

nmr (CDCl₃) δ 1.1–1.4 (m, 2 H), 1.9–2.3 (m, 4 H), and 2.5–3.0 (m, 2 H); mass spectrum parent *m/e* 108.

Anal. Calcd for C₇H₈O: C, 77.78; H, 7.41. Found: C, 77.68; H, 7.39.

3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane (4).—*p*-Toluenesulfonic acid (0.028 g) was added to a solution of 2.71 g (25 mmol) of tricyclo[3.2.0.0^{2,7}]heptan-3-one and 3.68 g of trimethyl orthoformate in 5 ml of anhydrous methanol. The reaction mixture was stirred at room temperature for 8 hr. Sodium methoxide (10 mg) was added to the reaction mixture. The resulting solution was put on a rotary evaporator to remove methanol and distilled under reduced pressure to give 3.27 g (85%) of 3,3-dimethoxytricyclo[3.2.0.0^{2,7}]heptane: bp 38–39° (4 mm); nmr (CDCl₃) δ 1.3–1.8 (m, 6 H), 2.35 (m, 2 H), 3.12 (s, 3 H), and 3.28 (s, 3 H); mass spectrum parent peak *m/e* 154; ir (CCl₄) 2815 (symmetric CH stretching for methoxyl group), 1150–1050 cm⁻¹ (C–O–C asymmetric stretching) and no carbonyl absorption.

Anal. Calcd for C₉H₁₄O₂: C, 70.13; H, 9.09. Found: C, 69.96; H, 9.12.

Reaction of 3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane (4) with Anhydrous Methanolic Sulfuric Acid.—Methanol was purified and dried by distilling Mallinkrodt AR methanol from magnesium turnings. In a 10-ml, round-bottomed flask equipped with magnetic stirring bar and drying tube was placed 3 ml of methanolic sulfuric acid solution (10% concentrated H₂SO₄ by weight). The dimethyl ketal (0.500 g) was added to this stirred solution at ice-water-bath temperature. The solution was stirred at room temperature for 2 hr. Water (6 ml) was added. After stirring for 15 min the solution was made basic with solid sodium bicarbonate and extracted with five 6-ml portions of ether. The ethereal extracts were combined, washed with two 5-ml portions of water, and dried over anhydrous magnesium sulfate. After filtration, the ether was removed by distillation at atmospheric pressure to give yellow liquid residue. The residue was distilled *in vacuo* [bulb to bulb distillation at 50–56° (5 mm)] to give 0.324 g of colorless liquid. This colorless liquid was analyzed by analytical glpc on a Hewlett-Packard high-efficiency packed column, 0.125 in. × 6 ft stainless steel packed with 10% UCON-98 on 80–100 Chromosorb W, indicating that only one compound was present. Thin layer chromatography of this colorless liquid also showed it to be one compound.

The analytical sample of **5** was obtained by preparative glpc (0.25 in. × 6 ft 17% SE-30 on 30–60 mesh Chromosorb P at 150°). The colorless liquid **5** has the following spectral properties: ir (CCl₄) 1745 (five-membered cyclic carbonyl stretching frequency), 1050–1150 (C–O–C stretching), and 2810 cm⁻¹ (symmetric CH stretching for methoxyl group); nmr (CDCl₃) δ 2.00–2.60 (m, 6 H), 2.80–3.00 (m, 2 H, fused ring junction protons), 3.26 (s, 3 H, methoxyl hydrogens), and 3.65 (m, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 140 (5), 71 (68), 58 (100), 41 (23) (see text for interpretation of spectra).

Anal. Calcd for C₈H₁₂O₂: C, 68.57; H, 8.57. Found: C, 68.30; H, 8.65.

Registry No.—**2**, 694-98-4; **3**, 37939-83-6; **4**, 39008-47-4; **5**, 39003-10-6.

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The Preparation of α,β-Unsaturated Aldehydes from Acid Chlorides

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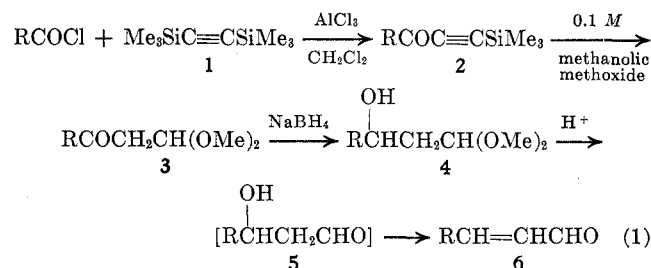
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We describe here a simple procedure for the preparation of α,β-unsaturated aldehydes which involves a

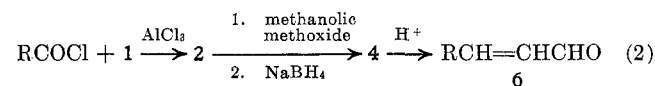
facile 2-carbon homologation of an acid chloride. The method, which we belatedly became aware, is related to that previously reported by Wakayama, *et al.*,¹¹ represents a useful alternative to those already available^{1a–m} since acid chlorides are usually easily prepared.

The method is summarized in the following generalized equation and is illustrated with *p*-biphenylcarbonyl chloride, benzoyl chloride, and cyclohexylcarbonyl chloride. It involves Friedel–Crafts alkylation of an acid chloride with bistrimethylsilyl acetylene (**1**) as first reported by Birkofer, *et al.*,² then by Walton and Waugh,³ followed by further sequential rapid transformation of the acyl trimethylsilylacetylene **2** to the β-keto acetal **3**, the β-hydroxy acetal **4**, the β-hydroxyaldehyde **5** and the α,β-unsaturated aldehyde **6**. Since the



alkynylation reaction appears to have appreciable scope,^{2–4} the outlined sequence would appear to be reasonably general.

The intermediates indicated in eq 1 were actually isolated and characterized in the case of R = *p*-biphenyl.⁵ For the other acid chlorides the sequence was telescoped as indicated in eq 2. The various



intermediates indicated in eq 1 are presumably also involved in these cases.

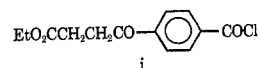
The fact that the foregoing method also provides a simple preparation of β-hydroxyaldehydes should not be overlooked. As indicated in the Experimental Section, mild acid hydrolysis of the hydroxy acetal **4** (R = *p*-biphenyl)⁵ gave the corresponding hydroxyaldehyde **5** (obtained in this case as the hydrate.)

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(2) L. Birkofer, A. Ritter and H. Uhlenbrauck, *Chem. Ber.*, **96**, 3280 (1963).

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(4) To the examples cited in ref 2 and 3 and *p*-biphenylcarbonyl chloride and cyclohexylcarbonyl chloride used here, we added the acid chloride **i** which



we found reacted in the anticipated manner with **1** at room temperature (2.25 hr) in CH₂Cl₂ in the presence of 3 molar equiv of aluminum chloride. (Very little if any reaction occurred with 1 molar equiv.)

(5) The detailed work was done in this series because of our interest in the products as chemical intermediates.

Experimental Section⁶

The general telescoped procedure is illustrated with biphenyl-carbonyl chloride as substrate as follows. To a stirred solution of 2 g (0.009 mol) of the acid chloride (G & C Chemical Co., Belleville, N. J.) and 1.7 g (0.01 mol) of bistrimethylsilylacetylene⁸ in 25 ml of methylene chloride (dried by storing over molecular sieves) cooled in ice-water was added 1.4 g (0.01 mol) of anhydrous aluminum chloride. After stirring for ca. 3 min, the cooling bath was removed. The reaction mixture was stirred at room temperature for 2 hr and then was poured into ice-water and the organic product was extracted into ether. Drying and evaporating the ether left the trimethylsilylacetylenic ketone **2** (R = biphenyl) which was treated with 20 ml of cold 0.1 M methanolic sodium methoxide. The cooling bath (ice-water) was removed after ca. 1 min and the mixture was stirred for 10 min to effect conversion to **3** (R = biphenyl). The resulting solution of **3** was cooled (ice-water), 1.2 g (0.031 mol) of solid sodium borohydride was added, the cooling bath was removed, the mixture was stirred for 20 min and poured into ice-water, and the β -hydroxy dimethyl acetal **4** (R = biphenyl) was isolated by extracting with ether and drying and evaporating the ethereal solution. Crude **4** was dissolved in 40 ml of dioxane, 20 ml of 4 N aqueous hydrochloric acid was added, and the mixture was heated on the steam bath at 80–85° (internal temperature) for 5 min and then allowed to cool for another 5 min. The reaction mixture was poured into ice-water to give the α,β -unsaturated aldehyde **6** (R = biphenyl) as an off-white solid, yield 1.55 g (84% from the acid chloride), mp 106–115°. Uv comparison with an analytical sample indicated it to be 81% pure. [Analytically pure aldehyde could be obtained by thick layer chromatography on 2-mm silica gel using *n*-hexane–EtOAc (4:1) for development; R_f ca 0.8.] It melted at 119–121° (lit.⁷ mp 120–121°), $\lambda_{\max}^{\text{MeOH}}$ 318 nm (ϵ 33,300).

Liquid aldehydes (e.g., cinnamaldehyde) were isolated from the hydrolysis mixture by extraction into ether.

With the biphenylchlorocarbonyl substrate the various intermediates involved in the conversion (eq 1) were isolated (by quenching in ice-water and extracting with ether after the appropriate time interval indicated in the telescoped procedure) and characterized.

***p*-C₆H₅C₆H₄C(=O)C≡CSiMe₃**.—The analytical sample melted at 71–73° (from petroleum ether, bp 30–60°): R_f on tlc (*n*-hexane–EtOAc) ca. 0.9; $\lambda_{\max}^{\text{KBr}}$ 4.7 (C=C, v weak), 6.13 (acetylenic ketone), and 6.25 μ (aromatic).

Anal. Calcd for C₁₅H₁₀OSi (278.41): C, 77.65; H, 6.52. Found: C, 77.74; H, 6.47.

***p*-C₆H₅C₆H₄C(=O)CH₂CH(OMe)₂**.—The analytical sample obtained by thick layer chromatography using *n*-hexane–EtOAc (4:1) for development melted at 35–38°: R_f ca. 0.3; $\lambda_{\max}^{\text{KBr}}$ 5.95 μ ; mass spectrum m/e 270 (M⁺), 75 [CH(OMe)₂].

Anal. Calcd for C₁₇H₁₈O₃ (270.31): C, 75.53; H, 6.71. Found: C, 75.23; H, 6.57.

***p*-C₆H₅C₆H₄CHOHCH₂CH(OMe)₂**.—The analytical sample obtained by thick layer chromatography (C₆H₆–EtOAc 4:1) melted at 57–59°, $\lambda_{\max}^{\text{KBr}}$ 3.0 μ (OH), R_f (C₆H₆–EtOAc 4:1) ca. 0.35.

Anal. Calcd for C₁₇H₂₀O₃ (272.33): C, 74.97; H, 7.40. Found: C, 74.92; H, 7.45.

***p*-C₆H₅C₆H₄CHOHCH₂CH(OH)₂**.—Treating **4** (R = biphenyl) dissolved in a small amount of ether with 6 N aqueous hydrochloric acid at room temperature for 15 min gave the hydrated aldehyde as a colorless solid, mp 135–140°, as indicated by ir, nmr, and mass spectral analysis. Treatment of the hydrated aldehyde with 4 N HCl–dioxane as described above gave the unsaturated aldehyde **6** (R = biphenyl) in 92% yield.

Cyclohexyl-COCl \rightarrow **Cyclohexyl-CH=CHCHO**.—Using the telescoped procedure described above, cyclohexylcarbonyl chloride (Eastman) was converted to β -cyclohexylacrolein⁸ in 40–45% yield. (The crude aldehyde was converted directly to its semicarbazone⁸ by the usual method.⁹ The yield of aldehyde indicated is based on the amount of semicarbazone obtained.)

(6) Melting points are uncorrected. The thin layer and thick layer (2 mm) plates used were obtained from Analtech Inc., Newark, Del. Uv light was used for spot visualization. Mass spectra were determined on an AEI MS-9 spectrometer at 70 eV.

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(8) E. D. Venus-Danilova, *J. Gen. Chem. USSR*, **4**, 866 (1934); *Chem. Abstr.*, **29**, 21523 (1935).

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Benzoyl Chloride \rightarrow **Cinnamaldehyde**.—Using the telescoped procedure, benzoyl chloride was converted to cinnamaldehyde in 78% yield. (Here too, as in the previous experiment, the yield was established by conversion to its semicarbazone derivative.)

Registry No.—**1**, 14630-40-1; **2** (R = biphenyl), 39703-85-0; **3** (R = biphenyl), 39703-86-1; **4** (R = biphenyl), 39703-87-2; **5** (R = biphenyl) hydrated aldehyde, 39703-88-3; **6** (R = biphenyl), 39703-89-4; biphenylcarbonyl chloride, 14002-51-8; cyclohexylcarbonyl chloride, 2719-27-9; β -cyclohexylacrolein, 935-03-5; benzoyl chloride, 98-88-4; cinnamaldehyde, 104-55-2.

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Photoinduced Reduction of Polyhalogenomethyl Groups

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Studies on the stereoselective synthesis of carbohydrates by telomerization of vinylene carbonate with polyhalogenomethanes¹ have shown the need for the mild and selective reduction of tri- or dihalogenomethyl groups to di- or monohalogenomethyls, and, among the reductive agents previously reported,² only Ni(CO)₄ is satisfactorily effective for the present purpose.³ The reduction of polyhalide is important as the preparative method for synthetically difficult lower halides.

In this paper we describe the smooth and mild conversion of polyhalogenomethyl groups to di- or monohalogenomethyls by simple irradiation with an ultraviolet lamp in tetrahydrofuran (THF). The solutions of tri- or dihalogenomethyl compounds (ca. 1 \times 10⁻¹ M) were irradiated either with a high- or low-pressure mercury lamp at room temperature and reduction is usually completed within several hours. This reaction does not proceed in the dark. The results are summarized in Table I.

Polyhalides such as 1,1,1,3-tetrabromononane, 1,1,1,3-tetrachlorooctane, and telomers of vinylene carbonate with CCl₄ (**1a** and **2a**)^{1,4} could be reduced exclusively to dihalogenomethyl compounds without any detectable amount of monohalogenomethyls, while the benzylic trichloromethyl compound underwent a smooth reductive dimerization to 1,1,2,2-tetrachloro-1,2-diphenylethane in analogy with the case by

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(4) T. Tamura, T. Kunieda, and T. Takizawa, in preparation.