melted at 232–234°, and after drying at 80° and 20 mm. for several hours it melted at 252–254°. Dovey and Robinson⁴ report m.p. 225–226° for a hydrate which furnished analytical figures corresponding to $C_{23}H_{17}OBF_4 \cdot 0.66H_2O$. The fluoborate was shaken with 3% sodium hydroxide solution and the ferrichloride was precipitated by addition of a saturated solution of ferric chloride in concentrated hydrochloric acid. After one recrystallization from acetone–benzene, the yellow needles melted at 273–275°; reported m.p. 277°.¹⁷ For further identification, the crude pyrylium fluoborate was converted to 2,4,6-triphenylpyridine, m.p. 138–139°, according to Dilthey.¹⁷

The two layers of the filtrate from the pyrylium fluoborate were separated. The benzene layer was washed with five 100-ml. portions of 5% sodium bicarbonate solution. On acidification of the bicarbonate extracts 1.30 g. of benzoic acid, m.p. and mixture m.p.'s with an authentic sample 121–123°, was obtained. After washing with water, the residue, after removal of the benzene, was distilled under reduced pressure through a 20-cm. Vigreux column. The first fraction (30 g., b.p. 90–100° (20–25 mm.)) was unreacted acetophenone. The second fraction (0.45 g., b.p. 110–150° (0.4–0.5 mm.)) was discarded. The third fraction, b.p. 151–175° (0.4–0.5 mm.), weighed 30.1 g. The residue was 40.1 g. of a brown glassy solid from which, after trituration with a mixture of 60 ml. of hexane and 10 ml. of benzene, 6.0 g. of crude 1,3,5-triphenylbenzene, m.p. 165–172°, was isolated. After recrystallization from benzene–hexane, it melted at 174–176°; reported m.p. 172°.¹⁸ Nitration of the substance gave 1-(*p*-nitrophenyl)-3,5-diphenylbenzene, m.p. 144–145°; reported m.p. 142–143°.¹⁸

The third fraction obtained above was carefully redistilled through a 20-cm. Vigreux column and separated into four fractions as presented in Table I. Each fraction was examined in the infrared and the spectra were compared

(17) W. Dilthey, *J. prakt. Chem.*, [2] **94**, 53 (1916).

(18) D. Vorlander, E. Fischer and H. Wille, *Ber.*, **62**, 2837 (1929).

with that of dypnone. The spectra of fractions I and II were similar to that of dypnone except that the peak at 3.35 μ . showed much stronger absorption and two new peaks at 5.86 and 5.95 μ . were present. The spectra of fractions III and IV were identical with that of dypnone. Fraction III gave a semicarbazone, m.p. and mixture m.p.'s with an authentic sample 150–152°, identical with the semicarbazone of dypnone.

TABLE I

Fraction	B.p., °C. at 0.3–0.5 mm.	n_D^{25}	Wt., g.
I	150–152	1.6060	1.99
II	152–154	1.6196	6.73
III	154–156	1.6245	5.90
IV	156–157	1.6278	13.45
Residue			2.09

Condensation of Dypnone in the Presence of Boron Trifluoride Etherate.—Dypnone (3.0 g., 0.00135 mole) was heated with 3.0 g. (0.00211 mole) of boron trifluoride etherate at 120–130° for ten minutes. After cooling, 10 ml. of benzene and 20 ml. of water were added to the mixture. The yellow precipitate (0.30 g., 11%) melted at 233–234° after recrystallization from 10 ml. of 95% ethanol. The mixture m.p. with authentic II was not depressed.

Reaction of Dypnone and Benzoyl Fluoride in the Presence of Boron Trifluoride Etherate.—Benzoyl fluoride was prepared by heating a mixture of benzoic anhydride (36.5 g., 0.162 mole) with 14 g. (0.245 mole) of potassium fluoride in a Woods metal-bath.¹⁹ Distillation of the fluoride began at 190° bath temperature. The slightly pink fluoride (13.1 g., 65%) boiled at 150–154°.

To a cooled mixture of dypnone (8.38 g., 0.04 mole) and benzoyl fluoride (4.96 g., 0.04 mole) was added slowly 14.20 g. (0.10 mole) of boron trifluoride etherate. The mixture was allowed to stand overnight at room temperature. After working up as in the preceding case, 2.00 g. (12.6%) of II, m.p. 229–233°, was obtained.

(19) A. I. Mashentev, *J. Gen. Chem. (USSR)*, **15**, 915 (1945).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

An Investigation of the Possibility of Benzopyrylium Salt Formation by Hydrocarbon Elimination from Chromens¹

BY ROBERT C. ELDERFIELD AND TE PIAO KING²

RECEIVED DECEMBER 23, 1953

In order to investigate possibilities of facile carbon–carbon bond cleavage with formation of benzopyrylium salts, 2,4-diphenyl-4-methyl-1,4-chromene and 2,4-diphenyl-2-methyl-1,2-chromene have been synthesized. No carbon–carbon bond cleavage in either of these compounds was noted under a wide variety of conditions. Alkaline and acid hydrolysis of ethyl α -cyano- β -(*o*-anisyl)- β -(9-fluorenyl)- β -phenylpropionate has been studied.

In the preceding paper³ evidence was presented to show that the formation of 2,4,6-triphenylpyrylium salts from acetophenone does not proceed by ejection of a methyl group from an intermediate pyran as had been suggested previously. Although such elimination of a hydrocarbon fragment does not occur in this particular instance, the possibility that, under favorable conditions, elimination of a methyl group from an oxygen heterocycle may occur as a result of the energy supplied by resonance stabilization of a resultant pyrylium salt remains.⁴

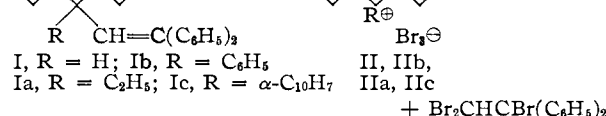
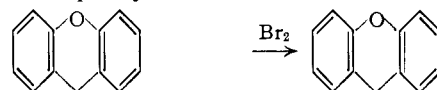
(1) The material here reported is taken from a dissertation presented by Te Piao King in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Parke–Davis and Company Fellow 1952–1953.

(3) R. C. Elderfield and T. P. King, *THIS JOURNAL*, **76**, 5437 (1954).

(4) For examples of such eliminations in other series, see ref. 3.

One case of carbon–carbon bond cleavage with the formation of an oxonium salt has been reported. Ziegler⁵ noted that when 9-(β,β -diphenylvinyl)-xanthene (I) or its 9-substituted analogs (Ia, Ib, Ic) were treated with bromine in ether at room temperature, xanthylum perbromide (II) or 9-substituted xanthylum perbromides (IIa, IIb, IIc) and 2,2-diphenyl-1,1,2-tribromoethane were formed.



(5) K. Ziegler, *Ann.*, **434**, 34 (1923).