that *tert*-BuOD was used instead of *tert*-BuOH in the dechlorination of 7,7-dimethoxy-1,2,3,4-tetrachloro-2-norbornene. The ketone was purified by preparative glpc: ir 1770 cm^{-1} (C=O); nmr τ 8.05 (m, 2 H, exo C-5 and C-6 protons) and 8.83 (m, 2 H, endo C-5 and C-6 protons). This spectrum indicated ≥95% D at all C-1, C-2, C-3, and C-4 positions.

2,3-Dideuterio-2-norbornen-7-one (11).—The vinyl protons of 7,7-dimethoxynorbornene[16] were exchanged with lithium cyclohexylamide-*N*-D and cyclohexylamine-*N*-D_2[20] at 25°. The ketal was purified by preparative glpc. The nmr spectrum indicated *ca.* 1.4 atom D per molecule in the olefinic region (τ 4.00), and only the vinyl protons were exchanged under these conditions. Mass spectral analysis (AEI Model MS 9) indicated that the total atom D per molecule was 1.38. The deuterio ketal was converted to **11** in the normal manner[16] and purified by preparative glpc: ir 1770 cm^{-1} (C=O); nmr indicated *ca.* 1.4 atom D per molecule in the olefinic region (τ 3.48).

7-Norbornanone (13).—Hydrogenation of **1** according to the procedure of Gassman and Pape[18] gave **13**: mp 77–79° (lit.[16] mp 79.5–80.5°); ir 1785 cm^{-1} (C=O); nmr (CS_2, external TMS) showed a multiplet at τ 7.80–8.60.

endo-**Tricyclo[3.2.1.$0^{2,4}$]octan-8-one (14)** was obtained from M. A. Battiste[21] and was purified by preparative glpc: mp 62–69° (lit. mp 58–61°[21] and 71–72°[22]); ir 1760 cm^{-1} (C=O); nmr (external TMS) τ 7.78 (m, 2 H) and 8.0–9.3 (m, 8 H).

2-Norbornenone (15) was obtained from R. K. Lustgarten and was purified by preparative glpc: nmr τ 3.48 (m, 1 H, olefinic proton), 3.90 (m, 1 H, olefinic proton), 6.85 (m, 1 H, bridgehead proton), 7.10 (m, 1 H, bridgehead proton), and 7.68–8.37 (m, 4 H).

9-Benzonorbornenone (2).—Oxidation of *anti*-9-benzonorbornenol[17] in the same manner as that described by Bartlett and Giddings[17] led to the desired product, which was purified by preparative glpc: ir 1770 cm^{-1} (C=O); nmr τ 2.82 (broad peak, 4 H, aromatic protons), 6.78 (m, 2 H, bridgehead protons), 7.92 (m, 2 H, exo C-2 and C-3 protons), and 8.76 (m, 2 H, endo C-2 and C-3 protons). *Anal.* Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.49; H, 6.27.

Esr Spectra.—The radical anions were prepared under vacuum (*ca.* 0.1 μ) by the reduction of ketones and diketones with alkali metals using standard procedures described elsewhere.[2a] All reactions were carried out in a sealed-off glass apparatus that included a cell for esr measurement. Esr spectra were obtained with a Varian 4502 spectrometer with a "field dial" using 100-kc field modulation. Low-temperature experiments were made using a Varian variable-temperature control unit. The temperature reading was found to be accurate within ±3°. Hyperfine frequencies were calibrated using a Harvey-Wells proton gaussmeter and a Beckman frequency counter.

A. Reduction of 7-Norbornenone (1).—The ketone (10 mg) in DME (*ca.* 2.5 ml) was treated with potassium at −78°. The solution became yellow-orange at 25° and the esr spectrum was resolved into a 1:2:1 triplet, a_H = 2.69 G (2 H). Each peak was further split into a 1:4:6:4:1 quintet, a_H = 0.44 G (4 H). A 1:1 doublet (a = 15.2 G) was detected that was symmetrically disposed about the center peak and slightly less intense.[14] The use of THF instead of DME as solvent gave similar results at 25°, a_H = 2.59 G (2 H) and a_H = 0.41 G (4 H). A 1:1 doublet, a = 15.2 G, was also observed. When the ketone (10 mg) in DME (*ca.* 2 ml) was treated with sodium at 25°, only a single peak (width *ca.* 13 G) was detected. All attempts to obtain a resolved spectrum at temperatures ranging from −80 to 50° failed.

B. Reduction of 9, 10, and 11.—The ketones in DME were treated with potassium at −78°. The following values were obtained at 25°: from **9**, a_H = 2.69 G (2 H) and a_H = 0.44 G (2 H); from **10**, a_H = 2.65 G (2 H) and a_H = 0.46 G (2 H); and from **11**, a_H = 2.68 G (2 H) and a_H = 0.4 G (2 H).

C. Attempted Reduction of 13, 14, and 15.—The ketones in DME were treated with potassium at −78°. No esr signals were observed at temperatures ranging from −78 to 25°. The results were the same when the solutions were maintained at 25° for several hours.

D. Reduction of Bicyclo[2.2.2]oct-5-ene-2,3-dione (7).—The diketone[9] (1 mg) in DME (*ca.* 1.5 ml) was treated with potassium at 25°. The spectrum was well simulated using values of a_H = 2.68 G (2 H) and a_H = 0.46 G (4 H). Additional hyperfine splitting of a = 0.1 *G* was also observed, but it was not possible to determine the multiplicity. This hyperfine splitting is most likely due to the potassium cation. When the signal level was increased by a factor of 100, the hyperfine splitting by ^{13}C in natural abundance was easily observed. The value obtained, a_C = 6.12 G, is attributed to the carbonyl carbon.[11]

E. Reduction of 9-Benzonorbornenone (2).—The ketone (25 mg) in DME (*ca.* 3.5 ml) was treated with potassium at −78°. The best resolved spectra were recorded at −40°, where a 1:2:1 triplet, a_H = 2.35 G (2 H), was observed. Each peak was split into 11 additional peaks and possibly more, with a separation of 0.09 G. Some of this additional hyperfine splitting is most likely due to the potassium cation. In another experiment, the ketone (10 mg) in DME (*ca.* 2 ml) was treated with sodium at 25°. At −40° the relative intensities of the various lines were in accord with a triplet splitting of a_H = 2.35 G (2 H) and a 1:1:1:1 quartet splitting of a_{Na} = 0.7 G (1 Na).

F. Reduction of Benzobicyclo[2.2.2]oct-5-ene-2,3-dione (8).—The diketone[9] (2 mg) in DME (*ca.* 2 ml) was treated with potassium at 25°, and a triplet, a_H = 2.35 G (2 H), was observed. Additional splitting, as found in the reduction of **2**, was detected. In another experiment, the diketone (2 mg) in DME (*ca.* 3 ml) was treated with sodium at 25°. The best resolved spectra were recorded at −20°, where the following values were obtained: a_H = 2.35 G (2 H), a_{Na} = 0.73 G (1 Na, 1:1:1:1 quartet splitting), a_H = 0.18 G (2 H), and a_H = 0.09 G (4 H).

Registry No.—**1**, 694-71-3; **2**, 6165-88-4; **3**, 17441-59-7; **4**, 17441-60-0; **7**, 17547-68-1; **8**, 17547-69-2; **9**, 28610-76-6; **10**, 28610-77-7; **11**, 28610-78-8.

Acknowledgment.—The following substances were obtained as gifts: **14** from Professor M. A. Battiste;[21] **15** from Dr. R. K. Lustgarten; and **7** and **8** from Professor G. A. Russell.[9] We are grateful to Professor Russell, who made available information prior to publication and provided helpful discussion.

(20) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *ibid.*, **84**, 244 (1962).
(21) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).
(22) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967).

Reactions of Some Methylene Ketones with Dimethyl Phthalate. A New Route to 2-Substituted 1,3-Indandiones

WILLIAM A. MOSHER* AND ROBERT W. SOEDER

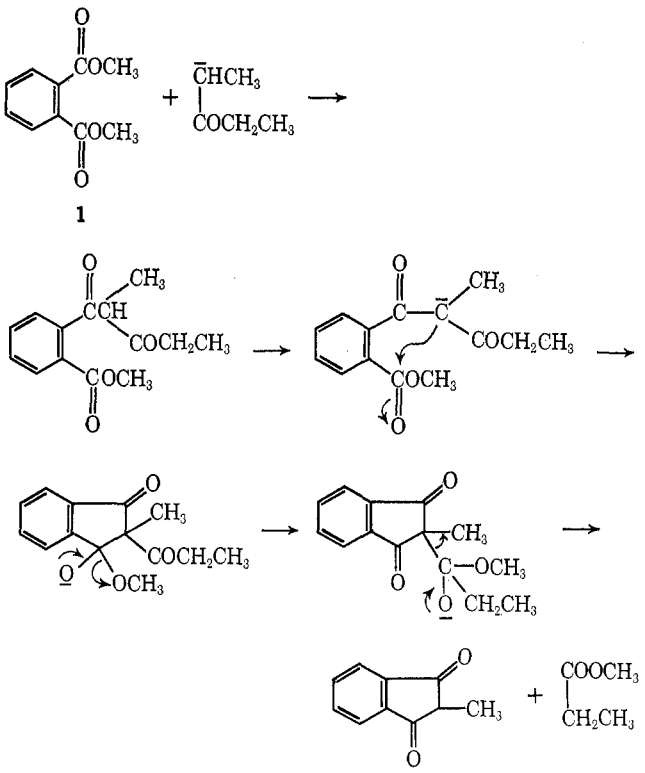
Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received September 8, 1970

The reactions of methyl ketones with dialkyl phthalates to yield 2-acyl-1,3-indandiones have been the object of several investigations.[1-3] The present note describes the reactions of ketones containing one or two methylene groups adjacent to the carbonyl, hereafter called methylene ketones, with dimethyl phthalate (**1**). Symmetric and unsymmetric methylene ketones have been condensed with **1** in the presence of sodium methoxide or sodium hydride. 3-Pentanone and 4-heptanone gave respectively 2-methyl- and 2-ethyl-1,3-indandione. The mechanism shown in Scheme I is

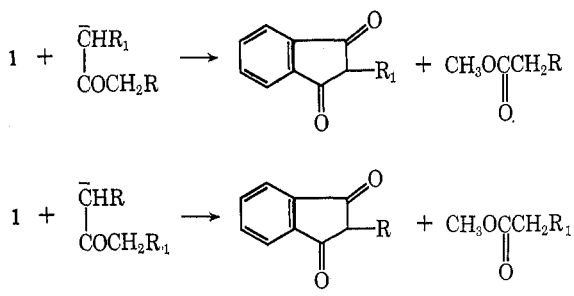
(1) E. Schwerin, *Chem. Ber.*, **27**, 104 (1894).
(2) L. B. Kilgore, J. Ford, and W. C. Wolfe, *Ind. Eng. Chem.*, **34**, 494 (1942).
(3) S. Shapiro, K. Geiger, and L. Freedman, *J. Org. Chem.*, **25**, 1860 (1960).

SCHEME I



suggested for the reaction of 3-pentanone with phthalate **1**. The identification of methyl propionate as one of the products of this reaction supports the above mechanism.

In the reaction of the unsymmetric methylene ketones with phthalate **1**, a combination of steric and electronic factors are involved, since there is the possibility of the formation of two different anions.



The reaction of 3-hexanone with **1** gave a mixture of 2-methyl- and 2-ethyl-1,3-indandiones in a ratio of 3.3:1. 1-Phenyl-2-butanone yielded 2-phenyl- and 2-methyl-1,3-indandiones in the ratio of 1.55:1. Reaction of **1** with methylene pyridyl ketones, such as 1-(2-pyridyl)- and 1-(4-pyridyl)-2-butanones and 1-phenyl-3-(2-pyridyl)- and 1-phenyl-3-(4-pyridyl)-2-propanones, gave 2-(2-pyridyl)- and 2-(4-pyridyl)-1,3-indandiones (**2** and **3**), respectively, indicating that the activating effect of the pyridine ring dictates which anion is formed.

Propiophenone, a methylene ketone containing one methylene group instead of two as the ketones above mentioned, reacted with **1** to give 2-methyl-1,3-indandione.

Experimental Section[4]

Reaction of 3-Pentanone with Phthalate 1.—To a dispersion of sodium hydride (50% in mineral oil, 24 g) in anhydrous benzene (500 ml) was added slowly a mixture of 3-pentanone (41 g) and phthalate **1** (100 g), and the mixture was refluxed for 15 hr. The deep red solid formed on cooling was collected by filtration, dried *in vacuo*, and dissolved in water (750 ml), and the solution was acidified with concentrated HCl to give a 68% yield of 2-methyl-1,3-indandione, mp 83–84°, identical (mixture melting point and ir) with an authentic sample.[5]

In a second preparation, using freshly distilled solvent and reactants, the reaction mixture, after the 15-hr refluxing period, was distilled almost to dryness. Four cuts were taken. The first three cuts contained benzene and a little methanol. The fourth cut contained methyl propionate, identified by comparison (vpc and ir) with an authentic sample.

Reaction of 4-Heptanone with Phthalate 1.—The crude product obtained by condensing 4-heptanone with phthalate **1** as in the procedure described above was chromatographed on alumina (elution with chloroform) to give a 54% yield of a pale yellow compound of mp 51–51.5°, identical (mixture melting point and ir) with an authentic sample of 2-ethyl-1,3-indandione.[5]

Reaction of 3-Hexanone with Phthalate 1.—A mixture of 3-hexanone (1 g), dimethyl phthalate **1** (1.94 g), benzene (1.5 ml), and sodium methoxide (0.54 g) was heated in a sealed tube at 100° for 48 hr. The cooled tube was opened, the charge filtered into a Dry Ice trap, the filtrate flash distilled into another Dry Ice trap, and the liquid analyzed by vapor phase chromatography. 2-Methyl- and 2-ethyl-1,3-indandione in molar ratio 3.3:1 were obtained.

Reaction of 1-Phenyl-2-butanone with Phthalate 1.—A mixture of 1-phenyl-2-butanone (19.8 g) and **1** (19.4 g) was added slowly to sodium methoxide (5.4 g) in anhydrous benzene (175 ml) and heated to reflux. After 48 hr, the red reaction mixture was cooled and the solid washed with ether, dried *in vacuo*, dissolved in water, and acidified with concentrated HCl. The resultant red oil was extracted with benzene and the benzene layer, after drying over sodium sulfate, was chromatographed on an alumina column made up with benzene. The first band gave 2-methyl-1,3-indandione (1 g), mp 80° [mmp (with an authentic sample) 79–80°] and the second band yielded 2-phenyl-1,3-indandione (2.15 g) as orange plates, mp 144–146° (ethanol) (lit.[6] 145°). The molar ratio of 2-phenyl- to 2-methyl-1,3-indandione was 1.55:1.

The dioxime of 2-phenyl-1,3-indandione melted at 197–199° (lit.[7] 193–196°).

2-(2-Pyridyl)-1,3-indandione (2). Method A.—A solution of 1-(2-pyridyl)-2-butanone[8] (14.9 g) and phthalate **1** (19.4 g) in anhydrous benzene (50 ml) was added to sodium methoxide (5.4 g) in anhydrous benzene (150 ml). The mixture was refluxed for 48 hr, then cooled, and filtered. The precipitate was dissolved in water. Neutralization of the aqueous solution with concentrated HCl gave **2** as a yellow solid, mp 278–281 (ethanol). An additional amount of **2** was obtained by extracting the mother liquor with water and neutralizing the aqueous solution with concentrated HCl. A total yield of 3.2 g was obtained. Compound **2** was identified by mixture melting point determination with an authentic sample prepared from phthalic anhydride and 2-picoline.[9]

Method B.—A solution of 1-phenyl-3(2-pyridyl)-2-propanone (14.5 g) (prepared by the procedure of Uhlemann,[10] with the exception that phenylacetyl chloride was used in place of ethyl phenylacetate) and compound **1** (13.3 g) in anhydrous benzene (100 ml) was added to sodium methoxide (4.0 g) in anhydrous benzene (125 ml) under nitrogen. The reaction mixture was refluxed for 88 hr, allowed to cool, and poured into water, and

(4) Melting points were taken in a Thomas-Hoover capillary melting point apparatus and are uncorrected. For high melting point compounds a sealed capillary tube was used. The infrared spectra were determined in potassium bromide pellets with a Baird Model B recording spectrophotometer. Elemental analyses were performed by Dr. A. Bernhardt, Microanalytisches Laboratorium Max Planck Institute für Kohlenforschung, Mulheim (Ruhr), West Germany.

(5) C. F. Koelsch and D. J. Byers, *J. Amer. Chem. Soc.*, **62**, 560 (1940).

(6) F. Nathanson, *Chem. Ber.*, **26**, 2576 (1893).

(7) A. Porai-Koshits and I. Chezhevskaga, *Zh. Obshch. Khim.*, **26**, 842 (1956).

(8) N. N. Goldberg, L. B. Barkley, and R. Levine, *J. Amer. Chem. Soc.*, **73**, 4301 (1951).

(9) K. Zalukaev and E. Vanag, *J. Gen. Chem. USSR*, **27**, 3314 (1957).

(10) I. E. Uhlemann, *J. Prakt. Chem.*, **14**, 281 (1961).

the benzene layer was extracted twice with water. The combined water layers were extracted with chloroform, treated with concentrated HCl to pH 7, and again extracted with chloroform. The chloroform layer was dried and chromatographed on an alumina column made up with benzene (elution with chloroform) to give, upon distillation of the solvent and recrystallization of the residue from ethanol–chloroform, 0.4 g of **2**, mp 278–280°, identical with an authentic sample (mmp 277–279°).

2-(4-Pyridyl)-1,3-indandione (3). Method A.—1-(4-Pyridyl)-2-butanone[11] was condensed with compound **1** following the procedure above described for compound **2** (method A). Recrystallization from ethanol gave **3** as yellow crystals, mp 309–312°. The identity of **3** was established by mixture melting point determination with an authentic sample prepared from phthalide and picolinaldehyde (see method C).

Method B.—1-Phenyl-3(4-pyridyl)-2-propanone, prepared by the procedure above reported for 1-phenyl-3(2-pyridyl)-2-propanone, was condensed with compound **1** under the conditions above described for compound **2** (method B). Chromatography and recrystallization from ethanol gave **3** as yellow crystals, mp 313–316°, identical (mixture melting point) with an authentic sample.

Method C.—This method is similar to that used by Horton and Murdock for preparing 2-aryl-1,3-indandiones.[12] Sodium methoxide (14 g) was added slowly to a solution of phthalide (33.5 g) and picolinaldehyde (27 g) in ethanol (100 ml) under nitrogen, and the mixture was heated at reflux for 3 hr. The red precipitate formed on cooling was collected by filtration and dissolved in hot water (750 ml), and the solution was made slightly acid with concentrated HCl. The precipitate crystallized from ethanol gave a 40% yield of **3** as yellow crystals, mp 312–314°.

Anal. Calcd for $C_{14}H_9NO_2$: N, 6.28. Found: N, 5.91.

Reaction of Propiophenone with Phthalate 1.—A mixture of propiophenone (33.5 g) and compound **1** (48.5 g) was added to a dispersion of sodium hydride (50% in mineral oil, 12 g) in anhydrous benzene (500 ml). The reaction mixture was refluxed for 22 hr, cooled, and filtered. The red solid was washed with ether, dried *in vacuo*, and dissolved in water, (800 ml), and the solution was acidified with concentrated HCl. Chromatography of the resultant yellow oil on an alumina column made up with benzene–hexane (elution with chloroform) gave 11 g (27.5%) of 2-methyl-1,3-indandione as yellow solid, mp 78–80°.

Registry No.—**1**, 131-11-3; 3-pentanone, 96-22-0; 4-heptanone, 123-19-3; 3-hexanone, 589-38-8; 1-phenyl-2-butanone, 1007-32-5; propiophenone, 93-55-0.

Acknowledgment.—We gratefully acknowledge the valuable assistance of Dr. Mario F. Sartori in connection with this research.

(11) C. Osuch and R. Levine, *J. Org. Chem.*, **22**, 939 (1957).
(12) R. L. Horton and K. C. Murdock, *ibid.*, **25**, 938 (1960).

Heterocyclic Analogs of Fulvene and Fulvalene. III. $\Delta^{3,3'}$-Bi-3*H*-indazole

JOHN H. M. HILL, D. M. BERKOWITZ, AND K. J. FREESE

Department of Chemistry, Hobart and William Smith Colleges, Geneva, New York 14456

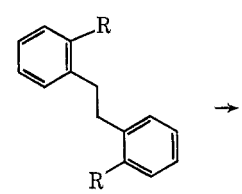
Received September 8, 1970

In an earlier part of this series we described the synthesis of $\Delta^{2,2'}$-bi-2*H*-benzimidazole (I).[1] Here we report the synthesis and properties of the remaining dibenzotetraazafulvalene, $\Delta^{3,3'}$-bi-3*H*-indazole (II). A common intermediate in all routes to this compound was 3,3′-bi-1*H*-indazole (III); the routes differed only in the method of synthesis of III and its subsequent oxidation.

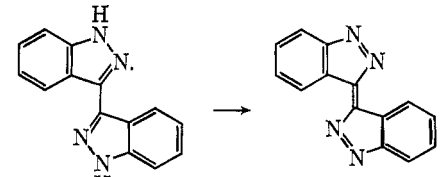
(1) J. H. M. Hill, *J. Org. Chem.*, **28**, 1931 (1963).

The most satisfactory of the several pathways to III investigated involved the direct synthesis of the biindazole from a suitably substituted bibenzyl derivative. 2,2′-Dinitrobibenzyl (IV) was simultaneously reduced and acetylated by catalytic hydrogenation in acetic anhydride, and the resulting 2,2′-diacetamidobibenzyl (V) was nitrosated with nitrosyl chloride. Nitrogen trioxide or nitrogen tetroxide was found to be less satisfactory in this particular case.[2] The resulting *N*,*N*′-dinitroso-2,2′-diacetamidobibenzyl (VI) was isomerized to bibenzyl-2,2′-diazoacetate (VII) by gentle warming in solution.[3] Cyclization of VII to III occurred when the temperature was raised to reflux.[4]

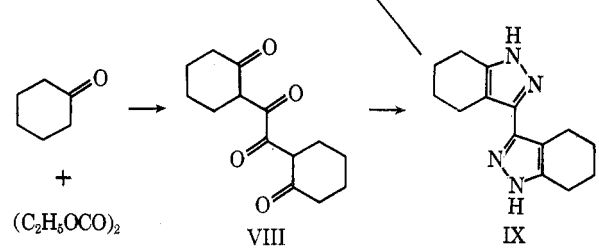
In this sequence all steps except the final ring closure proceeded with good yield. This last step gave erratic results and the reaction product was contaminated with appreciable amounts of tar, which was difficult to remove. Carrying out the rearrangement and cyclization in a variety of other solvents did not improve the yield or produce a cleaner product. The following yields are typical of those obtained in other solvents: C_6H_6, 29%; $CHCl_3$, 11%; CCl_4, 14%; *tert*-BuOH, 23%; C_6H_{12}, 14%.



IV, R = NO_2
V, R = $NHCOCH_3$
VI, R = $N(NO)COCH_3$
VII, R = N_2OCOCH_3



III II



$(C_2H_5OCO)_2$ VIII IX

A second successful stepwise route to III was developed: cyclohexanone condensed with ethyl oxalate to yield the tetraketone VIII. Examination of the –OH and –C=O absorbances in the infrared spectrum of VIII indicated that it was almost totally enolized. Treatment of VIII with hydrazine cyclized it to the bipyrazole (IX) which was aromatized to III by prolonged heating with palladium catalyst. Overall, this

(2) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).
(3) The loss of the nitroso function was monitored by infrared; this was complete in about 5 hr.
(4) R. Huisgen and H. Nakaten, *Justus Liebigs Ann. Chem.*, **586**, 84 (1954).