ester, b.p. 140–160° (1.5 mm.) was obtained. This was saponified by refluxing for eight hours with 150 ml. of ethanol, 40 ml. of water and 20 g. of potassium hydroxide. On working up in the usual manner, 19 g. of highly viscous dark brown acid, b.p. 165–180° (2.5 mm.) was obtained. The acid was mixed with 2.5 g. of 10% palladium charcoal and distilled over an open flame. Redistillation of the blue distillate yielded 3.5 ml. of a lower-boiling fraction containing little azulene (b.p. 70–100° at 1.5 mm.) and 3.1 ml. of a more viscous fraction containing the main portion of the azulene (b.p. 105–145°). Fraction I and the high-boiling residue were combined and subjected once more to the action of palladium–charcoal. This resulted in 3 ml. of low boiler and an additional 1.8 ml. of fraction II.

Fraction II was dissolved in 75 ml. of ethanol, mixed with 4 g. of trinitrobenzene in 125 ml. of warm ethanol and allowed to stand. The precipitate of trinitrobenzene complex weighed 2.4 g. The crude derivative was placed on an alumina column (240 × 20 mm.) and decomposed by eluting with 250 ml. of cyclohexane–benzene (2:1). Concentration of the eluate and distillation *in vacuo* yielded 0.96 g. of the desired azulene, b.p. 115–120° (1.5 mm.). The product was blue but its solutions had a violet tinge.

The trinitrobenzolate, violet-black needles from ethanol, melted at 181.5–182°.

Anal. Calcd. for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.70; H, 4.40; N, 11.06.

Purification of the picrate and tritylate proved somewhat more difficult due to their relatively great solubility in ethanol which caused coprecipitation of unreacted picric acid and trinitrotoluene. The picrate, yellowish-black needles, melted at 145°.

Anal. Calcd. for $C_{19}H_{17}N_3O_7$: C, 57.15; H, 4.29; N, 10.52. Found: C, 56.87; H, 4.34; N, 10.45.

The trinitrotoluene complex, violet-black needles, melted at 99.5–100°.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.57. Found: C, 60.49; H, 4.72; N, 10.50.

1,4-Dimethyl-8-isopropylazulene.—Reaction of 54 g. of 1,4-dimethyl-7-isopropylindan with six 10-g. portions of diazoacetic ester resulted in recovery of 16 g. of the indan (b.p. up to 120° at 2.5 mm.) and 50 g. of crude colored ester, b.p. 120–170° (1.5 mm.). Saponification of the product with 200 ml. of 80% ethanol containing 25 g. of potassium hydroxide yielded 22 g. of a very viscous brownish-green acid, b.p. 173–183° (3 mm.). Two decarboxylations and dehydrogenations in the manner described above, using 3 g. of 10% palladium–charcoal for the first run and 1.5 g. for the recovered non-azulenic material, gave 5 ml. of low-boiling material (b.p. up to 100° at 2.5 mm.) and 7.1 ml. of crude azulene, b.p. 100–146°. When solutions of the crude trialkylazulene in 50 ml. of ethanol and 4 g. of trinitrobenzene in 125 ml. of warm ethanol were mixed, 3.2 g. of trinitrobenzene complex precipitated.

The azulene was regenerated by chromatography over alumina, cyclohexane–benzene (2:1) serving as eluent. Distillation yielded 0.91 g. of viscous blue liquid boiling at 118–121° (1.6 mm.). Its solutions had a weak violet tinge. The derivatives of this azulene were more soluble in ethanol than those of the trimethyl analog so that purification proved difficult. The trinitrobenzolate, violet-black needles, melted at 147.5–148°.

Anal. Calcd. for $C_{21}H_{21}N_3O_6$: C, 61.34; H, 5.14; N, 10.21. Found: C, 60.98; H, 4.92; N, 10.03.

DEPARTMENT OF CHEMISTRY
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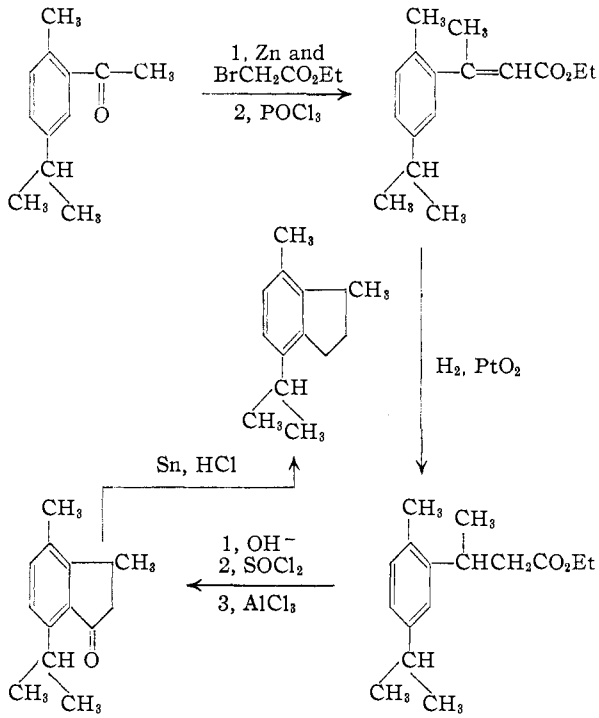
1,7-Dimethyl-4-isopropylindan

BY WERNER HERZ

In connection with another problem we had occasion to investigate the synthesis of 1,7-dimethyl-4-isopropylindan. The most obvious approach, *i.e.*, preparation of the indan by treatment of the previously reported 4-isopropyl-7-methylindanone[1,2] with the methyl Grignard reagent followed by dehydration and reduction, suffered from the low yields encountered in the preparation of the starting material. An attempt to prepare the indanone by condensation of *p*-cymene with β-chloropropionyl chloride[3] resulted in a mixture of the desired product with its isomer 4-methyl-7-isopropylindanone, although the Friedel–Crafts acylation of *p*-cymene ordinarily favors the position ortho to the methyl group.[4] A successful synthesis in 24% over-all yield was finally accomplished by means of the following sequence of reactions



Acknowledgment.—This work was aided by a grant from the Research Council of the Florida State University.

Experimental[5]

Ethyl β-(2-Isopropyl-5-methyl)-phenylcrotonate.—The Reformatsky reaction of ethyl bromoacetate with 2-aceto-*p*-cymene proved erratic when carried out in the usual way. The following method was satisfactory and reproducible. A mixture of 176 g. (1 mole) of 2-aceto-*p*-cymene,[6] 165 g. (1 mole) of ethyl bromoacetate and 350 ml. of benzene was refluxed for one hour in a flask fitted with a Stark and Dean moisture trap. A total of 65 g. of 20 mesh zinc, freshly cleaned with 5% hydrobromic acid, washed and dried in a vacuum, was then added in small portions. After the vigorous reaction had slackened, the mixture was refluxed for 15 minutes. Addition of 80 g. of ethyl bromoacetate and 33 g. of zinc was accompanied by another exothermic reaction. After an additional 15 minutes at reflux, 40 g. of bromoester and 17 g. of zinc was added. The mixture was refluxed for another hour and worked up in the usual manner.[7] Distillation of the dried ether extracts yielded 181 g. of a crude fraction boiling at 120–150° (3.5 mm.) which was dehydrated by refluxing with 80 ml. of phosphorus oxychloride and 1 l.

(1) J. W. Cook, C. L. Hewett, W. W. Mayneord and E. Roe, *J. Chem. Soc.*, 1727 (1934).
(2) O. Blum-Bergmann, *ibid.*, 1030 (1935).
(3) F. Mayer and P. Müller, *Ber.*, **60**, 2278 (1927).
(4) A. Claus, *ibid.*, **19**, 232 (1886).
(5) Melting points are uncorrected.
(6) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.
(7) "Organic Reactions" Vol. I, 1941, p. 17.

of benzene. The cold mixture was poured over ice and extracted with ether. The extracts were thoroughly washed with water, sodium bicarbonate solution and again with water. The dried ether solution was distilled, a fraction boiling at 115–125° (2 mm.) and weighing 136 g. (55%) being collected. The analytical sample boiled at 103–104° (1 mm.), $n^{25}D$ 1.5211.

Anal.[8] Calcd. for $C_{15}H_{22}O_2$: C, 78.02; H, 9.01. Found: C, 77.98; H, 8.79.

Ethyl β-(2-Isopropyl-5-methyl)-phenylbutyrate.—A solution of 32 g. of the unsaturated ester in 150 ml. of ethanol was reduced with 0.3 g. of platinum oxide. The calculated amount of hydrogen was taken up in three hours. Removal of solvent followed by distillation gave 30 g. of product (94%) boiling at 95–110° (1.3 mm.). The analytical sample boiled at 95–96° (1 mm.), $n^{25}D$ 1.4922.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.36; H, 9.74. Found: C, 78.04; H, 9.66.

β-(2-Isopropyl-5-methyl)-phenylbutyric Acid.—Saponification of 29 g. of the ester with 125 ml. of 90% ethanol containing 15 g. of potassium hydroxide yielded a viscous oil, b.p. 140–150° (2 mm.), wt. 21.8 g. (84%), which could not be induced to crystallize. The analytical sample boiled at 141–142° (1.8 mm.), $n^{25}D$ 1.5085.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.84; H, 8.93.

3,4-Dimethyl-7-isopropylindanone.—A mixture of 20 g. of the acid and 25 g. of thionyl chloride was heated on the steam-bath for 2 hours and allowed to stand overnight. Distillation gave 20.5 g. of acid chloride, b.p. 105–115° (2 mm.) which was poured cautiously into 50 ml. of dry benzene containing 15 g. of aluminum chloride. After 12 hours the mixture was decomposed with ice–hydrochloric acid and extracted with ether. Distillation of the washed and dried extracts gave 13.5 g. of indanone (73%), b.p. 95–115° (1.5 mm.). The analytical sample boiled at 96–98° (1 mm.), $n^{25}D$ 1.5412.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.11; H, 8.97. Found: C, 83.19; H, 8.81.

1,7-Dimethyl-4-isopropylindan.—Reduction of 88 g. of the indanone with amalgamated zinc in the manner described earlier[9] yielded 52 g. of a fraction boiling in the range 60–90° (2 mm.) and 23 g. boiling at 95–125° (2 mm.), apparently largely unreduced ketone. On redistillation 41 g. (79% based on recovered material) of indan was collected at 78–83° (2 mm.). The analytical sample boiled at 76–78° (1.5 mm.), $n^{25}D$ 1.5200.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.00; H, 10.72.

(8) Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

(9) W. Herz, THIS JOURNAL, **73**, 4295 (1951).

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The Purification and Stability of Hypophosphorous Acid

BY WILMER A. JENKINS AND RICHARD T. JONES

Hypophosphorous acid, H_3PO_2, has been the subject of extensive experimental investigation,[1] but to our knowledge, the acid previously used has always contained from one to five mole per cent. phosphorous acid. In the course of some kinetic and analytical investigations of this substance, it became necessary to prepare it in a very pure form. The following procedure was devised to meet the purpose, and represents, as far as we know, a method which has never before been tried with hypophosphorous acid. This method yields solid hypophosphorous acid containing less than 0.1 mole per cent. phosphorous acid and less than 0.1 mole per cent. phosphoric acid.

(1) Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, chapter 6.

Purification of Hypophosphorous Acid.—Hypophosphorous acid from almost any source will serve as a starting material, as long as it is about 10 *f*. The commercial grade 50% acid (Merck and Co., Inc.), which usually contains from two to three mole per cent. phosphorous acid, meets this requirement and was used in all of our preparations. If more dilute acid from another source is used, it is advisable to concentrate it by vacuum desiccation before proceeding with this purification method.

About 600 ml. of concentrated hypophosphorous acid is placed in a one-liter filtering flask, the side-arm of which is connected to a water aspirator. Through a two-hole stopper in the top of the flask run a thermometer and a coarse gas dispersion tube, which opens below the liquid surface and is connected to a source of dry nitrogen. The flask rests on a hot-plate. After all of the air has been thoroughly flushed out of the system with nitrogen, the aspirator and hot-plate are turned on, and the nitrogen flow is cut down to a small stream of bubbles. The hot-plate is regulated so that the temperature remains around 40° during the evaporation. The evaporation is continued until the volume of the solution is about 300 ml., at which point the evaporation will appear to cease. The hot-plate is now turned off and the solution allowed to cool. The nitrogen supply and the aspirator are then turned off and the liquid in the flask poured into a wide-mouthed erlenmeyer flask which is stoppered well and placed in a Dry Ice–acetone-bath. After a few hours in the bath, the contents of the flask will freeze; in some cases, it may be necessary to scratch the walls of the flask to induce solidification. The flask is then removed from the bath and allowed to stand in a cold room or refrigerator (~5°) for about 12 hours, after which time the flask contents should be from 30 to 40% liquid.

The following operations must be carried out in a cold room.[2] The mixture is now filtered by suction through a *rapid*, retentive paper such as Whatman No. 44. The filtrate is discarded, the solid pressed dry on the paper, transferred to a crystallizing dish, and allowed to stand in the cold until about 20 to 30% of it liquefies. It is then refiltered, allowed to stand to 30% liquefaction, and filtered a third time. After the last filtration, the solid is stored over $Mg(ClO_4)_2$ in an evacuated desiccator in a cold room.

This entire procedure is very empirical; nevertheless, it yields a very pure product. For best results, careful attention should be paid to the following points: (a) the temperature should not rise above 45° during the evaporation process. (b) If the evaporation is not continued until a minimal amount of water is left in the acid, the mixture may liquefy completely in a few hours after it is removed from the Dry Ice–acetone-bath. This can usually be avoided if the liquid is evaporated to about half its original volume, at which point the evaporation will appear to cease. (c) All operations involving solid hypophosphorous acid must be carried out at temperatures well below its melting point (26.5°). A cold room at 5° is entirely satisfactory in this regard.[2] (d) At least two or three filtrations, with partial liquefaction in between, are essential. The yield in this preparation is necessarily low, about 10%.

If large crystals of this product are desired, they can be prepared by recrystallizing the white solid from *n*-butanol. (The high solubility of hypophosphorous acid in the lower alcohols renders them impractical for recrystallization purposes.) Just enough *n*-butanol is added to the solid to dissolve it at room temperature, and the solution is then cooled in a salt-ice-bath (−20°) to deposit crystals. One of us (W. A. J.) carried out ten such cycles; analysis of the final product for phosphorous acid showed no increase in purity over that obtained from two filtrations as described above. No attempt was made to remove all of the *n*-butanol from the crystals, and it is not known whether or not the crystals contained *n*-butanol of crystallization.

Analysis of the Purified Product.—Aqueous solutions of the white solid from the above procedure were analyzed for hypophosphorous and phosphorous acids by an iodometric

(2) A referee has suggested to us that in lieu of a cold room, the apparatus described by Schwab and Wichers, *J. Research Natl. Bur. Standards*, **32**, 253 (1944), could be used. We feel that this point is well taken, but we cannot guarantee success if this method is used, since we have not tried it.