Anal. Calcd for $C_{24}H_{24}S_8O_9$: C, 52.16; H, 4.38. Found: C, 52.21; H, 4.28.

Tetrakis(benzenesulfonlyoxymethyl)methane was prepared by the method of Herzog.[19]

(2) The Polyazide Precursors of 1, 3, 5, and 7.—*Warning!* The handling of polyazides in large quantities may be harzardous, and the safety of the preparation described has not been fully established.

1,1,1-Tris(azidomethyl)ethane (10).—A mixture of crude **9** (73 g) and NaN_3 (44 g) in diethylene glycol (250 ml) was stirred under N_2 and maintained at 135° for 16 hr. After cooling, the mixture was poured into water (500 ml). The resulting orange-brown oil was collected, combined with a diethyl ether (100 ml) extract of the aqueous layer, and extracted with water. The ethereal solution was dried (Na_2SO_4), treated with activated charcoal and upon evaporation gave **10** an almost colorless oil (24.5 g, 93%): nmr ($CDCl_3$–TMS) τ 6.73 (s, 2, methylene) and 9.00 (s, 1, methyl); ir (neat) 2970, 2925, 2860 (CH), 2095 (vs, N_3), 1460, 1440, 1380 (CH) and 1285 cm^{-1} (vs, b, N_3).

The following were prepared in a similar manner.

2,2-Bis(azidomethyl)propane was obtained as a colorless oil (89%): nmr ($CDCl_3$–TMS) τ 6.82 (s, 2, methylene) and 9.06 (s, 3, methyl); ir (neat) 2970, 2930, 2870 (CH), 2100 (vs, N_3), 1470, 1445, 1390, 1345 (CH) and 1290 (sh), 1260 cm^{-1} (vs, b, N_3).

Tetrakis(azidomethyl)methane was prepared as colorless plates (85%): nmr ($CDCl_3$–TMS) τ 6.67 (s, methylene); ir (Nujol) 2200 (sh), 2100 (vs, N_3), and 1270 cm^{-1} (vs, b, N_3).

***cis,cis*-1,3,5-Triazidocyclohexane** was obtained (reaction mixture maintained at 100° for 6 hr) as a pale yellow oil (89%): nmr ($CDCl_3$–TMS) τ 6.58 [m, 1, methine (axial), J_{aa}^{vic} = 11, J_{ae}^{vic} = 4 Hz), 7.69 [m, 1, methylene (equatorial proton), J_{ae}^{gem} = 11, J_{ae}^{vic} = 4 Hz), and 8.71 [m, 1, methylene (axial proton), J_{ae}^{gem} = 11, J_{aa}^{vic} = 11 Hz); ir (neat) 2950, 2930, 2890 (CH), 2170 (sh), 2090 (vs, b, N_3), 1470, 1450, 1370, 1350 (sh) (CH) and 1290 (sh), 1250 cm^{-1} (vs, b, N_3).

(3) Aliphatic and Alicyclic Primary Polyamines 1, 3, 5, and 7.

1,1,1-Tris(aminomethyl)ethane (3).—A solution of **10** (33.6 g) in dry tetrahydrofuran (THF) (100 ml) which had been dried over molecular sieves was added slowly (2 hr) to a stirred suspension) of $LiAlH_4$ (27 g) in dry THF (500 ml). When the addition was complete the mixture was heated under reflux (18 hr). After cooling, water (27 ml), 15% NaOH solution (27 ml), and more water (81 ml) were added. The granular white solid was extracted for 24 hr in a Soxhlet thimble with THF from the refluxing motor liquor. The THF was evaporated and the resulting oil was dried by stirring with refluxing benzene (30 ml) and collecting the water in a Dean–Stark trap. Distillation gave 17.2 g (85%) of **3**: bp 81° (7 mm); nmr ($CDCl_3$–TMS) τ 7.50 (s, 2, CH_2), 8.77 (s, 2, NH_2), and 9.25 (s, 1, CH_3); ir (neat) 3350, 3280 (NH), 2900, 2850 (CH), 1580 (NH), 1460 (CH), and 1370 cm^{-1} (CH). The trihydrochloride of **3** was prepared by addition of concentrated HCl to a solution of **3** in methanol.

Anal. Calcd. for $C_5H_{18}N_3Cl_3$: C, 26.51; H, 8.01; N, 18.55. Found: C, 26.88; H, 8.02; N, 18.57.

The following were prepared in a similar manner.

2,2-Bis(aminomethyl)propane (1) (75%) had bp 157–159° (lit.[8] bp 151–153°) (737 mm); nmr ($CDCl_3$–TMS) τ 7.48 (s, 2, CH_2), 8.95 (s, 2, NH_2), and 9.17 (s, 3, CH_3); ir (neat) 3380 (NH), 3300 (NH), 2950 (CH), 2870 (CH), 1600 (b, NH), 1465 (CH), 1390 (CH), and 1360 cm^{-1} (CH). The dihydrochloride of **1**, recrystallized from C_2H_5OH (95%) gave white plates, mp 274–276° (lit. 256–257°,[3] 280–281°[2]).

Anal. Calcd for $C_5H_{16}N_2Cl_2$: C, 34.30; H, 9.21; N, 16.00. Found: C, 34.43; H, 9.25; N, 15.54.

Tetrakis(aminomethyl)methane (5).—The crude tetramine (80%) from the benzene azeotrope drying could not readily be distilled: nmr ($CDCl_3$–TMS) τ 7.36 (s, 1, CH_2) and 8.75 (s, 1, NH_2); ir (neat) 3370 (NH), 3290 (NH), 2910 (CH), 2860 (CH), 1600 (b, NH), 1460 (b, CH), and 1370 cm^{-1} (b, CH). The tetrahydrochloride of **5** on recrystallization from hydrochloric acid gave colorless plates, mp >300° but decomposes slowly above 250° (lit.[5] mp >300°, dec at 260°).

Anal. Calcd for $C_5H_{20}N_4Cl_4$: C, 21.60; H, 7.25; N, 20.15. Found: C, 21.74; H, 7.23; N, 19.76.

***cis,cis*-1,3,5-Triaminocyclohexane (7)** was obtained after extraction for 48 hr, yield 59%, bp 68° (0.08 mm). The trihydrochloride salt of **7** was prepared by addition of concentrated HCl to a solution of **7** in ethanol. Reprecipitation, by addition of ethanol to an ethanol–water solution of the trihydrochloride, and drying under vacuum at 100° resulted in an analytical sample of the trihydrochloride: nmr (D_2O–DSS) τ 6.45 [m, 1, methine (axial), J_{aa}^{vic} = 12, J_{ae}^{vic} = 4 Hz], 7.48 [m, 1, methylene (equatorial proton), J_{ae}^{gem} = 12, J_{ae}^{vic} = 4 Hz], 8.37 [m, 1, methylene (axial proton), J_{ae}^{gem} = 12, J_{aa}^{vic} = 12 Hz].

Anal. Calcd for $C_6H_8N_3Cl_3$: C, 30.20; H, 7.60; N, 17.61. Found: C, 30.05; H, 7.27; N, 17.40.

(19) Footnote *e*, Table I.

Registry No.—**1**, 29082-53-9; **3**, 31044-82-3; **5**, 14302-75-1; **7**, 26251-48-9; **9**, 31044-85-6; **10**, 31044-86-7; 2,2-bis(benzenesulfonyloxymethyl)propane, 31044-87-8; *cis-cis*-1,3,5-tris(benzenesulfonyloxy)cyclohexane, 31044-88-9; 2,2-bis(azidomethyl)propane, 31044-89-0; tetrakis(azidomethyl)methane, 31107-13-8; *cis,cis*-1,3,5-triazidocyclohexane, 31044-90-3.

Acknowledgments.—This work was supported by grants from the National Science Foundation and the National Institutes of Health.

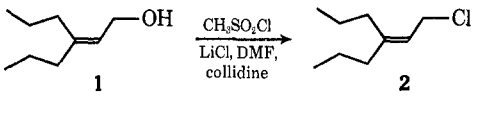
A Facile and Specific Conversion of Allylic Alcohols to Allylic Chlorides without Rearrangement[1]

E. W. COLLINGTON AND A. I. MEYERS*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received March 9, 1971

The perennial problem of converting allylic alcohols to their corresponding halides without allylic rearrangement has been the subject of considerable study.[2] In recent years several successful methods have been reported which in certain instances overcome this problem. The effort associated with the synthesis of 1,5-dienes in naturally occurring materials depends heavily upon a smooth conversion of allylic alcohols to allylic halides.[3] In connection with studies on insect pheromones, a mild and efficient technique was developed for performing this task. A considerable quantity of the allylic chloride **2** was required and in this regard various methods were investigated utilizing the allylic alcohol **1** as the precursor. It was found that the latter



1 **2**

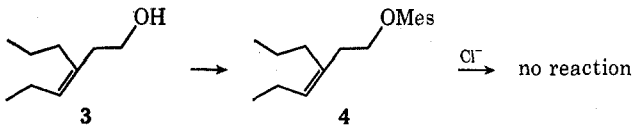
was readily transformed in excellent yield into the allylic chloride using methanesulfonyl chloride and a mixture of lithium chloride, dimethylformamide, and collidine at 0°. The product showed no contamination by rearranged chloride. An interesting feature of this process is the fact that any *nonallylic alcohol present*

(1) This study was supported by the National Institutes of Health (NIH GM-17941-01) and the National Science Foundation (NSF GP-22541).

(2) For a recent discussion of this problem, see "Advanced Organic Chemistry, Reactions, Mechanisms, and Structure," J. March, Ed., McGraw-Hill, New York, N. Y., 1968, p 270.

(3) The following articles appeared while this work was in progress: G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Lett.*, 1393 (1969); E. H. Axelrod, G. M. Milne, and E. E. van Tamelan, *J. Amer. Chem. Soc.*, **92**, 2139 (1970).

in the starting material is not converted to the allylic chloride. Thus, **1**, which was shown by vpc to contain 10% of the homoallylic alcohol **3**, gave 83% of **2** and 10% of the mesylate **4**. The mild conditions employed

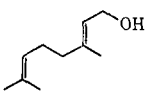
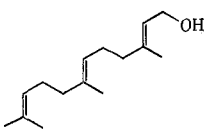
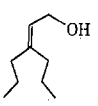
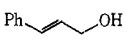
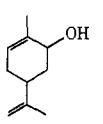


retard displacement of saturated mesylates by chloride ion, while allowing the more labile allylic mesylate to react. The use of *s*-collidine rather than pyridine as the hydrogen chloride scavenger is based upon the observation that its poorer nucleophilic properties fail to allow quaternization of the allylic chloride, once it is formed. When pyridine was utilized, the allylic chloride was formed, albeit in poorer yield (40–50%), the remainder of the material being lost in aqueous work-up as the *N*-allylic pyridinium salt. The function of lithium chloride was established when, in its absence, a distinct increase in the amount of rearranged chloride was noted. This indicated that the SN2 process involving chloride ion on the initially formed mesylate was giving way to a unimolecular ionization of the allylic mesylate and therefore to rearrangement. Addition of 1.0 equiv of lithium chloride in a minimum amount of dimethylformamide provided the chloride ion nucleophile in sufficient quantity to effect a clean bimolecular displacement of the mesyl group. In this fashion, the total products recovered exhibited the ratio of homoallylic mesylate to allylic chloride in close agreement to the ratio of starting homoallylic alcohol to allylic alcohol. Several different allylic alcohols were subjected to this technique and all behaved similarly under identical experimental conditions (Table I).

The method described herein allows allylic alcohols, even though they may be contaminated by their homoallylic isomers, to be converted in the same ratio as the isomeric mixture to allylic chlorides and homoallylic mesylates. The latter may be removed in a subsequent operation such as passage through silica gel if the allylic chloride is sufficiently stable. However, only relatively few allyl halides will tolerate this treatment (entry 5). The allyl chlorides were also found, as expected, to be highly sensitive toward distillation and vpc analyses, although all were quite stable at room temperature and may be utilized with the homoallylic mesylate present if the next synthetic step is sufficiently selective.

TABLE I

CONVERSION OF ALLYLIC ALCOHOLS TO ALLYLIC CHLORIDES

Entry	Alcohol	Homollylic isomer present, %[a]	Chloride, %[e]	Homollylic mesylate, %[g]
1		21[b]	87	20 ± 2
2		10[b]	84	7 ± 2
3		10[c]	83	8 ± 2
4			82	
5		10[d]	50[f]	9 ± 2[h]

[a] Isomer distribution determined by vpc (10% UC-W98, 80-100S). [b] Commercial products distilled before use. [c] Obtained by reduction of corresponding α,β-unsaturated aldehyde with sodium borohydride in aqueous ethanol (pH 7). [d] Obtained by reduction of *d*-carvone with sodium borohydride in aqueous ethanol (pH 7), bp 65° (0.3 mm). The allylic alcohol contained a mixture of geometric isomers (E. Geunther and D. Althausen, "Essential Oils," Vol. II, Van Nostrand, New York, N. Y., 1949. [e] Yield based upon per cent of allylic alcohol present in starting material. [f] Mixture of geometric isomers. [g] Determined by integration of the CH_3SO_2OR singlet in the nmr spectrum of the allyl chloride. [h] The mesylate removed by rapid elution of the crude chloride through silica gel in a hexane solution.

Experimental Section

Allylic Chlorides. General Procedure.—A stirred mixture of the allylic alcohol (0.10 mol) and *s*-collidine (0.11 mol) under nitrogen was treated with lithium chloride (0.10 mol) dissolved in a minimum amount of dry dimethylformamide. On cooling to 0°, a suspension was formed which was treated dropwise with methanesulfonyl chloride (0.11 mol). Stirring was continued at 0° for 1–1.5 hr, when the pale yellow reaction mixture was poured over ice-water. The aqueous layer was extracted with cold ether–pentane (1:1) and the combined extracts were washed successively with saturated copper nitrate solution. This was continued until no further intensification of the blue copper solution occurred, indicating complete removal of *s*-collidine. The organic extracts were dried (Na_2SO_4) and concentrated at room temperature, providing a residue of the allyl chloride. Spectral data for the allylic chlorides are given in Table II.

TABLE II

Entry	Ir, film (C=C), cm^{-1}	Nmr (CCl_4), τ
1	1675	4.43-4.8 (1, t) 4.8-5.2 (1, m) 5.9-6.1 (2, d, J = 8 Hz) 7.76-8.06 (4, m) 8.16-8.53 (9, m)
2	1675	4.4-5.15 (3, m) 5.82-6.15 (2, d, J = 8 Hz) 7.8-8.2 (8, m) 8.2-8.6 (12, m)
3	1650	4.2-4.6 (1, t, J = 5 Hz) 5.7-6.0 (2, d, J = 5 Hz) 7.7-8.1 (4, m) 8.1-8.8 (4, m) 8.8-9.3 (6, m)
4	1665	2.55-2.93 (5, m) 3.23-4.1 (2, m) 5.8-5.96 (2, d, J = 6 Hz)
5	1655	4.33-4.56 (1, m) 5.2-5.36 (2, broad s) 5.5-5.7 (1, m) 7.3-8.5 (11, m)

Registry No.—**1** chloride, 4490-10-2; **2** chloride, 6784-45-8; **3** chloride, 30808-78-7; **4** chloride, 2687-12-9; **5** chloride, 30808-80-1.