CO)$^+$], 221 [(M − C_4H_7)$^+$], and 165 [(221 − 2CO)$^+$]. *Anal.* Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.64; H, 5.71.

2-Phenyl-2-(2-hydroxy-2-methyl-3-bromopropyl)indan-1,3-dione (2). The addition of 5.80 g (36.2 mmol) of Br_2 in 10 ml of HOAc to a suspension of 1 (10.0 g, 36.2 mmol) in 50 ml of HOAc was accompanied by decoloration, dissolution of the solid, a mild exotherm, and the evolution of HBr. After 1.5 hr at 25°, the mixture was poured into 250 ml of H_2O, and the crude solid thus obtained was recrystallized from 50 ml of EtOH, yield 10.34 g (29.0 mmol, 80%) of **2** as colorless crystals:[7] mp 143–145° dec; ν_{max} (KBr) 3400, 1705, 1265, 1240 cm^{-1}; λ_{max} 332 nm (ϵ 329), 287 (1510), and 248 (11,900); ^{1}H nmr δ 8.00–7.50 (m, C_6H_4), 7.33–7.17 (m, C_6H_5), 3.73 (s, CH_2Br), 2.87 (s, CH_2), and 1.27 ppm (s, CH_3); mass spectrum *m/e* 444 and 446 after silylation [(M + TMS)$^+$], 372 and 374 (M$^+$), 293 [(M − Br)$^+$], 279 [(M − CH_2Br)$^+$], and 275 [(293 − H_2O)$^+$]. *Anal.* Calcd for $C_{19}H_{17}BrO_3$: C, 61.14; H, 4.59; Br, 21.41; *m/e* 372.0361. Found: C, 61.47; H, 4.26; Br, 21.33; *m/e* 372.0363.

2-Phenyl-2-[2-hydroxy-2-methyl-3-(1-piperidinyl)propyl]-indan-1,3-dione (3). A mixture of bromo compound **2** (3.57 g, 10 mmol), DMF (5 ml), and piperidine (2.1 g, 25 mmol) was left at 25° for 4 days.[1] The crude product, isolated by dilution of the mixture with H_2O, was recrystallized from 15 ml of EtOH, yield 3.08 g (8.2 mmol, 82%) of colorless needles[8] of **3**: mp 130–131°; ν_{max} ($CHCl_3$) 1720 cm^{-1}; λ_{max} 331 nm (ϵ 405), 293 (1610), and 247 (11,600); ^{1}H nmr δ 8.58 (broad, OH), 8.03–7.40 (m, C_6H_4), 7.20 (s, C_6H_5), 3.13–2.52 (AB, exocyclic NCH_2), 2.65 (m, ring NCH_2), 2.40 (s, acyclic CH_2), 1.40 (m, ring CH_2), and 1.15 ppm (s, CH_3); mass spectrum *m/e* 377 (M$^+$) and 98 [($C_6H_{12}N$)$^+$, base peak]. *Anal.* Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71; *m/e* 377.1989. Found: C, 76.30; H, 6.98; N, 3.60; *m/e* 377.2013.

Registry No.—**1**, 26151-51-9; **2**, 51270-74-7; **3**, 51270-75-8; piperidine, 110-89-4.

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(6) Literature values for **1** are mp 100–101°; ν_{max} (Nujol) 1744 and 1710 cm^{-1}; λ_{max} (EtOH) 336 nm (ϵ 2000) and 226 (3600).
(7) Literature values for **4** are mp 141–142°; ν_{max} (Nujol) 3430 and 1712 cm^{-1}; λ_{max} (EtOH) 291 nm (ϵ 900) and 249 (11,500); formula $C_{19}H_{15}BrO_2$.
(8) Liteeature values for **5** are mp 138–139°; ν_{max} (Nujol) 1708 cm^{-1}; λ_{max} (EtOH) 294^s nm (ϵ 1700) and 248 (11,800); formula $C_{24}H_{25}NO_2$.

Halogenation of Carbonyl Compounds *via* Silyl Enol Ethers[1]

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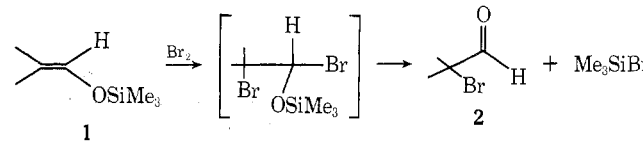
In connection with other studies we needed several α-bromo aldehydes and, since such compounds are prepared by bromination of aldehydes only with difficulty,[2] we sought an alternative method. Several recent syntheses have been described,[3] but they represent homologation reactions. Vinyl acetates and enamines of the corresponding aldehyde have also been used to prepare the desired compounds.[4] In line with our interest in electrophilic additions to olefins,[5] it occurred to us that bromination of silyl enol ethers (**1**) followed by spontaneous β cleavage of volatile trimethylbromosilane[6] should afford the desired product (**2**). Since the silyl enol ethers are readily generated in high yield,[7] this method would provide a simple route to synthetically useful[8] α-bromo aldehydes.

Table I
Synthesis of α-Haloaldehydes from the Corresponding Aldehyde *via* Silyl Enol Ethers

$$R_1R_2CHCHO \xrightarrow[Et_3N]{Me_3SiCl} R_1R_2C{=}CHOTMS \xrightarrow{X_2} \underset{R_1R_2CCHO\ (X = Br, Cl)}{\overset{X}{|}}$$

Entry	X_2	R_1	R_2	% yield of **2**
1	Br_2	$PhCH_2$	H	77
2	Br_2	Ph	Me	75
3	Br_2	C_6H_{17}	H	94
4	Br_2	$-CH_2CH_2CH{=}CHCH_2-$		57[a]
5	Br_2	$-CH_2CH_2CH_2\underset{CO_2C_2H_5}{\overset{}{|}}CHCH_2-$		62
6	Br_2	Me	Me	51[b]
7	Cl_2	$PhCH_2$	H	95
8	Br_2	$(CH_2)_4CN$	H	42[c]

[a] Some bromination of the double bond observed in the crude product. [b] Low yield of distilled product due to high volatility; reaction performed in Et_2O. [c] Ca. 10% yield of an unknown aldehyde was also obtained.



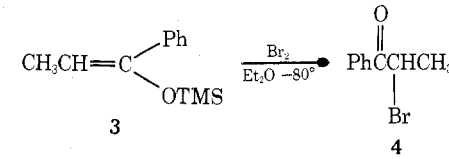
1 2

Our expectations were confirmed as shown in Table I. The silyl enol ethers were prepared according to the method of House[7] and were found to react instantaneously with 1 equiv of bromine in carbon tetrachloride at room temperature. The product was isolated by evaporating the solvent and trimethylbromosilane (bp 85°) and distilling the aldehyde. The technique is applicable to a wide range of aldehydes as well as to ketones. Particularly noteworthy is the bromination at the α position of the aldehyde in the presence of a double bond (see Table I) and an ester function (entry 5). α-Chloro aldehydes are obtained by using chlorine[9] in place of bromine (entry 7), although neither iodine nor iodine monochloride was reactive.

A limitation of the method is indicated by the fact that the silyl enol ethers of crotonaldehyde, 6-ketoheptanal (aldehyde silyl enol ether), and citronellal afforded polymeric products even when bromination was carried out at −80°.

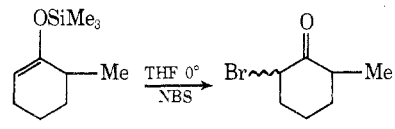
While bromination of ketones generally presents no major problem,[2] various synthetic procedures have been devised for specific bromination where more than one regioisomer is possible.[2,10] Bromination of silyl enol ethers enables regiospecific halogen introduction since methods are available[7] for the synthesis or isolation of silyl enol ether regioisomers. A recent communication describes the bromination of lithium enolates, derived from silyl enol ethers, to afford α-bromo ketones.[11] However, we have found that preparation of the enolate is unnecessary.

The use of silyl enol ethers for the bromination of ketones is demonstrated by the quantitative conversion of silyl enol ether **3** to α-bromopropiophenone (**4**)[12] and the



3 4

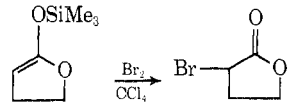
formation of 2-bromo-6-methylcyclohexanone (6) from enol ether 5 upon treatment with *N*-bromosuccinimide (95% yield).[13] Addition of Br_2 to 5 afforded an 85% yield



5 6

of predominantly 6, but the isomeric 2-bromo-2-methyl ketone as well as dibromo derivatives were observed. Bromo ketone 6 has been reported[11,14] to be readily isomerized in the presence of acid, and we found this to be true even on distillation of 6.

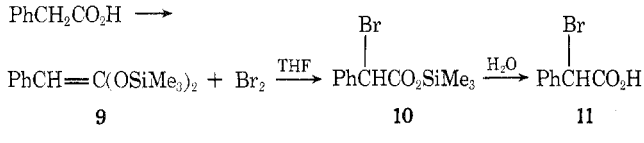
We have further investigated the use of trimethylsilyl derivatives for introducing an α-bromide in other carbonyl compounds. Thus, reaction of the ketene trimethylsilyl acetal 7 (from butyrolactone)[15] with 1 equiv of Br_2 afforded 2-bromobutyrolactone (8) in 84% yield. However,



7 8

further investigation of this method was considered unwarranted because Rathke[16] has shown that ester enolates which are the precursors of ketene trimethylsilyl acetals[17] can be brominated directly in high yield.

The synthesis of α-bromocarboxylic acids may also be accomplished *via* ketene bis(trimethylsilyl) acetals. Treatment of 9[15,17] with 1 equiv of Br_2 followed by hydrolysis of the trimethylsilyl ester 10 with a few drops of water[18] afforded α-bromophenylacetic acid (11) in 81% yield.



9 10 11

The results described herein demonstrate that halogenation of trimethylsilyl derivatives of carbonyl compounds represents a convenient procedure for the regiospecific synthesis of α-halocarbonyl compounds.

Experimental Section[19]

Preparation of Silyl Enol Ethers. House's[7] procedure was used to afford products in yields of 60–80%.

Bromination of Silyl Enol Ethers. To a stirred solution of the compound in carbon tetrachloride was added slowly, over several hours, 1 equiv of bromine in carbon tetrachloride. The rate of addition was maintained such that the solution was always colorless to pale orange.

A. 2-Bromo-3-phenylpropanal (Entry 1). From 6.2 g of the silyl enol ether was obtained 4.9 g (77%) of colorless liquid: bp 70–75° (2 Torr); nmr ($CDCl_3$) δ 3.3 (m, 2, CH_2), 4.35 (m, 1, CH), 7.15 (s, 5, Ph), 9.35 (d, 1, CHO).

Anal. Calcd for C_9H_9BrO: C, 50.66; H, 4.23; Br, 37.60. Found: C, 50.41; H, 4.29; Br, 37.42.

B. 2-Bromo-2-phenylpropanal (Entry 2). From 6.2 g of silyl enol ether was obtained 4.8 g (75%) of colorless liquid: bp 68–71° (2 Torr); nmr ($CDCl_3$) δ 2.2 (s, 3, Me), 7.4 (m, 5, Ph), 9.55 (s, 1, CHO). The product was identical with that previously reported.[20]

C. 2-Bromodecanal (Entry 3). From 6.8 g of silyl enol ether was obtained 6.6 g (94%) of colorless liquid: bp 72–76° (0.5 Torr); nmr ($CDCl_3$) δ 0.85 (m, 3, Me), 1.2 (broad, 12, $(CH_2)_6$), 1.9 (m, 2, CH_2), 4.15 (m, 1, CH), 9.3 (d, 1, CHO).

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.07; H, 8.09; Br, 34.03. Found: C, 51.04; H, 8.14; Br, 34.10.

D. 4-Bromo-4-formylcyclohexene (Entry 4). From 5.45 g of silyl enol ether was obtained 3.25 g (57%) of colorless liquid: bp 45° (2 Torr); nmr ($CDCl_3$) δ 2.15 (broad, s, 4, $(CH_2)_2$), 2.7 (broad, s, 2, CH_2), 5.65 (broad, s, 2, -CH=CH-), 9.35 (s, 1, CHO).

Anal. Calcd for C_7H_9BrO: C, 44.43; H, 4.76; Br, 42.35. Found: C, 44.36; H, 4.76; Br, 42.30.

E. Ethyl (3-Bromo-3-formyl)cyclohexanecarboxylate (Entry 5). From 2.35 g of silyl enol ether was obtained 1.5 g (62%) of colorless liquid: bp 91–95° (0.1 Torr); nmr ($CDCl_3$) δ 1.2 (t, 3, CH_3); 1.0–3.0 (m, 9, ring H's), 4.1 (q, 2, OCH_2), 9.3 (two singlets, 1, CHO, axial and equatorial isomers).

Anal. Calcd for $C_{10}H_{15}BrO_3$: C, 45.65; H, 5.70; Br, 30.40. Found: C, 45.41; H, 5.79; Br, 30.47.

F. 2-Bromo-2-methylpropanal (Entry 6). From 2.6 g of silyl enol ether was obtained 1.4 g (51%) of colorless liquid: bp 47° (70 Torr); nmr ($CDCl_3$) δ 1.75 (s, 6, Me_2C), 9.25 (s, 1, CHO). The compound was identical with that previously reported.[21]

G. 2-Chloro-3-phenylpropanal (Entry 7). A solution of 1.0 g of silyl enol ether in CCl_4 was treated with gaseous chlorine until a yellow-green color persisted. Evaporation of excess chlorine and solvent and distillation of the residue at 100° and 5 Torr afforded 0.8 g (95%) of product. The nmr was identical with that previously reported.[22]

H. 2-Bromo-6-cyanohexanal (Entry 8). From 0.98 g of silyl enol ether was obtained 0.61 g of colorless liquid (bp 100° (0.5 Torr)) consisting of two compounds in a 7 to 3 ratio. The major component (42% yield) was the title compound: nmr ($CDCl_3$) δ 1.8 (m, 6, $(CH_2)_3$), 2.5 (m, 2, CH_2CN), 4.4 (t, 1, CHCHO), 9.45 (d, 1, J = 2 Hz, CHO). The second was an unidentified aldehyde: nmr ($CDCl_3$) δ 1.8 (m, 6), 2.5 (m, 2), 3.5 (t, 1), 9.25 (s, 1).

α-Bromopropiophenone (4). The silyl enol ether 3 (0.95 g) in 25 ml of ether at −80° was stirred and treated dropwise with bromine (0.25 ml) in 40 ml of Et_2O over several hours. The resulting colorless solution was warmed to room temperature and the solvent removed *in vacuo*. Distillation at 80° and 0.2 Torr afforded 1.0 g (100%) of product which was identical with an authentic sample: nmr ($CDCl_3$) δ 1.85 (d, 3, Me, J = 7.4 Hz), 5.3 (q, 1, CH, J = 7.4 Hz), 7.5 (m, 3, aromatic H's), 8.1 (m, 2, aromatic H's).

2-Bromo-6-methylcyclohexanone (6). To 0.35 g (1.9 mmol) of silyl enol ether 5 in 20 ml of anhydrous THF at 0° was added 0.35 g (2.0 mmol) of NBS. After stirring for 15 min, the solution was poured into aqueous $NaHCO_3$ and NaCl. The mixture was extracted with petroleum ether, dried over Na_2SO_4, and dried under vacuum to afford 0.34 g (95%) of pale yellow liquid 6. The nmr indicated a mixture of 60% axial bromide and 40% equatorial bromide and was consistent with that published.[14] Distillation afforded 0.32 g (89%) which contained *ca.* 20% of 2-bromo-2-methylcyclohexanone.

2-Bromobutyrolactone (8). To 0.8 g (5 mmol) of 7[23] in 25 ml of CCl_4 was added dropwise with stirring 0.27 ml (5 mmol) of Br_2 in 5 ml of CCl_4. Addition was complete after 3 hr. The solvent was removed *in vacuo* and the residue distilled in a Kugelrohr at 100° and 0.5 Torr to afford 0.7 g (84%) of colorless liquid 8. The nmr was identical with that reported.[24]

α-Bromophenylacetic Acid (11). To 0.68 g (2.4 mmol) of 9[17] in 15 ml of anhydrous THF was added dropwise with stirring a solution of 0.13 ml (2.4 mmol) of Br_2 in 15 ml of anhydrous THF. After addition was complete (30 min), the solution was stirred for 2 hr and treated with a few drops of H_2O. The solvent was evaporated to give 0.53 g of pale orange solid. Recrystallization from petroleum ether gave 0.43 g (81%) of white solid 11 which was identical with an authentic sample (Aldrich).

Acknowledgment. Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

Registry No.—R_1R_2CHCHO (R_1 = $PhCH_2$, R_2 = H), 104-53-0; R_1R_2CHCHO (R_1 = Ph, R_2 = Me), 93-53-8; R_1R_2CHCHO (R_1 = C_8H_{17}, R_2 = H), 112-31-2; R_1R_2CHCHO (R_1,R_2 = CH_2CH_2CH=$CHCH_2$-), 100-50-5; R_1R_2CHCHO (R_1R_2 = $CH_2CH_2CH_2CH(CO_2C_2H_5)CH_2$-), 51075-21-9; R_1R_2CHCHO (R_1 = R_2 = Me), 78-84-2; R_1R_2CHCHO (R_1 = $(CH_2)_4CN$, R_2 = H), 18214-15-8; R_1R_2C=CHOTMS (R_1 = $PhCH_2$, R_2 = H), 51075-22-0; R_1R_2C=CHOTMS (R_1 = Ph, R_2 = Me), 51075-23-1; R_1R_2C=CHOTMS (R_1 = C_8H_{17}, R_2 = H), 51075-24-2; R_1R_2C=CHOTMS (R_1,R_2 = $-CH_2CH_2CH$=$CHCH_2$-), 51075-25-3; R_1R_2C=CHOTMS (R_1,R_2 = $-(CH_2)_3CH(CO_2C_2H_5)CH_2$-), 51075-26-4; R_1R_2C=CHOTMS (R_1 = R_2 = Me), 6651-34-9; R_1R_2C=CHOTMS (R_1 = $(CH_2)_4CN$, R_2 = H), 51075-27-5; 2-bromo-3-phenylpropanal, 51075-28-6; 2-bromo-2-phenylpropanal, 51075-29-7; 2-bromodecanal, 51157-27-8; 4-bromo-4-formylcyclohexene, 51075-30-0; ethyl (3-bromo-3-formyl)cyclo-

hexanecarboxylate, 51075-31-1; 2-bromo-2-methylpropanal, 13206-46-7; 2-chloro-3-phenylpropanal, 19261-37-1; 2-bromo-6-cyanohexanal, 51157-28-9.

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An Improved Synthesis of Benzenetricarbonylchromium[1]

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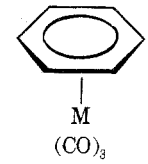
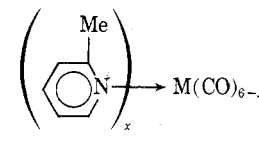
Received July 23, 1973

Since the discoveries of arenetricarbonylmetal complexes in the late 1950's,[2-6] this class of organometallic compounds has been rather extensively investigated.[7] The parent member of this series, benzenetricarbonylchromium (**1**), has been shown to undergo a variety of interesting reactions, including ligand exchange,[8,9] Friedel–Crafts acetylation,[10-12] and reactions with *n*-butyllithium resulting either in metalation[13,14] or nucleophilic addition to a carbonyl ligand to form a carbene–chromium complex.[15] Additional studies concerning the reactivity of **1** in which benzene serves as a π-coordinated ligand in transition metal chemistry would seem highly desirable. Unfortunately, most of the previously reported syntheses of **1** involve high-pressure, autoclave-type carbonylation reactions. The single report by Nicholls and Whiting[3] that **1** can be prepared in 30% yield from a reaction at reflux of benzene and hexacarbonylchromium in diethylene glycol dimethyl ether has proven to be unreliable in our laboratory, and the reaction is furthermore complicated by the rapid and extensive sublimation of hexacarbonylchromium from the reaction flask.

In this note, we describe a convenient and improved synthesis of **1** which should make this organochromium compound readily available for further study. This procedure has been extensively checked by students in our undergraduate organic chemistry laboratory and has been found to be very reliable. The method is based on a general synthesis of arenetricarbonylmetal complexes originally developed by Pruett, *et al.*,[16,17] and involves the refluxing under nitrogen of equivolume amounts of benzene and 2-picoline containing hexacarbonylchromium. Under these conditions, carbon monoxide is rapidly evolved, and little or no sublimation of hexacarbonylchromium occurs. These results are due presumably to the intermediate formation of (2-picoline)pentacarbonylchromium (**4**)[18] or related complexes which subsequently react with benzene present to form high yields of **1**.



1, M = Cr
2, M = Mo
3, M = W



4, M = Cr; $x = 1$
5, M = Mo; $x = 2$
6, M = W; $x = 1$

Several attempts to extend this procedure to the synthesis of benzenetricarbonylmolybdenum (**2**) and benzenetricarbonyltungsten (**3**) resulted instead in the formation of the 2-picoline complexes bis(2-picoline)tetracarbonylmolybdenum (**5**) and (2-picoline)pentacarbonyltungsten (**6**), respectively, as the only identifiable products. Complex **6**, a yellow, air-stable solid, was identified by elemental analysis, a molecular weight determination, and its nmr spectrum. Complex **5**, a dark-yellow solid, was found to be moderately sensitive to air, and was best handled and stored under nitrogen. It was only very slightly soluble in organic solvents, and its solutions were very air sensitive. A related complex, bis(pyridine)tetracarbonylmolybdenum, has been previously prepared both by photochemical[19] and thermal[20] reactions between pyridine and hexacarbonylmolybdenum.

Additional studies concerning the chemistry of **1** are in progress and will be reported in subsequent papers.

Experimental Section

Reaction of Benzene, 2-Picoline, and Hexacarbonylchromium. Into a 500-ml, single-necked flask was added 100 ml of 2-picoline, 100 ml of benzene, and 8.80 g (0.04 mol) of hexacarbonylchromium. After addition of several boiling chips, a wide-bore condenser fitted on the top with a three-way stopcock was inserted, and the system was evacuated under reduced pressure until boiling had commenced. Nitrogen was then bled into the system to equalize the pressure. This process was repeated about ten times to ensure an oxygen-free atmosphere. The reaction mixture was then heated to reflux for 96 hr, during which time carbon monoxide was evolved and the color turned to dark red.[21] After this period, the reaction mixture was allowed to cool to room temperature under nitrogen. The flask was transferred to a rotary evaporater and the excess benzene, 2-picoline, and hexacarbonylchromium were removed under water aspirator pressure with gentle heating on a steam bath. The yellow-green residue was extracted repeatedly with hot ethyl ether and the extracts were filtered. This process was repeated until the extracts were virtually colorless. The combined extracts were subsequently evaporated to dryness and the residue was washed with pentane to remove any remaining 2-picoline. After drying, there remained 7.75 g (91%) of yellow crystals of benzenetricarbonylchromium (**1**), mp 160–161° dec (lit.[6] mp 162–163°).