furic acid saturated with sodium chloride. Purification was accomplished by washing with water and repeatedly precipitating the polymer from carbon disulfide solution by adding the copolymer solutions to acetone. Copolymer absorption spectra were obtained with a Cary recording spectrophotometer, Model 11, using solutions in tetrahydrofuran. The solvent was purified by distillation from calcium hydride and was used immediately thereafter. Peroxides present in solvent which has not been freshly distilled cause gelation of butadiene copolymers.

Naphthalene.—Technical naphthalene was recrystallized from ethanol and sublimed. A monomer and solvent charge consisting of 2.0 g. of naphthalene, 5.0 ml. of benzene and 8.0 g. of butadiene was employed. After tumbling for 15.75 hours a 63% conversion was obtained. After four precipitations the copolymer exhibited no absorption maxima in the range 2300–4000 Å. (concentration 17 g. per liter).

Phenanthrene.—Phenanthrene was purified by repeated distillation from sodium,[12] treatment with maleic anhydride and refluxing benzene,[13] subsequent extraction with 10% sodium hydroxide and crystallization from ethanol. A charge containing 10 ml. of benzene, 2.0 g. of phenanthrene and 8.0 g. of butadiene in the usual medium was tumbled 13 hours to yield a copolymer in 41% conversion. The purified copolymer exhibited no absorption maxima in the range 2300–4000 Å. (concentration 6.1 g. per liter). Similar results were obtained using a sample of synthetic phenanthrene.

Fluorene.—A charge consisting of 35 ml. of soap solution, 2.0 ml. of potassium persulfate solution, 0.050 g. of mercaptan, 10.0 ml. of benzene, 2.0 g. of fluorene (m.p. 112–113°) and 18.0 g. of butadiene yielded a polymer in 28% conversion after tumbling for 12.75 hours. After six precipitations the polymer showed absorption maxima at 3025, 2910, 2665, 2640 and 2580 Å. Four more precipitations produced no further change in the intensity of these maxima. Fluorene must therefore be chemically incorporated in the polymer. The spectrum of 9-methylfluorene[8] agrees well with that of the polymer.

***trans*-Stilbene.**—Eastman Kodak Company white label *trans*-stilbene was recrystallized from ethanol before use. The usual amounts of emulsifier, initiator and modifier, 10 ml. of benzene, 1.0 g. of *trans*-stilbene and 9.0 g. of butadiene were tumbled for 11 hours to yield a copolymer in 40% conversion having absorption maxima at 2690, 2590 and 2530 Å. (concentration 15 g. per liter). Bibenzyl exhibits absorption maxima at 2695, 2645, 2620, 2590, 2540 and 2490 Å. Repetition of the copolymerization with the *trans*-stilbene charge increased to 2.0 g. and butadiene decreased to 8.0 g. gave a copolymer having maxima at 2690, 2655, 2620, 2590, 2540 and 2480 Å. (concentration 16 g. per liter). After correction for the absorption due to polybutadiene the stilbene content of the copolymer prepared from the 20% stilbene charge was calculated from the extinction coefficient of bibenzyl and found to be about 1%.

***cis*-Stilbene.**—This monomer was prepared by the method of "Organic Syntheses."[14] One gram of *cis*-stilbene, 10 ml. of benzene, 9.0 g. of butadiene in the previously described emulsion yielded a product in 41% conversion after tumbling for 11 hours. No absorption maxima were noted in the range 2300–4000 Å. (concentration 15 g. per liter).

Pyrene.—Thirty-five grams of the "pure" grade of pyrene from the Gesellschaft für Teerverwertung was refluxed in 400 ml. of toluene with 5 g. of maleic anhydride for four days. To the toluene solution was added 150 ml. of 5% potassium hydroxide and the mixture was refluxed for five hours with occasional shaking. After the aqueous layer was rejected, the toluene layer was thoroughly washed with water, concentrated to about 100 ml. and allowed to cool. The crystals of pyrene were removed by filtration and recrystallized twice from ethanol to give light yellow crystals, m.p. 148.5–149.5°, having an ultraviolet spectrum in good agreement with that given by Clar[15] for pyrene free of anthracene derivatives.

Copolymers were prepared from a charge containing 10 ml. of benzene, 1.0 g. of pyrene and 9.0 g. of butadiene in the previously described recipe. After seven precipitations the copolymer exhibited absorption maxima at 3420, 3015 and 2600 Å. It is to be noted that these absorptions do not rule out 4,5-attack since 4,5-dihydropyrene has been found to absorb at nearly the same wave lengths.[16]

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[12] A. Jeanes and R. Adams, THIS JOURNAL, **59**, 2615 (1937).

[13] L. F. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1938.

[14] R. E. Buckles and K. Bremer, *Org. Syntheses*, **33**, 70 (1953); R. E. Buckles and N. G. Wheeler, *ibid.*, **33**, 85 (1953).

[15] E. Clar, *Ber.*, **69**, 1677 (1936).

[16] H. Fromherz, L. Thaler and G. Wolf, *Z. Elektrochem.*, **49**, 389 (1943).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of Indone and Some Related Compounds[1]

BY C. S. MARVEL AND C. W. HINMAN

RECEIVED JULY 6, 1954

An improved synthesis of indone has been described and this ketone has been further characterized. Some intermediates and derivatives have also been reported. Indone homopolymerized with extreme ease under a variety of conditions but copolymers with butadiene were not obtained.

Indone (I), a cyclic α,β-unsaturated ketone, was desired in order that it might be compared with benzalacetophenone[2] as a comonomer in butadiene polymerization. The literature contains one account by Stoermer and Asbrand[3] of its preparation in low yields from the condensation of indene and *p*-nitrosodimethylaniline followed by hydrolysis. We have found that indone can be prepared in fair yields from indanone (II) by conversion to 2-acetoxyindanone (III) with subsequent elimination of acetic acid. It has also been prepared by the dehydrobromination of 3-bromoindanone (IV) with *sym*-collidine and by the debromination of 2,3-dibromoindanone with sodium iodide, but these do not seem to be satisfactory synthetic reactions because of the difficulty of obtaining these bromo compounds.

Indone is a light yellow oil which polymerized with extreme ease at ordinary temperatures even in diffused light. It is a powerful vesicant and lachrymator. Inhibitors such as hydroquinone, copper, copper salts and *t*-butylcatechol would not keep it from polymerizing. Trinitrobenzene would prevent polymerization if the ketone was stored at

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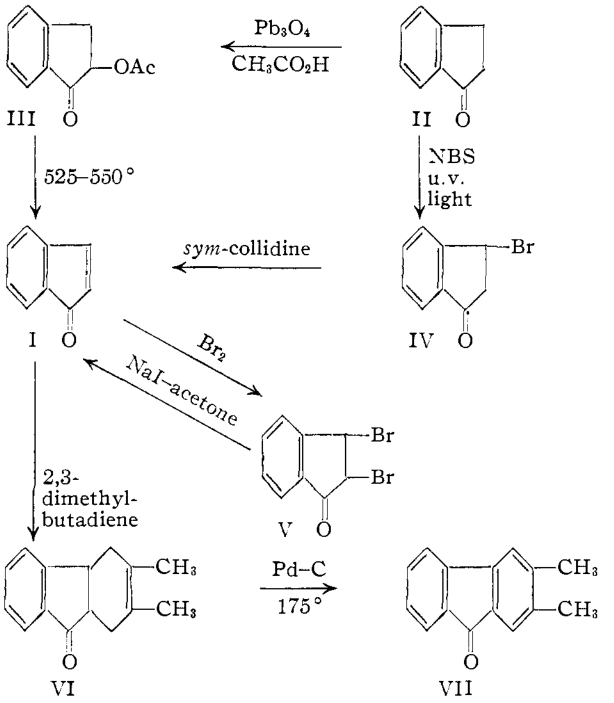
[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber in connection with the Government Synthetic Rubber Program.

[2] C. S. Marvel, W. R. Peterson, H. K. Inskip, J. E. McCorkle, W. K. Taft and B. G. Labbe, *Ind. Eng. Chem.*, **45**, 1532 (1953).

[3] R. Stoermer and E. Asbrand, *Ber.*, **64**, 2796 (1931).



0° or below but would not stabilize the monomer at room temperature. Indone homopolymerizes alone at room temperature to give a white powdery polymer which shrinks at 220° and melts at 305–310° in a capillary melting point tube. The polymer is insoluble in alcohol, acetone, ether and benzene, but dissolves in chloroform and to a lesser extent in carbon tetrachloride and carbon disulfide. The polymerization seems to be more rapid when initiated with free radicals, Lewis acids or bases, but due to the rather rapid spontaneous polymerization, it was difficult to evaluate the different types of initiation.

The structure of indone was confirmed by converting it to the known dibromo derivative[3] V which had the correct melting point and composition. It combined with 2,3-dimethyl-1,3-butadiene in the Diels–Alder reaction to yield an adduct which was readily dehydrogenated to give the known 2,3-dimethylfluorenone (VII). Infrared absorption at 1715 cm.$^{-1}$ indicates a phenyl group conjugated with carbonyl and an ultraviolet maximum at 3160 Å. further confirms the indone structure.

3-Bromoindanone was obtained by the action of N-bromosuccinimide on indanone. Its structure as the 3-bromo compound was established by the fact that it was a monobromo compound which gave phthalic acid in oxidation and it was not identical with the known 2-bromoindanone which melts much lower.

Experimental

2-Acetoxyindanone (III).—2-Acetoxyindanone was prepared essentially by the method of Criegee and Klonk,[4] but it was found that higher yields of the desired compound could be obtained by using the variation of forming the lead tetraacetate in solution from red lead and glacial acetic acid described in preparation of acetoxyacenaphthene.[5] The reaction gave the best yields when carried out at 70°. The yield of 2-acetoxyindanone, b.p. 122–123.5° at 0.30 mm., was 40% of the theoretical amount.

Pyrolysis of 2-Acetoxyindanone (III).—At a rate of about one drop per second 25 g. of 2-acetoxyindanone was dropped into a 25-mm. Pyrex column externally heated to 550 ± 5° by a Hoskins furnace and packed to a depth of 12 in. with $^1/_{16}$-in. Pyrex helices. The cracking was conducted in an inert atmosphere by introducing a slow stream of oxygen-free nitrogen at the top of the column. The pyrolysate was collected in a 50-ml. flask containing a few crystals of *sym*-trinitrobenzene cooled in a Dry Ice–acetone-bath. The pyrolysis products were washed free of acetic acid with distilled water, extracted with peroxide-free ether, washed several times with water and finally with a saturated sodium chloride solution. Final drying was effected over anhydrous magnesium sulfate. After removal of the ether under reduced pressure the residue was distilled at low pressure making no attempt to fractionate. The boiling point of the indone portion of the distillation was 58–73° at 0.9 mm. The distillate was then fractionally distilled through a 6-in. Vigreux column at low pressure. The fraction collected as pure indone weighed 3.5 g. (20.5% of the theoretical), and boiled at 61–63° at 0.9 mm., $n^{20}{}_{\mathrm{D}}$ 1.5981; infrared band at 1715 cm.$^{-1}$, ultraviolet absorption at 3160 Å.

Anal. Calcd. for C_9H_6O: C, 83.10; H, 4.66. Found: C, 83.05; H, 4.73.

A considerable amount of the ester was recovered during the distillation and when this was taken into consideration the yield approximated 50% of the theoretical amount.

Homopolymerization of Indone.—Homopolymers of indone formed readily when initiated by light at room temperature, by benzoyl peroxide at 50°, by persulfate at 30°, by mesitylmagnesium bromide at −70°, by traces of sulfuric acid at room temperature or by zinc chloride at room temperature. These polymers were white powders when precipitated from a chloroform solution by pouring the solution into methanol, and they had inherent viscosities which ranged from 0.462 to 0.478 in chloroform solution (0.25 g. polymer in 100 ml. of solvent). The melting point of the homopolymer was 305–310° with shrinking noticed at 220°. The homopolymers could be formed in bulk, solution or emulsion systems.

Attempted Copolymerization of Indone.—Several attempts were made to copolymerize indone with butadiene using the Mutual recipe.[6] A charge ratio of 90/10 butadiene/indone was used in these experiments. In each case two homopolymers were formed rather than a copolymer and these were separated into a powdery polymer and a rubbery polybutadiene when the crude product was dissolved in chloroform and poured into methanol. The twice reprecipitated polybutadiene portion gave no carbonyl absorption in the infrared.

2,3-Dibromoindanone (V).—To about 0.5 g. of indone was added dropwise a bromine–carbon tetrachloride solution until the color of the bromine solution persisted. Upon evaporation of the solution yellow crystals formed and after recrystallization from high petroleum ether these melted at 63°. This agrees with the reported melting point of 2,3-dibromoindanone.[3]

Anal. Calcd. for $C_9H_6OBr_2$: C, 37.26; H, 2.09; Br, 55.13. Found: C, 37.51; H, 2.30; Br, 54.78.

Debromination of 2,3-Dibromoindanone (V).—Four grams of 2,3-dibromoindanone was dissolved in 15 ml. of acetone and to this was added 20 ml. of sodium iodide–acetone solution (15 g. NaI/100 ml. acetone). The resulting solution was shaken and heated to the boiling point of acetone and then allowed to stand undisturbed for one-half hour. The sodium bromide was collected on a filter, and the filtrate evaporated under vacuum to remove the acetone. The residue was then taken up in ether and washed with aqueous sodium thiosulfate, water and a saturated sodium chloride solution. Final drying was effected over anhydrous magnesium sulfate. After removal of the ether under reduced pressure the residue was distilled at reduced pressure, yielding indone, b.p. 59.5–61° at 0.9 mm., $n^{20}{}_{\mathrm{D}}$ 1.5980.

Upon treatment of this product with a bromine–carbon tetrachloride solution, 2,3-dibromoindanone was again formed.

1,4,10,11-Tetrahydro-2,3-dimethylfluorenone (VI).—One gram of indone and 1.6 g. of 2,3-dimethyl-1,3-butadiene

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[4] R. Criegee and K. Klonk, *Ann.*, **564**, 1 (1949).

[5] J. Cason, *Org. Syntheses*, **21**, 1 (1941).

[6] J. W. Wilson and E. S. Pfau, *Ind. Eng. Chem.*, **40**, 530 (1948).

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 $C_{15}H_{16}O$: 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 $C_{15}H_{12}O$: 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 C_9H_7OBr: C, 51.19; H, 3.34; Br, 37.88. Found: C, 51.53; H, 3.45; Br, 37.55.

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., $n^{20}{}_D$ 1.5982.

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

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

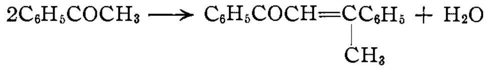
The Condensation of Acetophenone with Itself in the Presence of Lewis Acids[1]

BY ROBERT C. ELDERFIELD[2] AND TE PIAO KING[3]

RECEIVED DECEMBER 23, 1953

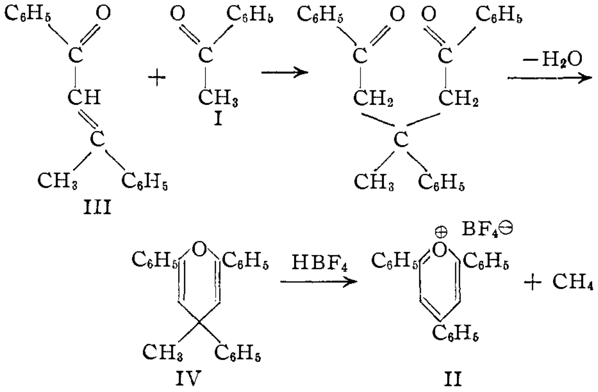
The reaction by which acetophenone condenses with itself in the presence of boron trifluoride has been reinvestigated. From a study of the by-products of the reaction, a revised reaction sequence which accounts for the formation of 2,4,6-triphenylpyrylium fluoborate has been suggested.

Dovey and Robinson[4] 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 Reihm[5] 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



$$\underset{\text{I}}{2C_6H_5COCH_3} \longrightarrow \underset{\text{III}}{C_6H_5COCH{=}\underset{CH_3}{\underset{|}{C}}C_6H_5} + H_2O$$

I III



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 Armstrong[6] and

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[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).

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