A Procedure for Acetate Pyrolysis. The Preparation of 2-Cyclohexenone

KENNETH L. WILLIAMSON, RICHARD T. KELLER, GUNTHER S. FONKEN, JACOB SZMUSZKOVICZ, AND WILLIAM S. JOHNSON

Departments of Chemistry of the University of Wisconsin, Madison, Wis., and of Stanford University, Stanford, Calif.

Received December 12, 1961

Pyrolysis of 2-acetoxycyclohexanone by conventional procedures gave poor yields of 2-cyclohexenone accompanied by much cyclopentene. Pyrolysis at reduced pressure in a recycling apparatus described here, however, afforded 2-cyclohexenone in yields exceeding 90%.

The course of the pyrolysis of 2-acetoxycyclohexanone by the usual procedure—*i.e.*, allowing the ester to flow down a hot tube packed with glass beads—was found to be particularly dependent upon the amount of carbon deposited in the pyrolysis tube, which in turn is a function of the pyrolysis temperature and contact time. At 330° the yield of cyclohexenone was 25%; 52% of the acetate was recovered. Increasing the temperature to 500° caused a reduction in the yield of cyclohexenone to 22–36%.[1] At this temperature no unpyrolyzed acetate could be recovered; however, a low-boiling substance was formed in 25–62% yield. This material was cyclopentene as shown by comparison of the dibromide and the 2,4-dinitrobenzenesulfenyl chloride adduct with authentic derivatives.[1c] Phenol was also formed either by disproportionation of cyclohexenone as noted by Bartlett and Woods[2] in the dehydration of 2-hydroxycyclohexanone over alumina at 310–320°, or by dehydrogenation of cyclohexenone catalyzed by the carbon which was produced in the pyrolysis column (see below). The infrared absorption spectrum of a sample of the noncondensable gaseous fraction produced on pyrolysis of the keto acetate at 500° indicated the presence of carbon monoxide, carbon dioxide, and methane.

It seemed reasonable that cyclohexenone might be the precursor of cyclopentene, especially in view of the photolysis of cyclohexanone to cyclopentane at 140–325°.[3] In an effort to test this hypothesis, cyclohexenone was treated at 510–520°, in a clean pyrolysis apparatus, in a manner analogous to the pyrolysis of 2-acetoxycyclohexanone. However, no low-boiling product was obtained, and the cyclohexenone was recovered unchanged except for a small amount of the disproportionation products mentioned above. Cologne and Dubin[1c] have reported similar results. When cyclohexenone was pyrolyzed at 450° over lump coconut charcoal in the recycling pyrolysis apparatus (see below), the only volatile organic product isolated was phenol; surprisingly no cyclopentene was detected. The production of phenol is probably the result of dehydrogenation of cyclohexenone rather than disproportionation, because cyclohexanone was not found.

In the pyrolysis of the acetoxy ketone, lower temperatures gave higher yields of product, but the conversion was low. Therefore, it was decided to investigate a procedure that was reported for 2-acetoxycyclopentanone, namely pyrolysis at 10 mm. by allowing the acetate to boil up into a column packed with activated carbon heated to 180–190°.[4]

In order to pyrolyze 2-acetoxycyclohexanone under comparable conditions, a recycling pyrolysis apparatus was constructed in which the higher boiling unpyrolyzed acetoxy ketone could be separated in the fractionating column from the lower boiling product and returned to the pot after passage through the pyrolysis column, the low-boiling product being continuously removed as formed (see Fig. 1). When 2-acetoxycyclohexanone was thus pyrolyzed at 8–10 mm. through a column packed with lump carbon and heated to 180°, the yield of cyclohexenone was 14% and of cyclopentene 18%.[5] This is in marked contrast to the 65% yield of cyclopentenone obtained under similar conditions from 2-acetoxycyclopentanone.[4]

---

(1) The pyrolysis of other α-acetoxy ketones to α,β-unsaturated ketones by conventional means has given similarly low yields. (a) C. S. Marvel and C. W. Hinman, *J. Am. Chem. Soc.*, **76**, 5435 (1954), have prepared indone in 20% yield from 2-acetoxyindanone by pyrolysis at 550°; (b) E. W. Warnhoff and W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 494 (1953), have prepared 2-methyl-2-cyclohexenone in 14–38% yield accompanied by up to 8% of a dimer of 2-methylenecyclohexanone by pyrolysis of 2-acetoxy-2-methylcyclohexanone at 350–450°. The low yield in this last case was surely due, at least in part, to the fact that the acetate used was not pure and contained considerable 2-methyl-6-acetoxycyclohexanone which we have recently shown, by NMR spectroscopy, is the correct structure for the 54.4–54.7° substance erroneously described in the 1953 publication as the 2-acetoxy isomer. The production of the 6-acetoxy compound from 2-chloro-2-methylcyclohexanone constitutes another example of abnormal substitution in α-halo ketones [*cf.*, K. L. Williamson and W. S. Johnson, *J. Org. Chem.*, **26**, 4563 (1961)]; (c) Since the completion of the present work, J. Cologne and J. C. Dubin, *Compt. rend.*, **250**, 553 (1960), reported the pyrolysis of 2-acetoxycyclohexanone to give cyclohexenone in 33% yield and cyclopentene in 30% yield. No experimental details were recorded.

(2) P. D. Bartlett and G. F. Woods, *J. Am. Chem. Soc.*, **62**, 2933 (1940).

(3) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942).

(4) H. W. Wanzlich, G. Gollmer, and H. Milz, *Ber.*, **88**, 69 (1955).

(5) Cyclopentadiene was not detected in this pyrolysis experiment. N. I. Shuikin and T. 1. Naryshina, *Doklady Akad. Nauk, S.S.S.R.*, **135**, 105 (1960) [*Chem. Abstr.*, **55**, 13332c (1961)], have shown that cyclopentene on pyrolysis at 450–600° over carbon gives a 53% yield of cyclopentadiene. These workers found furthermore that when the pyrolysis was conducted over powdered quartz, only traces of dehydrogenated products were formed.

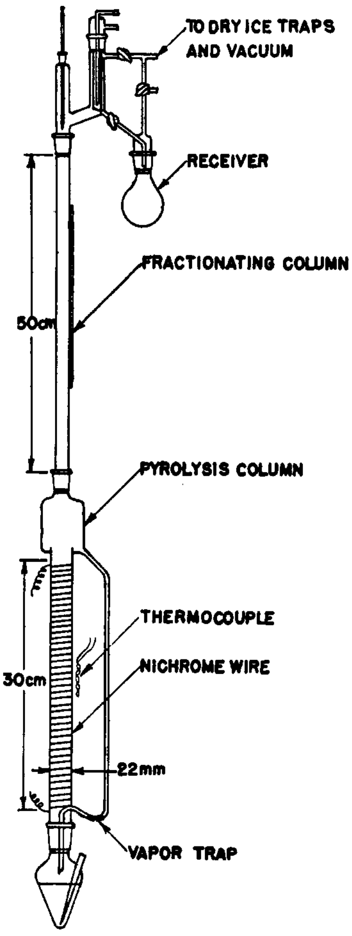

Figure 1

Similarly, in the pyrolysis of 2-acetoxycyclohexanone by the conventional downflow procedure, we noted a decrease in the yield of cyclohexenone (from 36 to 22%) in successive runs as the column became more carbonized.[6]

Replacement of the lump carbon by clean Pyrex glass helices in the recycling apparatus changed the course of pyrolysis markedly. At 180°, no pyrolysis was evident; at 350°, forty-eight hours were required for consumption of all of the starting material; and at 450°, the pyrolysis was substantially complete after six hours. When a column temperature of 450° and a pressure of 10 mm. were employed, 2-acetoxycyclohexanone was pyrolyzed cleanly to cyclohexenone; gas chromatography of the crude reaction mixture gave only two peaks corresponding to cyclohexenone and acetic acid. The yield of pure distilled cyclohexenone was 91%.[7] The glass helices in the pyrolysis column were perfectly clean throughout the reaction, showing no trace of carbon or decomposition products.

It is evident that the pyrolysis of 2-acetoxycyclohexanone in the presence of carbon, either deliberately added or formed by decomposition, can alter the product composition.[8] By conducting the pyrolysis at low pressures so that no carbon is formed on the column and by recycling unpyrolyzed keto acetate, an efficient synthesis of cyclohexenone[9] can be realized. This procedure should be generally applicable to pyrolyses in which the product can be separated from the starting material by distillation.

Experimental

2-Acetoxycyclohexanone.[10]—A solution of 100 g. (1.02 moles) of freshly fused potassium acetate and 132 g. (1.0 mole) of 2-chlorocyclohexanone[11] in 250 ml. of glacial acetic acid was refluxed for 6 hr. Most of the acetic acid was removed by distillation under reduced pressure, the mixture was diluted with 250 ml. of water, and was extracted with three 50-ml. portions of ether. The combined ether layers were washed with saturated sodium chloride solution and filtered through anhydrous sodium sulfate. Distillation afforded 125 g. (80% yield) of colorless 2-acetoxycyclohexanone, b.p. 120–123° (12 mm.), m.p. 36–38° (reported, 35°[10]; 35.5–36°[7]; and 41–42°[12]), which became pink on standing.

Anal. Found: C, 61.3; H, 7.9.

Pyrolysis of 2-Acetoxycyclohexanone. A. Conventional Procedure.—The pyrolyses were carried out at atmospheric pressure by slowly dropping the molten ester through a vertical 2.5 × 90 cm. Pyrex tube packed with glass beads and surrounded by an electric heating jacket. A slow stream of oxygen-free nitrogen was passed downward through the tube during the reaction. The pyrolysate was passed through a water-cooled condenser and collected in a series of three traps, the first being cooled with ice and the second and third with Dry Ice. The product was fractionally distilled through a 19-cm. Widmer column.

A run in which 312 g. (2.00 moles) of 2-acetoxycyclohexanone was pyrolyzed over a period of 48 hr. through a clean column at 490–510° gave a pyrolysate which on

---

(6) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955), have shown in the synthesis of strained cyclic dienes that the optimum yield (based on recovered starting material) was obtained when only 60–70% of the theoretical acetic acid was eliminated and substantially no carbonization occurred. When a higher percentage of acetic acid was eliminated, carbonization occurred in the column and the course of the reaction was altered to give isomerization and aromatization of the substrate, along with the formation of spurious gaseous products.

(7) C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959), have reported a conversion of 96% in the pyrolysis by conventional means of 2-acetoxycyclohexanone to cyclohexenone at 510° through a glass helices-packed column. The yield was not stated.

(8) The amount of carbonization occurring during a pyrolysis may account for the discrepancies in product composition reported by various authors (see ref. 7, footnote 22).

(9) For previous syntheses of 2-cyclohexenone, each by a different procedure, see footnotes 2, 4, and 7 as well as (a) C. Courtot and J. Pierron, *Bull. soc. chim. France*, **45** (4), 286 (1929); (b) F. C. Whitmore and G. W. Pedlow, Jr., *J. Am. Chem. Soc.*, **63**, 758 (1941); (c) A. J. Birch, *J. Chem. Soc.*, 593 (1946); (d) W. Treibs, G. Franke, G. Leichsenring, and H. Roder, *Ber.*, **86**, 616 (1953); (e) H. Born, R. Pappo, and J. Szmuszkovicz, *J. Chem. Soc.*, 1779 (1953); (f) A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953); (g) I. N. Nazarov, L. D. Bergel'son, I. V. Torgov, and S. N. Ananchenko, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 889 (1953); *Chem. Abstr.*, **49**, 1082 (1955); (h) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 607 (1954); (i) M. Mousseron, R. Jaquier, A. Fontaine, and R. Zagdoun, *Bull. soc. chim. France*, 1246 (1954); (j) M. Mersohn, *J. Am. Chem. Soc.*, **83**, 2136 (1961). In addition, see W. F. Gannon and H. O. House, *Org. Syntheses*, **40**, 14 (1960).

(10) For an alternative synthesis, see H. J. Shine and G. E. Hunt, *J. Am. Chem. Soc.*, **80**, 2434 (1958).

(11) M. S. Newman, M. D. Farbman, and H. Hipsher, *Org. Syntheses*, Coll. Vol. III, 188 (1945).

(12) M. Bergmann and M. Gierth, *Ann.*, **448**, 48 (1926).

fractionation yielded 38.8 g. (28.5% yield) of crude cyclopentene, b.p. 41–43° (740 mm.); about 70 g. of acetic acid; 69 g. (36% yield) of crude 2-cyclohexenone, b.p. 35–66°, mostly at 60° (11 mm.); and 31.5 g. of higher boiling residue. A second run with 304 g. (1.96 moles) of 2-acetoxycyclohexanone was carried out over a 40-hr. period at 495–505° in the same apparatus, with the column now well carbonized from the first run. Fractional distillation of the pyrolysate yielded 82 g. (62% yield) of crude cyclopentene; about 75 g. of acetic acid; 42.3 g. (23% yield) of crude 2-cyclohexenone; and about 20 g. of higher boiling residue. The gases produced during pyrolysis were collected over saturated sodium chloride solution. The spectrum, determined on a Baird spectrophotometer with a sodium chloride prism, showed absorption in the 2.7–2.8, 4.3, 13.9, and 15-μ regions, indicating carbon dioxide. A maximum at 7.67 μ along with the 3.3–3.4-μ C—H stretching band indicated methane. The characteristic doublet of carbon monoxide at 4.7 μ was also evident.

Redistillation of the combined cyclopentene fractions of the above two runs through a 19-cm. Widmer column gave 105 g. of cyclopentene, n^{20}_{D} 1.4220 (reported,[13] n^{20}_{D} 1.422), b.p. 42–43° (738 mm.) [reported,[13] 44.4° (760 mm.)]. The 2,4-dinitrobenzenesulfenyl chloride adduct was prepared by a modification of the general procedure of Kharasch[14] by refluxing 1 g. of the reagent with 0.30 g. of the cyclopentene fraction in 15 ml. of carbon tetrachloride on a steam bath for 2 hr. The cooled solution was filtered and the filtrate evaporated to give a yellow oil which slowly crystallized, yielding 1.36 g. of crude derivative. One recrystallization from petroleum ether (b.p. 90–95°) gave 0.76 g. of yellow needles, m.p. 78–79°, undepressed on admixture with a sample prepared from authentic cyclopentene.[15] An analytical sample prepared by repeated crystallization from petroleum ether (b.p. 90–95°) melted at 80.2–80.6°.

Anal. Calcd. for $C_{11}H_{11}O_4ClN_2S$: C, 43.64; H, 3.66. Found: C, 43.9; H, 3.7.

The dibromide of cyclopentene was prepared by the addition of a carbon tetrachloride solution of bromine to an equimolar amount of cyclopentene. Distillation afforded 82% of 1,2-dibromocyclopentane, b.p. 76–78° (12 mm.). A center cut of redistilled material had b.p. 77° (12 mm.) [reported,[16] b.p. 83° (16 mm.)]; m.p. −13° to −12° (reported,[17] m.p. 12.2°); n^{25}_{D} 1.5475 (reported,[16] n^{25}_{D} 1.5444); M_D: calcd., 38.62; found, 38.86 (reported,[18] M_D 38.86). The melting point was not depressed on admixture with a sample prepared from authentic cyclopentene.

The cyclohexenone fractions were dissolved in ether, washed with 10% sodium hydroxide solution, then with water, and dried over anhydrous magnesium sulfate. Distillation at 730 mm. through a 1 × 47-cm. Fenske column packed with glass helices did not effect a good separation as shown by a gradual increase in the boiling point, n_D, and in the intensity of ultraviolet absorption at 225 mμ of successive fractions. The contaminant was probably cyclohexanone. A 2,4-dinitrophenylhydrazone prepared from the first fraction of the distillation, b.p. 153–154° (730 mm.), n^{25}_{D} 1.4472, was recrystallized from ethanol to a constant melting point of 152–153.5°. The mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of cyclohexanone, m.p. 160.5–162°, was 152–157°. Chromatography did not improve the melting point of the derivative in question but sharpened the melting point to 153–153.5°.

Distillation of the higher boiling residues yielded 10.4 g. of crude 2-acetoxycyclohexanone, b.p. 117–125° (12 mm.). From the forerun of this distillation, 4.8 g. of phenol, m.p. 39–42°, was isolated by extraction with 10% sodium hydroxide solution. (The tribromo derivative had m.p. 91.5–92.5° after one recrystallization from ethanol–water.)

To test the effect of shorter contact time, 79 g. of 2-acetoxycyclohexanone was passed through the carbonized column at 500° over a period of 50 min., giving, after fractionation, 8.4 g. (24.5% yield) of crude cyclopentene and 17.0 g. (35% yield) of crude cyclohexenone, b.p. 55–73° (20 mm.), which on redistillation gave material, b.p. 63–69° (17–20 mm.), n^{25}_{D} 1.4797, $\lambda_{\max}^{95\%\ C_2H_5OH}$ 225 mμ (ϵ 10,070). A sample of 2-cyclohexen-1-one prepared by the method of Whitmore and Pedlow[9b] had b.p. 78° (34 mm.), n^{25}_{D} 1.4859, $\lambda_{\max}^{95\%\ C_2H_5OH}$ 225 mμ (ϵ 10,600).

In a run at 330°, 104 g. of the acetate yielded after fractionation 55 g. (53% yield) of recovered acetate, b.p. 117–125° (12 mm.), and 16.2 g. (25% yield) of cyclohexenone, b.p. 48–51° (7–8 mm.), $\lambda_{\max}^{95\%\ C_2H_5OH}$ 225 mμ (ϵ 10,270).

B. Over Carbon Employing Recycling Apparatus.—The procedure is that which Wanzlich, Gollmer, and Milz[4] used to prepare cyclopentenone.

The apparatus employed in this and subsequent runs was that depicted in Fig. 1. The pyrolysis column was packed with Fisher coconut charcoal lumps ($^1/_{16}$–$^1/_8$ in.). The column was wound on the outside with No. 22 B and S gauge Nichrome wire, resistance 1.02 ohms/ft., approximately 12-ft. long. The column temperature was measured by an external copper–constantan thermocouple placed at the midpoint, and maintained at a constant value (± 2°) by a Micromax control unit. A column temperature of 450° required 78 v. at 3.8 amp. Insulation was provided by a double wrapping of asbestos cloth tape and a 3-in. thick layer of Pyrex wool. The stainless steel saddle-packed fractionating column mounted above the pyrolysis column was provided with an external heater and its temperature measured by an external thermometer.

Into the pear-shaped distillation flask was placed 30.0 g. of 2-acetoxycyclohexanone, b.p. 113–114° (8 mm.). The oil bath temperature was maintained at 165°, the pressure of the system at 8–10 mm., and the temperature of the pyrolysis column at 180°, while a very slow stream of prepurified nitrogen was passed through the capillary. The temperature of the fractionating column was maintained at 90° so that unpyrolyzed acetoxy ketone did not distil but was returned to the pot *via* the external return tube while the product was collected in the receiver. At the end of 10 hr., when product formation had virtually ceased, the pyrolysis was stopped. In the receiver was 6.31 g. of a clear liquid, in the Dry Ice traps 14.08 g. of a clear, less viscous liquid, and from the apparatus was washed out 4.15 g. of a dark oil, to give a total recovery of 24.54 g. (82% material balance). The ultraviolet spectrum of the material in the receiver showed $\lambda_{\max}^{95\%\ C_2H_5OH}$ 224 mμ (ϵ 2600), corresponding to an 8.7% yield of cyclohexenone (ϵ 10,600). The ultraviolet spectra of the material in the Dry Ice traps showed $\lambda_{\max}^{95\%\ C_2H_5OH}$ 224 mμ (ϵ 650), corresponding to 5% of cyclohexenone for a total yield of 13.7%. The ultraviolet spectrum of the pot residue showed $\lambda_{\max}^{95\%\ C_2H_5OH}$ 217 mμ (ϵ 2260). The 6.31- and 14.08-g. fractions were combined and distilled: fraction no. 1, 2.36 g., b.p. 41.5–44°; 2, 0.74 g., b.p. 44–110°; 3, 5.12 g., b.p. 110–124°; 4, 2.10 g., b.p. 124–130°; 5, 5.32 g., b.p. up to 80° (10 mm.); 6, 0.97 g., b.p. 80–125° (10 mm.).

Fraction 1 was shown to be cyclopentene (18% yield), reported b.p.[13] 44–46°, by gas chromatographic comparison with an authentic sample. Fractions 2, 3, and 4 were combined and titrated with 0.1 *N* sodium hydroxide and found to consist of 82.5% acetic acid or 57% of the theoretical amount from 2-acetoxycyclohexanone. Fraction 5 was a

---

(13) G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Co., New York, 1940, p. 306.

(14) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

(15) B. B. Corson and V. N. Ipatieff, *Org. Syntheses*, Coll. Vol. II, 151, Note 1 (1943).

(16) J. Weinstock, S. N. Lewis, and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 6072 (1956).

(17) This melting point reported by D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943), was perhaps meant to be −12.2°.

(18) N. D. Zelinsky and R. J. Lewina, *Ber.*, **66**, 477 (1933).

mixture containing 34% cyclohexenone as shown by the ultraviolet spectrum or 39% by gas chromatographic analysis; the other larger peak in the gas chromatograph corresponded in position to cyclohexanone.

C. Over Glass Helices Employing Recycling Apparatus.—The same recycling pyrolysis apparatus was employed except that the pyrolysis column was packed with clean $^3/_{16}$-in. i.d. Pyrex glass helices.

The distillation flask was charged with 60 g. of 2-acetoxycyclohexanone, b.p. 113–114° (8 mm.), the oil bath maintained at 170°, system pressure at 10 mm., fractionating column temperature at 85°, and pyrolysis column temperature at 450°. Under these conditions the product distilled at a rate of about 3 drops per min. at a still head temperature of 60°. Over half the material had pyrolyzed in 3 hr.; after 6 hr. only about 5 ml. of material was left in the flask and at the end of 19 hr. it was dry.

The receiver contained 47.57 g. of a slightly yellow liquid, and the Dry Ice traps contained 8.8 g. of liquid, also slightly yellow. The apparatus was washed out thoroughly with ether to give 1.75 g. of brown residue for a material balance of 58.12 g. (97%). There was no charring evident in the pyrolysis column. Gas chromatography of the combined 47.57- and 8.8-g. material showed only two peaks, one corresponding to acetic acid, the other to cyclohexenone. Careful distillation of this material through a 2-ft. stainless steel saddle-packed column gave 33.40 g. (90.5% yield) of cyclohexenone, b.p. 60.5–62° (10 mm.), $\lambda_{\max}^{95\%\ C_2H_5OH}$ 224 mμ (ε 10,600), 2,4-dinitrophenylhydrazone, m.p. 162.6–164°. Reported values are b.p. 61–63° (14 mm.), 2,4-dinitrophenyl hydrazone, m.p. 163°.[2]

Pyrolysis of Cyclohexenone. A. Over Glass Helices.—A 40.3-g. sample of cyclohexenone, b.p. 72–74° (24 mm.), $n^{25}\text{D}$ 1.4830, $\lambda_{\max}^{95\%\ C_2H_5OH}$ 225 mμ (ε 9370), was passed through the pyrolysis apparatus described above during a period of 3.25 hr. at 510–520° in a slow stream of nitrogen (which was prepurified by passage through 20% sodium hydroxide solution, two bottles of Fieser's solution, two bottles of lead acetate, concentrated sulfuric acid, and a calcium chloride tower). Both Dry Ice traps were empty. Distillation of the material collected in the ice-cooled trap through a semimicro column[19] gave the following fractions: No. 1, 1.28 g., b.p. 50–70° (26 mm.), $n^{25}\text{D}$ 1.4730; 2, 16.95 g., b.p. 70–73° (26 mm.), $n^{25}\text{D}$ 1.4810; 3, 12.15 g., b.p. 73–77° (26 mm.), $n^{25}\text{D}$ 1.4850; 4, 3.17 g., boiling point to about 100° (forced) (26 mm.), $n^{25}\text{D}$ 1.4990. These fractions appeared to be mainly unchanged starting material.

B. Over Carbon.—An 8.7-g. sample of 2-cyclohexenone, b.p. 61–62° (15 mm.), was pyrolyzed at 20 mm. in the recycling apparatus. The pyrolysis column was packed with lump coconut charcoal; and the column temperature was maintained at 450°. After 4 hr. the distillation flask was empty and a solid crystalline material had collected in the fractionating head condenser. The liquid nitrogen-cooled traps contained no material boiling below 100° and an infrared spectrum of the product (1.8 g.) collected in these traps indicated the presence of cyclohexenone, a small amount of a saturated ketone, and phenol. The pyrolysis apparatus, including the fractionating head condenser, was washed out with ether, and the ether was removed by distillation to give 2.2 g. of a light yellow oil. The infrared spectrum of this oil indicated the presence of only two components, phenol, and cyclohexenone. The 1.8 g. from the traps was combined with the 2.2 g. from the apparatus, diluted with ether, and extracted with 5% sodium hydroxide solution. These aqueous extracts were acidified to Congo red with hydrochloric acid and the turbid solution was extracted with ether. The ether extracts were combined, dried over anhydrous sodium sulfate, and the ether was distilled to give 2.4 g. of a clear oil. The infrared spectrum of this clear oil was identical in all respects with the infrared spectrum of a sample of authentic phenol.

Acknowledgment.—This study was supported in part by grants from the National Institutes of Health, the National Science Foundation, and the Wisconsin Alumni Research Foundation.

---

(19) C. W. Gould, Jr., G. Holzman, and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

The *n*-Butylthiomethylene Blocking Group[1]

ROBERT E. IRELAND AND JAMES A. MARSHALL[2]

Department of Chemistry, The University of Michigan, Ann Arbor, Mich.

Received October 11, 1961

The chemical and physical properties of several representative 2-*n*-butylthiomethylene ketones are described, together with methods of preparation of this derivative. The use of the *n*-butylthiomethylene grouping as a "blocking group" during ketone methylation reactions is delineated. Several of the blocked ketones have been converted to α-methyl ketones by reductive desulfurization of the derivative.

In considering approaches to the total synthesis of polycyclic natural products, such as the di- and triterpenes, we adopted a plan[3–5] that would construct first the A/B ring system, which could then be elaborated further to the desired end product. Such a general scheme has not only been successful in our hands[4,5] but has also led to the syntheses of α-onocerin,[6] olean-11,12;13,18-diene,[7] and pentacyclosqualene[8] by other workers. One[3] of the paths we chose for the preparation of such an A/B ring system necessitated the intro-

---

(1) Preliminary communications: (a) R. E. Ireland and J. A. Marshall, *J. Am. Chem. Soc.*, **81**, 6336 (1959). (b) *Chem. & Ind.* (London), 1534 (1960).

(2) Public Health Service Research Fellow of the National Heart Institute, 1958–1960.

(3) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1620 (1962).

(4) R. F. Church, R. E. Ireland, and J. A. Marshall, *Tetrahedron Letters*, 34 (1961).

(5) R. F. Church and R. E. Ireland, *ibid.*, 493 (1961).

(6) G. Stork, J. E. Davies, and A. Meisels, *J. Am. Chem. Soc.*, **81**, 5516 (1959); N. Danieli, Y. Mazur, and F. Sondheimer, *Tetrahedron Letters*, 310 (1961).

(7) E. J. Corey, H. Hess, and S. Proskow, *J. Am. Chem. Soc.*, **81**, 5258 (1959).

(8) E. J. Corey and R. R. Sauers, *ibid.*, **81**, 1739 (1959); A. Eschenmoser, P. A. Stadler, A. Nechvatal, and A. J. Frey, *Helv. Chim. Acta*, **40**, 1900 (1957).