

References and Notes

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Iodide Catalysis of Oxidations with Dimethyl Sulfoxide. A Convenient Two-Step Synthesis of α Diketones from α -Methylene Ketones

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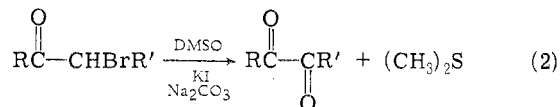
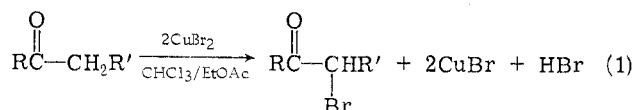
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Received January 24, 1975

α diketones are not only interesting with regard to conformational analysis,¹ electronic spectroscopy,² and photochemistry,³ but also because they are versatile synthetic intermediates and they undergo a variety of unique reactions, including the benzil-benzilic acid rearrangement⁴ and dioxaphospholene formation.⁵

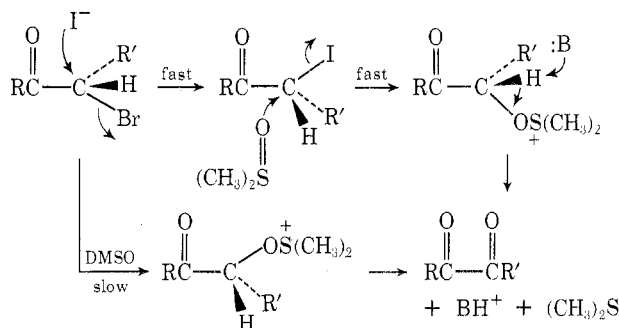
In connection with our synthesis of macrotricyclic hydrocarbons, we needed large amounts of several cyclic α diketones, including 1,2-cyclooctanedione and 1,2-cyclododecanedione. One synthesis involved an acyloin condensation, followed by oxidation with cupric acetate;^{6,7} another was the selenium dioxide oxidation of the corresponding cyclic ketones.⁷ Our attempts to reproduce the selenium dioxide oxidations led to products in moderate yields, but these products were contaminated with selenium which proved extremely difficult to remove.⁸ The acyloin condensation, while providing higher purity, was much more difficult to carry out and gave frustratingly low yields. The observation that primary and secondary halides and sulfonate esters could be oxidized to aldehydes and ketones with dimethyl sulfoxide (DMSO)⁹ led several groups to prepare α diketones via the DMSO oxidation of α -bromo ketones.¹⁰ Unfortunately, the DMSO oxidation, because it requires SN2 attack by the sulfoxide oxygen at the brominated carbon, is sensitive to the steric environment of that center. Thus, while primary halides and tosylates provide aldehydes in decent yields, oxidation of secondary systems, as required to make diketones, is often sluggish. This low reactivity can be partially overcome by promoting the oxidation with silver salts such as silver perchlorate¹¹ or silver nitrate,¹² but such reagents are not economical on the mole scale. We wish to report a convenient, high-yield process

for conversion of α -methylene ketones to α diketones, using only inexpensive, common reagents.



Of the many ways to α -brominate ketones, we have had uniformly excellent results with cupric bromide in refluxing chloroform-ethyl acetate.¹³ For the five ketones listed in Table I, the isolated yield of α -bromo ketone ranged from 90 to 97%, and the slowest reaction required 8 hr (2,2,5,5-tetramethyl-3-hexanone). The success of the sequence thus depended only on the oxidation step. Our attempts to oxidize these α -bromo ketones directly with DMSO gave only slow reactions in the cases of the third and fourth entries in Table I, and essentially no reaction in the first, second, and fifth cases.

It has been noted¹⁴ that DMSO is a weaker nucleophile than even bicarbonate in at least one instance. It seemed reasonable that the oxidation step could be catalyzed by a species that was a better nucleophile than DMSO and a better leaving group than bromide. Iodide ion fits this description well, for it is not only a powerful nucleophile (by virtue of high polarizability and low solvation), but also a highly reactive leaving group in nucleophilic displacements (because of the weakness of the C-I bond).¹⁵ Thus, the slow direct attack by DMSO on the α -bromo ketone could be circumvented by two faster displacements involving iodide.



The catalytic effect of iodide was dramatic. The second, third, and fourth entries in Table I reacted completely within 10 min at ambient temperature. The first entry, for reasons that are not clear, required 60 min at 120°, but still gave a reasonable yield. Not unexpectedly the 4-bromo-2,2,5,5-tetramethyl-3-hexanone (a new compound, entry 5) failed to react even after 25 hr at 150°. Although there was evidence that attack by iodide occurred (see Experimental Section), attack by DMSO was apparently precluded by the neopentyl nature of the reaction center.¹⁶ We were able to oxidize 4-bromo-2,2,5,5-tetramethyl-3-hexanone in 47% yield using silver nitrate in DMSO.¹² This is probably the method of choice when dealing with highly hindered α -halo ketones.

With the exception of the above compound, overall yields of the α diketones ranged from 65 to 92%. Both reactions are simple to perform and the required reagents and solvents are economical to use. The only disadvantages of this procedure are (1) certain α -bromo ketones (Table I, entries 1 and 2) are somewhat unstable and should not be stored for long periods before carrying out the oxidation, (2) some α -bromo ketones and α diketones undergo side reactions such as aldol condensations in DMSO, so the oxi-

Table I
Two-Step Conversion of Ketones to α Diketones

Entry	Starting ketone	Registry no.	Step 1		Step 2		Overall yield, %	Registry no.
			Time, hr	Yield, %	Time, min.	Yield, %		
1		830-13-7	3.5	90	60 ^a	71	65	3008-41-1
2		502-49-8	5.0	90	4-5 ^b	65	59	3008-37-5
3		451-40-1	5.0	97	5-10 ^b	95	92	134-81-6
4		93-55-0	5.0	95	5-10 ^b	90	86	579-07-7
5		868-91-7	8.0	93	c	c	c	

^a 120°. ^b Ambient temperature. ^c No reaction, even after 25 hr at 150°; see text.

dation step should be monitored with TLC and stopped when complete, and (3) ketones with nonidentical α -methylene groups will give mixtures of monobromo derivatives, and hence mixtures of isomeric diketones. Only if the isomers are separable at one stage or the other will this synthesis be of use.

Experimental Section

The following instruments were employed: Beckman IR-12 (calibrated with polystyrene); Varian A-60 (δ , parts per million downfield from internal Me₄Si); Bruker HFX-90 (¹³C data are given in parts per million upfield from CS₂); Hitachi RMU-7 (70 eV unless otherwise noted). All starting materials, reagents, and solvents were obtained from Aldrich Chemical Co. or Matheson Scientific unless otherwise noted. Melting and boiling points are not corrected. The elemental analysis was performed by Chemalytics, Inc., Tempe, Ariz.

2-Bromocyclododecanone. Cyclododecanone (9.1 g, 0.050 mol), chloroform (50 ml), and ethyl acetate (50 ml) were placed in a 250-ml three-necked flask equipped with magnetic stirrer, nitrogen inlet tube, and reflux condenser. Powdered cupric bromide (22.3 g, 0.10 mol) was added in small portions over a 2-hr period, with the reaction mixture maintained at 75–80° while a constant stream of nitrogen gas was bubbled through the reaction solution.¹³ The green color from each portion was allowed to disappear before the next portion was added. After the addition was completed, the solution was heated for 1.5 hr until the green color and dark cupric bromide disappeared, cooled, and filtered, and the colorless solid cuprous bromide was washed with 25 ml of chloroform. The combined filtrate and washings were rotary evaporated and the oily residue was redissolved in 200 ml of diethyl ether, washed with water (50 ml), 5% sodium bicarbonate (2 × 50 ml), and brine (50 ml), then dried over sodium sulfate. After filtration, rotary evaporation of solvent, and cooling (–10°), the resulting oil solidified to give cream-colored crystals (11.8 g, 90%) of 2-bromocyclododecanone, mp 52–53° (lit.¹⁷ mp 53–54°). The product could also be recrystallized from pentane at –78°.

Spectral data for 2-bromocyclododecanone¹⁸ include: ir (CHCl₃) 1713 cm^{–1}; ¹H NMR (CDCl₃) 1.33 (s, $\Delta\nu_{1/2}$ = 4.5 Hz, 14 H), 1.65–2.25 (br m, 4 H), 2.76 (m, 2 H), 4.43 (d of d, J = 4 Hz, 1 H); ¹³C NMR (CS₂) –10.1, 155.2, 156.2, 164.2, 165.5, 167.1 ppm; mass spectrum m/e (rel intensity) 262/260 (M⁺, 33/33), 180 (100).

1,2-Cyclododecanedione. To a stirred mixture of potassium iodide (8.3 g, 0.05 mol), sodium carbonate (5.3 g, 0.05 mol), and dimethyl sulfoxide (170 ml) at 120° under nitrogen was added 2-bromocyclododecanone (13.05 g, 0.05 mol) at once. After stirring for 1 hr, the mixture was rapidly cooled and then poured into ice-cold brine (300 ml), and the mixture was extracted with diethyl ether (2 × 100 ml). The combined extracts were washed with water (100 ml), brine (100 ml), 5% sodium bicarbonate (100 ml), and brine (100 ml), then dried (Na₂SO₄) and filtered. Rotary evaporation left an oil which was chromatographed through alumina (Alcoa), using benzene–diethyl ether (2:1 v/v) as the eluent, to yield 7.0 g (71%) of

bright yellow 1,2-cyclododecanedione, which crystallized upon removal of the solvent: mp 43° (lit.^{6,7} mp 44°); ir (cyclohexane) 1708 cm^{–1}; ¹H NMR (CDCl₃) 1.29 (s, $\Delta\nu_{1/2}$ = 3.5 Hz, 12 H), 1.53–1.93 (br m, 4 H), 2.75 ppm (t of t, J = 6 Hz, 4 H); ¹³C NMR (CS₂) –8.0, 153.9, 163.4, 164.5, 166.0, 167.3 ppm; mass spectrum m/e (rel intensity) 196 (M⁺, 100).

2-Bromocyclooctanone. The preceding method was employed on the 0.10-mol scale to prepare 2-bromocyclooctanone, bp 54–55° (0.1 mm) [lit.¹⁹ bp 79–81° (1 mm)], yield 18.4 g (90%), from cyclooctanone. Addition required 3.5 hr, and this was followed by stirring for 1.5 hr.

Spectral data^{18,19} include: ir (neat) 1710 cm^{–1}; ¹H NMR (CDCl₃) 1.67 (m, 8 H), 2.10–2.90 (m, 4 H), 4.36 ppm (t, 1 H); mass spectrum m/e (rel abundance) 206/204 (M⁺, 30/30), 98 (100).

1,2-Cyclooctanedione was prepared on the 20-mmol scale from 2-bromocyclooctanone. Reaction time was ~4–5 min at 20–23°. The work-up procedure was the same as described in the previous example: yield 2.0 g (74%); bp 44–45° (0.4 mm) [lit.⁷ bp 59–60° (1.5 mm)].

Spectral data include: ir (CCl₄) 1701 cm^{–1}; ¹H NMR (CDCl₃) 1.70 (s, $\Delta\nu_{1/2}$ = 7.0 Hz, 8 H), 2.30–2.71 ppm (m, 4 H); mass spectrum m/e (rel abundance) 140 (M⁺, 100).

2-Bromo-2-phenylacetophenone was prepared on the 50-mmol scale from deoxybenzoin. Addition required 3.5 hr, with 1.5 hr of additional stirring. After the usual work-up, 13.4 g (97%) of opaque product was isolated, mp 55–56° (lit.²⁰ mp 54–55°). The ir [(CCl₄) 1701 cm^{–1}], ¹H NMR [(CDCl₃) 6.45 (s, 1 H), 7.30–8.15 ppm (m, 10 H)], and TLC of the purified product were identical with those of an authentic sample of 2-bromo-2-phenylacetophenone (Eastman Organic Chemical Co.).

Benzil was prepared on the 10-mmol scale from 2-bromo-2-phenylacetophenone at ambient temperature for 5–10 min. After the usual work-up, 2.0 g (95%) of benzil was isolated, mp 95–96° (lit.²¹ mp 95–96°).

The ir [(CCl₄) 1677, 1684 cm^{–1}], ¹H NMR [(CDCl₃) 7.50–8.15 ppm (m, 10 H)], and TLC of the purified product were identical with those of an authentic sample of benzil (Eastman Organic Chemical Co.).

α -Bromopropiophenone was prepared on the 100-mmol scale (addition 1.5 hr, stirring 1.5 hr): yield 95%; bp 64–66° (1 mmHg) [lit.²² bp 110–111° (3 mmHg)].

The ir [(neat) 1710 cm^{–1}], ¹H NMR [(CDCl₃) 1.88 (d, J = 6 Hz, 3 H), 5.20 (q, J = 6 Hz, 1 H), 7.36–8.15 ppm (m, 5 H)], and TLC of the purified product match the data obtained from an authentic sample (Aldrich Chemical Co.).

1-Phenyl-1,2-propanedione was prepared on the 20-mmol scale exactly as in the preparation of benzil: yield 90%; bp 60–62° (0.5 mmHg) [lit.²³ bp 101° (12 mm)].

The ir [(neat) 1673, 1712 cm^{–1}], ¹H NMR [(CDCl₃) 2.53 (s, 3 H), 7.35–8.15 ppm (m, 5 H)], and TLC of the purified product match those data obtained on an authentic sample (Eastman Chemical Co.).

2,2,5,5-Tetramethyl-3-hexanone was prepared by the "Jones reagent"²⁴ oxidation of 2,2,5,5-tetramethyl-3-hexanol (Chemical

Samples Co.): bp 160–161° (lit.¹⁶ bp 161°); ir (CHCl₃) 1705 cm⁻¹; ¹H NMR (CDCl₃) 1.05 (s, 9 H), 1.10 (s, 9 H), 2.40 ppm (2 H); mass spectrum *m/e* (rel abundance) 156 (M⁺, 40), 57 (100).

4-Bromo-2,2,5,5-tetramethyl-3-hexanone was prepared from the above ketone on the 50-mmol scale. The reaction was notably slower than the other reactions, with addition requiring 8 hr. Work-up as usual gave 10.9 g (93%) of the bromo ketone as clear, colorless oil: bp 31° (0.10 mm); ir (CHCl₃) 1709 cm⁻¹; ¹H NMR (CDCl₃) 1.16 (s, 9 H), 1.25 (s, 9 H), 4.53 ppm (s, 1 H); mass spectrum *m/e* (rel abundance) 236/234 (M⁺, 60/60), 151/149 (M – C₄H₉CO, 70/70), 57 (100).

Anal. Calcd for C₁₀H₁₉BrO: C, 51.07; H, 8.14; Br, 33.98. Found: C, 51.04; H, 8.11; Br, 34.04.

Attempted Preparation of 2,2,5,5-Tetramethyl-3,4-hexanedione via Iodide-Catalyzed Oxidation. When the usual reaction was attempted on the above bromo ketone, even after reaction times of up to 25 hr at 150°, no diketone could be isolated, although there was development of some yellow color. The liquid reisolated from the reaction (105% based on mass of starting bromo ketone), which had an NMR identical with that of starting material, was shown by GLC (12% Carbowax 20M) to be a 55:45 mixture of α-bromo and α-iodo ketone: mass spectrum *m/e* 282 (RI), 236/234 (RBr), 197 (RI – C₄H₉CO), 151/149 (RBr – C₄H₉CO).

2,2,5,5-Tetramethyl-3,4-hexanedione was prepared by Kornblum's method;¹² 4-bromo-2,2,5,5-tetramethyl-3-hexanone (2.35 g, 10 mmol) was dissolved in 15 ml of acetonitrile, and a solution of silver nitrate (1.87 g, 11 mmol) in 15 ml of acetonitrile was added. After stirring for 60 hr at ambient temperature the mixture was filtered, the silver bromide was washed with diethyl ether, and the combined filtrate and washing were rotary evaporated (water aspirator, 30°). The residue was taken up in ether, washed with water, and dried, and the solvent was removed. The crude nitrate ester was dissolved in 70 ml of DMSO and then a suspension of sodium acetate trihydrate (0.20 g) in 20 ml of DMSO was added. After stirring for 5–10 min at room temperature, the reaction mixture was worked up in a similar manner to the previously mentioned DMSO oxidation reactions: yield 0.80 g (47%); bp 38–40° (5 mm) [lit.¹ bp 59–62° (14 mm)]; ir (neat) 1700 cm⁻¹; NMR (CCl₄) 1.18 ppm (s); mass spectrum *m/e* (rel abundance) 170 (M⁺, 6), 57 (100).

Acknowledgment. We wish to thank PHS, NIH, for their generous support of this work (Grant 5 R01 AI 11690-02 MCHB).

Registry No.—2-Bromocyclododecanone, 31236-94-9; 2-bromocyclooctanone, 39261-18-2; 2-bromo-2-phenylacetophenone, 1484-50-0; α-bromopropiophenone, 2114-00-3; 2,2,5,5-tetramethyl-3-hexanol, 55073-86-4; 4-bromo-2,2,5,5-tetramethyl-3-hexanone, 55073-87-5; 4-iodo-2,2,5,5-tetramethyl-3-hexanone, 55073-88-6; 2,2,5,5-tetramethyl-3,4-hexanedione, 4388-88-9.

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Oxidation of Alcohols with Acetyl Hypoiodite

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Received December 13, 1974

This report covers the reaction of a variety of alcohols with acetyl hypoiodite and the subsequent decomposition of the alkyl hypoiodite that was formed. The formation and decomposition of the alkyl hypoiodite product was done in the absence of metal salts. Previous reported reactions of steroid alcohols with acetyl hypoiodite involved the preparation and decomposition of the products in the presence of mercury, silver, or lead salts.¹ These salts very likely have a direct effect on the product composition.

To determine the generality of preparing alkyl hypoiodites from acetyl hypoiodite and alcohols, we have treated several alcohols with acetic acid solutions of acetyl hypoiodite. Solutions of acetyl hypoiodite were prepared by treating silver acetate with a 5% molar excess of iodine in glacial acetic acid.² The molar amount of precipitated silver iodide accounted for more than 99% of the starting silver acetate.

The alcohols to be oxidized were selected so that the proposed alkyl hypoiodite intermediates would break down to products in a variety of ways. Good yields of products were obtained by irradiating the cooled (20–25°) reaction mixtures immediately after the alcohols were mixed with the acetyl hypoiodite solutions. The product yields were cut approximately in half when the reaction mixtures were irradiated and heated (90–100°), and yields were very low (10–20%) when the reaction mixtures were run in the dark at ambient temperatures.

A general sequence for the reaction between acetyl hypoiodite and an alcohol is suggested below. The acetyl hypoiodite reacts with the alcohol to give an equilibrium with the alkyl hypoiodite and acetic acid. The O–I bond of the alkyl hypoiodite then is cleaved homolytically by visible light to produce alkoxy radicals. The alkoxy radicals have several decomposition pathways available to them.



The oxidations of 3-ethyl-3-pentanol, 1-pentanol, and benzyl alcohol with acetyl hypoiodite will be discussed in some detail. The only detectable products from the reaction of 3-ethyl-3-pentanol with acetyl hypoiodite were 3-pentanone and iodoethane. The 3-pentanone is formed from β-scission³ of the intermediate alkoxy radical **2**, while the iodoethane is produced when the ethyl radical and the hypoiodite **1** collide.