phase was separated and the aqueous layer was extracted with ether. The combined organic fractions were washed with water and dried over $MgSO_4$. Solvent removal followed by distillation gave 3.4 g (95%) of cyclopropylcyclooctatetraene, bp 40–43° (0.01 mm), nmr δ 5.8 (7 H, s), 1.6 (1 H, m), 0.7 (4 H, m).

Anal. Calcd for $C_{11}H_{12}$: C, 91.66; H, 8.34. Found: C, 91.33; H, 8.06.

N,N-Diethylaminocyclooctatetraene.—Over a period of 1 hr, 5.6 g (0.05 mol) of potassium *tert*-butoxide was added in small portions to a solution of 9.2 g (0.05 mol) of bromocyclooctatetraene in a mixture of 50 ml of diethylamine and 150 ml of ether at 0°. The suspension was stirred for 3 hr at 0°, and allowed to warm overnight to room temperature. Rapid vacuum filtration to remove precipitated potassium bromide followed by solvent removal gave an orange-brown residue. Attempted distillation, even at 1 μ, resulted in rearrangement to α-*N,N*-diethylaminostyrene. However, the nmr spectrum of the crude preparation is consistent with the *N,N*-diethylaminocyclooctatetraene structure: δ 5.9 (6 H, d, COT protons), 4.5 (1 H, d, enamine proton), 3.2 (4 H, q), 1.2 (6 H, t, ethyls).

N,N-Dimethylaminocyclooctatetraene.—Repetition of the above preparation, except that 200 ml of a saturated ether solution of dimethylamine was used, gave from 9.2 g of bromocyclooctatetraene 5.8 g (79%) of *N,N*-dimethylaminocyclooctatetraene by evaporative distillation (<30°) at 0.01 mm: nmr δ 5.8 (6 H, d), 4.4 (1 H, d), 2.6 (6 H, s). The analysis was poor but the assigned structure is supported by the nmr spectrum and by the mass spectral parent peak at *m/e* 147.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 81.11; H, 9.23.

Reaction of Cyclooctatetraenyllithium with Iron Pentacarbonyl.—A solution of 0.05 mol of cyclooctatetraenyllithium in 100 ml of ether at −70° was added dropwise to 19.5 g of iron pentacarbonyl in 100 ml of ether maintained at −70°. The deep red mixture was stirred for 3 hr at −70° and hydrolyzed with 15 ml of acetic acid. The solution was poured onto 250 ml of water and extracted with ether. The combined ether fractions were dried over $MgSO_4$ and the ether was removed under vacuum. The red residue was chromatographed over silica gel with a 5% methylene chloride–pentane mixture, giving 6.1 g (45%) of (formylcyclooctatetraene)iron tricarbonyl.

Cyclooctatetraenealdehyde.—To 100 ml of methyl formate at −30° was added a solution of 0.05 mol of cyclooctatetraenyllithium in 100 ml of ether over a period of 1 hr. The solution was stirred for 3 hr at 0° and hydrolyzed with 100 ml of water. The product was taken up in ether and dried with $MgSO_4$. Distillation of the orange residue after solvent removal gave 5.2 g (79%) of cyclooctatetraenealdehyde, bp 40–45° (0.5 mm), ir 1685 cm^{-1} (C=O).

Anal. Calcd for C_9H_8O: C, 81.81; H, 6.06. Found: C, 81.69; H, 5.98.

Cyclooctatetraenenitrile.—A mixture of 9.2 g of bromocyclooctatetraene, 7.8 g of potassium cyanide, and 22.2 g of $K_4Ni_2(CN)_6$ in 300 ml of absolute methanol was stirred for 8 hr at room temperature. The yellow suspension was poured into water and extracted with ether. The organic phase was washed with water and dried with $MgSO_4$. Solvent removal followed by chromatography of the residue with pentane over silica gel gave 0.52 g (8%) of cyclooctatetraenenitrile.

Cyclooctatetraenenitrile from Cyclooctatetraenyllithium.—Cyanogen was bubbled into 100 ml of ether until a saturated solution was obtained. This solution was cooled to −70°, and 0.05 mol of cyclooctatetraenyllithium in 100 ml of ether at −70° was added dropwise over a period of 20 min. The mixture was stirred for 2 hr at −70°, warmed to room temperature, and hydrolyzed with 200 ml of water. Upon standing overnight to decompose excess cyanogen, the organic phase was separated, washed with water, and dried. After the ether was removed, evaporative distillation of the residue at 1 mm (bath temperature, 40°) gave 1.6 g (25%) of cyanocyclooctatetraene. This sample was identical with the product obtained from $K_4Ni_2(CN)_6$, ir 2190 cm^{-1} (C≡N). Yields up to 40% have been obtained by first converting cyclooctatetraenyllithium to the corresponding Grignard reagent by the addition of anhydrous magnesium bromide.

Anal. Calcd for C_9H_7N: C, 83.72; H, 5.43. Found: C, 83.67; H, 5.51.

Registry No.—Bromocyclooctatetraene, 7567-22-8; *p*-methoxyphenylcyclooctatetraene, 23697-18-9; vinylcyclooctatetraene, 37164-12-8; cyclopropylcyclooctatetraene, 37164-13-9; *N,N*-diethylaminocyclooctatetraene, 37164-14-0; *N,N*-dimethylaminocyclooctatetraene, 37164-15-1; cyclooctatetraenealdehyde, 30844-12-3; cyanocyclooctatetraene, 37164-17-3.

A New Synthesis of 2-Hydroxy-3-methylcyclopent-2-en-1-one. III[1]

KIKUMASA SATO,* SEIICHI INOUE, TAKAYUKI KITAGAWA, AND TADASHI TAKAHASHI

Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama, Japan

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A new synthesis of 2-hydroxy-3-methylcyclopent-2-en-1-one (**7**) is described. The Mannich reaction of cyclopentane-1,2-dione (**3**) with morpholine and formalin gave a Mannich base **6**, which was hydrogenolized to afford **7**. However, the Mannich reactions of keto enamines **5a–c**, which are enamino derivatives of **3**, gave the Mannich bases **9a–c**, respectively, which were similarly hydrogenolized to afford 3,5-dimethyl-2-hydroxycyclopent-2-en-1-one (**10**).

2-Hydroxy-3-methylcyclopent-2-en-1-one (**7**) is a flavor constituent, for example, in coffee aroma[2] and maple flavor.[3] Erickson and Collins[4] have utilized **7** as an intermediate in a synthesis of dihydrojasmone, which is useful in perfumery.

Previous papers[1,5] described several routes to synthesize **7** from 2-carbethoxy-2-methylcyclopentanone.[6] In this paper, we wish to report a new synthesis of **7** from cyclopentanone (**1**).

Cyclopentanone (**1**) is monobrominated with dioxane dibromide in ether and 2-bromocyclopentanone (**2**) is oxidized by ferric chloride to afford cyclopentane-1,2-dione (**3**), which exists almost entirely in the enolic form.[7]

In an earlier paper,[1] we reported that the treatment of 2,5-dibromocyclopentanone (**4**) with excess morpholine in ether gives 2-morpholinocyclopent-2-en-1-one (**5a**) in good yield. Cyclopentane-1,2-dione (**3**) is also obtained by the hydrolysis of **5a** in 20% hydrochloric acid.

(1) For previous paper, see K. Sato, Y. Kojima, and H. Sato, *J. Org. Chem.*, **35**, 2374 (1970).

(2) M. A. Gianturco, A. S. Giammarino, and R. G. Pitcher, *Tetrahedron*, **19**, 2051 (1963).

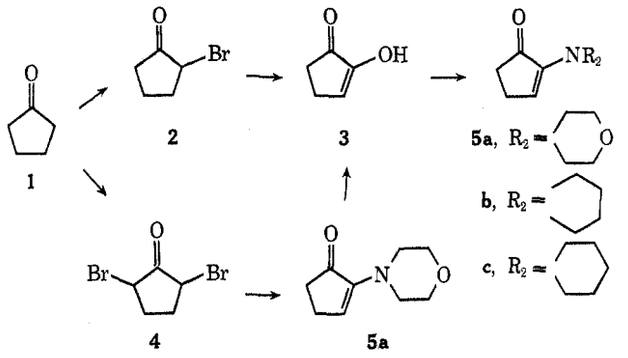
(3) V. J. Filipic, J. C. Underwood, and C. O. Willits, *J. Food Sci.*, **30**, 1008 (1965).

(4) J. L. E. Erickson and F. E. Collins, Jr., *J. Org. Chem.*, **30**, 1050 (1965).

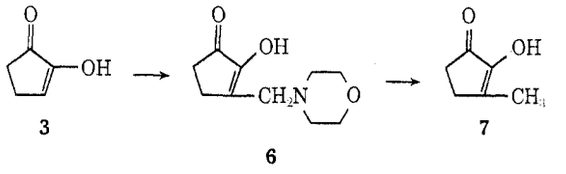
(5) K. Sato, S. Suzuki, and Y. Kojima, *ibid.*, **32**, 339 (1967).

(6) C. M. Leir has recently reported the synthesis of **7** from 2-carbomethoxy-2-methylcyclopentanone [*J. Org. Chem.*, **35**, 3203 (1970)].

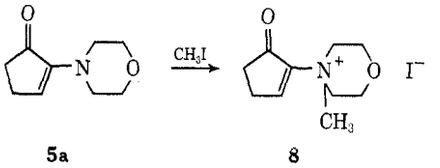
(7) C. W. N. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 2067 (1965).



The Mannich reaction[8] of **3** with 1 equiv each of morpholine and formalin in dioxane afforded 2-hydroxy-3-morpholinomethylcyclopent-2-en-1-one (**6**). Since the Mannich base **6** precipitates very rapidly during the reaction, no more reaction occurs even with excess morpholine and formalin. The Mannich base **6** was treated with zinc powder in glacial acetic acid to afford **7** in 58% yield.



The direct methylation of **5a**, which might be a key intermediate in the above-described synthesis of **7**, was also examined. The reaction of **5a** with methyl iodide in acetonitrile gave no C-methylated compound, but did give N-methylated compound, *N*-methyl-*N*-(1-oxo-2-cyclopenten-2-yl)morpholinium iodide (**8**), almost quantitatively.



We studied the indirect methylation of keto enamine **5a**, using the Mannich reaction. The behavior of keto enamines in the Mannich reaction has not been investigated. The Mannich reaction of **5a** with morpholine and formalin in dioxane afforded 3,5-bismorpholinomethyl-2-hydroxycyclopent-2-en-1-one (**9a**). The product gave a positive ferric chloride reaction and had characteristic absorption at 3400 cm^{-1}. The structure of **9a** was assigned on the basis of its nmr, ir, and uv spectra. This reaction was examined with various ratios of reagents, that are listed in Table I.

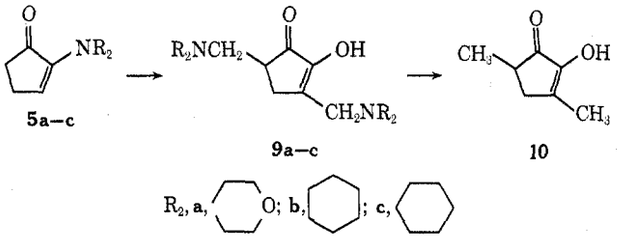


TABLE I
THE MANNICH REACTION OF KETO ENAMINES 5a–c UNDER VARIOUS CONDITIONS

Keto enamine	Formalin, equiv	Amine	Equiv	Mannich base	Yield, %
5a	1.0	Morpholine	1.0	**9a**	32
	2.0		1.0		45
	2.0		2.0		73.5
	1.0		None		
	2.0		None		
5b	1.0	Pyrrolidine	1.0	**9b**	23.8
	2.0		1.0		41.6
	2.0		2.0		61.5
5c	2.0	Piperidine	1.0	**9c**	44.1
	2.0		2.0		61.2

The formation of **9a** was not observed in the absence of morpholine and even with insufficient reagents no mono-Mannich derivative was obtained, while the best yields were obtained with 2 molar equiv each of morpholine and formalin. Moreover, the reaction of **5a** with morpholine and paraformaldehyde in various solvents, for example, ether, ethanol, THF, and dioxane, afforded **9a** in low yield.

Dione **3** reacted with the secondary amines, morpholine, pyrrolidine, and piperidine, to form enamine derivatives **5a–c**. Although 2,5-dibromocyclopentanone (**4**) and excess morpholine gave **5a**, as described above, **4** and the other secondary amines, pyrrolidine and piperidine, gave only trace amounts of the corresponding enamine derivatives (**5b** and **5c**), which were identified by vpc and ir with **5b** and **5c**, synthesized by the above-mentioned method. Then the Mannich reactions of **5b** and **5c** were examined. They also gave bis Mannich bases, **9b** and **9c**.

The hydrogenolysis of the Mannich bases **9a–c** afforded 3,5-dimethyl-2-hydroxycyclopent-2-en-1-one (**10**). The nmr spectrum of this product showed a doublet peak at δ 1.18 corresponding to the 5-methyl group and a singlet peak at δ 2.00 corresponding to the 3-methyl group.

On the basis of these facts we deduced concerning the production of **9a–c** that the first aminomethylation occurs through the normal enolization mechanism. It is not easily explained whether the first aminomethylation occurs at the enol site or at the enamine site. The problem of determining which course, A → B → D or A → C → D, is actually being followed is under investigation. The second aminomethylation followed by hydrolysis during work-up would then lead to the Mannich base (Scheme I).

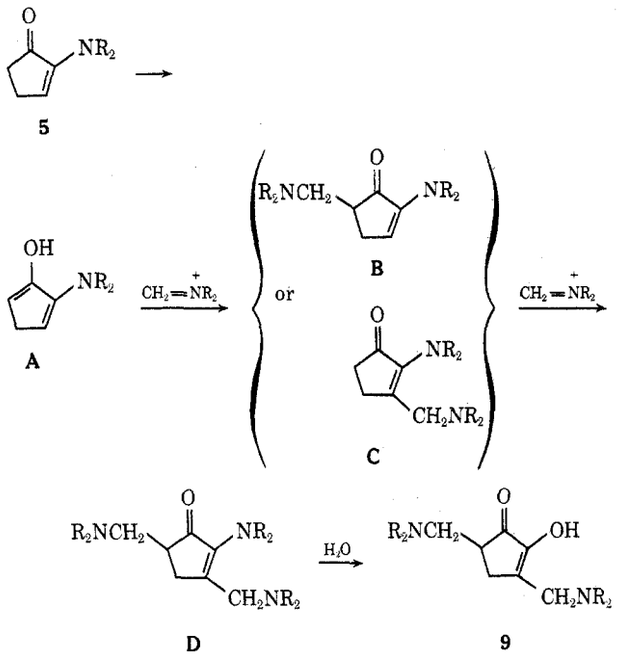
Experimental Section

General.—Boiling points and melting points are uncorrected. The infrared (ir) spectra were recorded on a Hitachi Model 215 spectrophotometer. The ultraviolet (uv) spectra were recorded on a Hitachi Model EPS-3T spectrophotometer. The nuclear magnetic resonance (nmr) spectra were obtained on a JEOL Model C-60 spectrometer (tetramethylsilane as internal standard). Vapor phase chromatographic (vpc) analysis was performed on a Shimadzu Model GC-1C instrument using a 3 mm × 260 cm column of 25% silicon DC-200 on Celite 545 with He as the carrier gas.

Cyclopentane-1,2-dione (3). A.—A mixture of 10 g (60 mmol) of **5a** and 100 ml of 20% HCl was stirred at room temper-

(8) K. Tonari, I. Ichimoto, H. Ueda, and C. Tatsumi, *Nippon Nogei Kagaku Kaishi*, **44**, 55 (1970), report the Mannich reaction of **7**.

SCHEME I



ature for 3 hr. The solution was cooled, neutralized with concentrated NaOH solution, and extracted with ether. After evaporation, the residue afforded crystalline product, which was recrystallized from petroleum ether (bp 40–60°), affording 2.5 g (41% yield) of pure **3**: mp 54–55° (lit.[7] mp 50–52°, lit.[9] mp 55–56°).

B.—**3** was prepared by the procedure of Acheson[9] from 15.6 g (96 mmol) of 2-bromocyclopentanone (**2**) and 42 g (0.80 mol) of ferric chloride in water at 95–98° for 10 min. Distillation of the dried extract gave 5.6 g (59.8% yield) of **3**, bp 84–86° (8 mm) [lit.[9] bp 78–86° (8 mm)]. The distillate solidified spontaneously.

2-Morpholinocyclopent-2-en-1-one (5a). A.—To a stirred solution of 23.2 g (95 mmol) of **4** in 100 ml of dry ether and 20 ml of dry acetone was added dropwise 41.5 g (0.48 mol) of morpholine in 50 ml of dry ether at 0–5°. The precipitated morpholine hydrobromide was filtered, and solvents and the surplus morpholine were removed under reduced pressure. The residue was recrystallized from ethanol to afford 13.0 g (82% yield) of **5a**, mp 63–64° (lit.[1] mp 63°).

B.—A mixture of 2.0 g (20 mmol) of cyclopentane-1,2-dione (**3**), 2.1 g (25 mmol) of morpholine, and 40 ml of benzene was refluxed with removal of water for 1 hr. The benzene and the surplus morpholine were removed and the residue was cooled in a Dry Ice box. The precipitated solid was collected and recrystallized from isopropyl ether to afford 3.6 g (61.5% yield) of **5a**.

2-Pyrrolidinocyclopent-2-en-1-one (5b).—The preparation of **5b** was carried out according to procedure B described above. A mixture of 5.7 g (58 mmol) of **3**, 5.0 g (70 mmol) of pyrrolidine, and 60 ml of benzene was refluxed for 3.5 hr. After removal of benzene and the surplus pyrrolidine, distillation of the residue gave 6.2 g (72% yield) of **5b**: bp 81–84° (0.23 mm); $n^{20}D$ 1.5401; uv max (99% EtOH) 316 nm (ε 3400); ir (neat) 1680, 1600, 1380, 1300, 1150, 760 cm^{-1}; nmr (CCl_4) δ 5.55 (t, 1, J = 3 Hz), 3.20 (m, 4), 2.35 (m, 4), 1.80 (m, 4).

Anal. Calcd for $C_9H_{13}ON$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.05; H, 8.71; N, 9.31.

2-Piperidinocyclopent-2-en-1-one (5c).—The preparation of **5c** was carried out according to procedure B described above. **3** (2.5 g, 26 mmol) and 2.6 g (31 mmol) of piperidine gave 3.6 g (85.4% yield) of **5c**: bp 88–89° (0.25 mm); $n^{20}D$ 1.5296; uv max (99% EtOH) 288 nm (ε 3650); ir (neat) 1710, 1610, 1110, 1005, 780 cm^{-1}; nmr (CCl_4) δ 5.91 (t, 1, J = 3 Hz), 2.90 (m, 4), 2.33 (m, 4), 1.52 (m, 6).

Anal. Calcd for $C_{10}H_{15}ON$: C, 72.69; H, 9.15; N, 8.48. Found: C, 73.09; H, 8.86; N, 8.60.

2-Hydroxy-3-morpholinomethylcyclopent-2-en-1-one (6).—To 4.9 g (50 mmol) of **3** in 6 ml of dioxane and 4.3 g (50 mmol) of morpholine was added dropwise slowly at room temperature 4.0 g (50 mmol) of formalin. Soon the mixture crystallized, and the crystals were recrystallized from ethanol to afford 6.3 g (60% yield) of **6**: mp 141.5°; uv max (99% EtOH) 261 nm (ε 12,100); ir (KBr) 3400, 1690, 1650, 1110 cm^{-1}; nmr ($CDCl_3$) δ 7.84 (s, 1), 3.83 (m, 4), 3.45 (s, 2), 2.61 (m, 4), 2.42 (s, 4).

Anal. Calcd for $C_{10}H_{15}O_3N$: C, 60.90; H, 7.76; N, 7.10. Found: C, 61.03; H, 7.71; N, 6.67.

2-Hydroxy-3-methylcyclopent-2-en-1-one (7).—A mixture of 6.3 g (30 mmol) of **6**, 50 ml of glacial acetic acid, and 13 g (0.20 g-atom) of zinc powder was stirred at 80° for 5 hr. After zinc was filtered off and acetic acid was removed under reduced pressure, a small amount of water was added. The solution was extracted with chloroform. After drying, the chloroform was evaporated and the residue was recrystallized from water to afford 2.0 g (58% yield) of **7**: mp 102–103° (lit.[10] mp 102–104°).

***N*-Methyl-*N*-(1-oxo-2-cyclopenten-2-yl)morpholinium Iodide (8).**—To 0.8 g (4.8 mmol) of **5a** in 10 ml of acetonitrile was added 2.3 g (16 mmol) of methyl iodide, and the mixture was heated with stirring under reflux for 6 hr. The mixture was kept overnight at room temperature. The precipitated solid was recrystallized from ethanol to afford 1.4 g (93% yield) of **8**: mp 165°; ir (KBr) 1720, 1625, 1115 cm^{-1}; nmr (D_2O) δ 8.38 (t, 1, J = 1.5 Hz), 4.60–3.66 (m, 8), 3.55 (s, 3), 3.08–2.60 (m, 4).

Anal. Calcd for $C_{10}H_{16}O_2NI$: C, 38.85; H, 5.22. Found: C, 38.87; H, 5.20.

3,5-Bismorpholinomethyl-2-hydroxycyclopent-2-en-1-one (9a).—To 5.0 g (30 mmol) of **5a** in 10 ml of dioxane and 5.2 g (60 mmol) of morpholine was added dropwise slowly at room temperature 4.9 g (60 mmol) of formalin. The precipitated solid was recrystallized from isopropyl ether to afford 6.5 g (73.5% yield) of **9a**: mp 126–127°; uv max (99% EtOH) 266.5 nm (ε 5100); ir (KBr) 3400, 1695, 1115 cm^{-1}; nmr ($CDCl_3$) δ 7.45 (s, 1), 3.85 (m, 8), 3.50 (m, 4), 2.61 (m, 8), 2.46 (m, 3).

Anal. Calcd for $C_{15}H_{24}O_4N_2$: C, 60.79; H, 8.16; N, 9.45. Found: C, 60.73; H, 8.68; N, 9.56.

3,5-Bispyrrolidinomethyl-2-hydroxycyclopent-2-en-1-one (9b).—The preparation of **9b** was carried out according to the procedure described above. From 3 g (20 mmol) of **5b** in 15 ml of dioxane, 2.8 g (40 mmol) of pyrrolidine, and 3.2 g (40 mmol) of formalin, 3.1 g (61.5% yield) of **9b** was obtained after recrystallization from ethanol: mp 127–128°; uv max (99% EtOH) 263 nm (ε 6040); ir (KBr) 2950, 2770, 2550–2300, 1690, 1660, 1410, 1340 cm^{-1}; nmr ($CDCl_3$) δ 8.17 (s, 1), 3.43 (m, 1), 2.76–2.10 (m, 12), 1.93–1.46 (m, 10).

Anal. Calcd for $C_{15}H_{24}O_2N_2$: C, 68.15; H, 9.15; N, 10.60. Found: C, 68.27; H, 9.59; N, 10.28.

3,5-Bispiperidinomethyl-2-hydroxycyclopent-2-en-1-one (9c).—The preparation of **9c** was carried out according to the procedure described above. From 1.2 g (7.3 mmol) of **5c** in 10 ml of dioxane, 1.3 g (15 mmol) of piperidine, and 1.2 g (15 mmol) of formalin, 1.3 g (61.2% yield) of **9c** was obtained after recrystallization from isopropyl ether: mp 133–134°; uv max (99% EtOH) 262 nm (ε 5560); ir (KBr) 3500, 2900, 1690, 1650, 1340, 1100 cm^{-1}; nmr ($CDCl_3$) δ 6.10 (s, 1), 3.30 (m, 1), 2.80–2.00 (m, 12), 1.96–1.08 (m, 14).

Anal. Calcd for $C_{17}H_{28}O_2N_2$: C, 69.83; H, 9.65; N, 9.58. Found: C, 70.19; H, 10.05; N, 9.76.

3,5-Dimethyl-2-hydroxycyclopent-2-en-1-one (10). A.—A mixture of 6.0 g (20 mmol) of **9a**, 50 ml of glacial acetic acid, and 13 g (0.20 g-atom) of zinc powder was stirred at 80° for 5 hr. After zinc was filtered off, acetic acid was removed under reduced pressure, a small amount of water was added, and the solution was extracted with chloroform. After drying, the chloroform was evaporated to dryness and the residue was recrystallized from water to afford 0.8 g (32% yield) of **10**: mp 91–92°; uv max (99% EtOH) 261 nm (ε 12,100) [lit.[10] mp 91–91.5°; uv max (EtOH) 259 nm (ε 11,800)]; ir (KBr) 3250, 1690, 1640, 1130 cm^{-1}; nmr (CCl_4) δ 6.48 (s, 1), 2.97–1.85 (m, 3), 2.00 (s, 3), 1.18 (d, 3, J = 6 Hz).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.58; H, 8.25.

B.—Similarly, from 1.6 g (6.1 mmol) of **9b**, 20 ml of glacial acetic acid, and 4.0 g (0.061 g-atom) of zinc powder, 0.3 g (39.5% yield) of **10** was obtained.

C.—Similarly, from 1.5 g (5.1 mmol) of **9c**, 20 ml of glacial

(9) R. M. Acheson, *J. Chem. Soc.*, 4232 (1956).

(10) M. A. Gianturco and P. Friedel, *Tetrahedron*, **19**, 2039 (1963).

acetic acid, and 3.3 g (0.051 g-atom) of zinc powder, 0.25 g (38.5% yield) of **10** was obtained.

Acknowledgment.—The authors wish to thank Mr. T. Morofushi for his technical assistance.

Registry No.—**5a**, 24454-33-9; **5b**, 36287-24-8; **5c**, 37150-25-7; **6**, 37150-26-8; **7**, 80-71-7; **8**, 37160-44-4; **9a**, 37164-08-2; **9b**, 37164-09-3; **9c**, 37164-10-6; **10**, 21834-98-0.

Mono- and Di-2,2,2-trichloroethyl Acetals as Protecting Groups

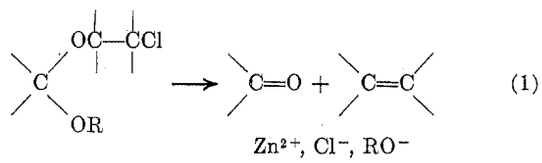
JOHN L. ISIDOR AND ROBERT M. CARLSON*

Department of Chemistry, University of Minnesota, Duluth, Minnesota 55812

Received August 7, 1972

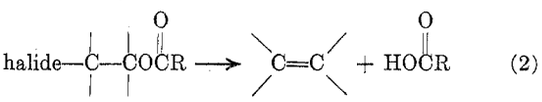
Mono- and di-2,2,2-trichloroethyl acetals have been selectively prepared in good yields by acid-catalyzed alcohol exchange with 2,2,2-trichloroethanol and dimethyl or diethyl acetals. A nonacidic and aprotic reductive cleavage using activated zinc dust in ethyl acetate or THF regenerates the carbonyl.

In connection with other synthetic work in these laboratories it was desirable to have available a protecting group for aldehydes that could be removed in a mild, selective, and nonacidic manner. The title compounds were therefore developed on the basis that the known reductive elimination of β-alkoxy halides[1] could, in the case of acetals, regenerate the carbonyl (eq 1). Reduction has previously been used



(1)

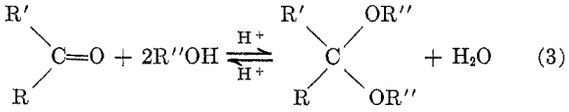
effectively in the removal of the 2-haloethyl carbonate (carbamate) protecting group from alcohols (amines), and the removal of the 2-haloethyl group from esters (eq 2).[2]



(2)

We would like to report the success of this overall design whereby a convenient, general synthesis of both the mono- and bis-2,2,2-trichloroethyl acetals has been developed and the optimum conditions for removal of the protecting group have been determined for a variety of systems.

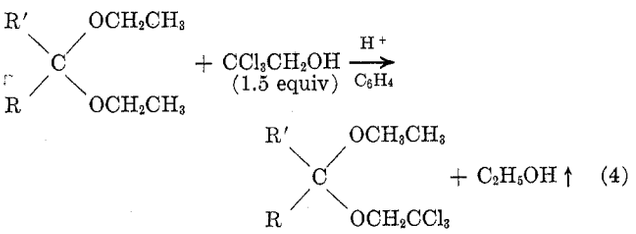
Traditionally, an acetal is most expeditiously prepared from the aldehyde or ketone by treatment with the corresponding alcohols and a strong acid under conditions which would favor the equilibrium shown below (eq 3). Such methods as the use of excess alcohol, the use of a water scavenger such as triethyl orthoformate, or the azeotropic removal of water have all been employed.[3] These published techniques were found to be unsatisfactory with trichloroethanol, however, presumably due to the inductive ($-I$) effect of the trichloromethyl group which makes trichloroethanol less nucleophilic and less able to stabilize any intermediate carbonium ion. The use of tris-2,2,2-trichloroethyl orthoformate as a water scavenger was considered impractical due to its difficulty in preparation and its great stability to acid.[4]



(3)

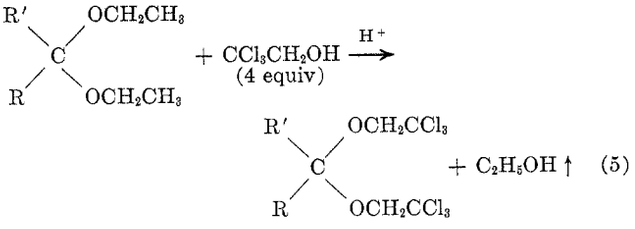
The method of choice for the preparation of trichloroethyl acetals proved to be a *p*-toluenesulfonic acid catalyzed alcohol exchange of a diethyl (or dimethyl) acetal with trichloroethanol in benzene or xylene. In this conversion, commerically available dimethyl or diethyl acetals were used whenever possible. However, in the majority of cases the free aldehyde or ketone was converted into the diethyl acetal with triethyl orthoformate and used without isolation in the subsequent alcohol exchange with trichloroethanol.

In the synthesis of the trichloroethyl acetals shown in Table I, advantage was taken both of the high boiling point of trichloroethanol, which allowed continuous removal of ethanol as an azeotrope, and of the acid stability of trichloroethyl ethers, which permitted the introduction of either one or two trichloroethoxy groups. For example, the use of 1.5 equiv of trichloroethanol in benzene gave the mixed acetal almost exclusively (eq 4), while the use of 4 equiv of trichloroethanol in



(4)

xylene gave good yields of the bistrichloroethyl acetals (eq 5).



(5)

A systematic search for the best experimental conditions for elimination soon focused on the use of ac-

(1) See, for example, O. Grummitt, *et al.*, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 748, and references cited therein.

(2) E. Kasafirek, *Tetrahedron Lett.*, **20**, 2021 (1972); M. F. Semmelhack and G. E. Heinsohn, *J. Amer. Chem. Soc.*, **94**, 5139 (1972), and references therein.

(3) C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley, New York, N. Y., 1970, Chapter 9.

(4) A. Kankaanpira and M. Lahti, *Suom. Kemistilehti B*, **42**, 406 (1969).