TABLE I[a]

AMINE HYDROPOLYSULFIDE + n-$C_4H_9Cl \rightarrow (C_4H_9)_2S_x$

Amine hydropolysulfide	g	Solvent	Reaction conditions Temp, °C	Time, hr	Yields of $(C_4H_9)_2S_x$,[b] g $x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$
$EN.H_2S_3$	7.9	DMF	30	2	0	6.5	0	0	0
$EN \cdot H_2S_3$	7.9	DMF	50	2	0	7.5	0	0	0
$EN \cdot H_2S_3$	7.9	EN	30	2	9.6	0.3	0	0	0
$EN \cdot H_2S_3$	7.9	EN	50	2	10.1	0.2	0	0	0
$EN \cdot H_2S_3$	7.9	BN	50	2	8.4	0.8	0	0	0
1,3-$PN \cdot H_2S_x$	4.2	DMF	30	2	0	1.2[c]	1.4[c]	1.4[c]	0
$HN \cdot H_2S_5$	8.8	DMF	30	2	0	0	0.4[c]	2.2[c]	0.4[c]

[a] EN, ethylenediamine; PN, propanediamine; HN, hexamethylenediamine; BN, n-buthlamine; DMF, dimethylformamide. [b] $(C_4H_9)_2S_x$ ($x = 1$) not isolated. [c] Value from nmr analysis.

TABLE II[a]

AMINE + S_8 + n-$C_4H_9Cl \rightarrow (C_4H_9)_2S_x$

Amine	Reaction condition Temp, °C	Time, hr	Yields of $(C_4H_9)_2S_x$,[b] g $x = 2$	$x = 3$
EN	30	1	4.7	2.2
EN	30	8	9.2	0.5
EN	50	3	10.6	0.2
1,3-PN	30	1	4.2	2.5
1,3-PN	50	3	9.4	0.4
HN	60	3	9.2	0.6
DETN	30	1	3.4	2.8
DETN	50	3	8.6	0.9
XDN	50	3	5.2	2.4
BN	30	1	1.8	2.0
BN	50	3	5.9	3.6

[a] DETN, diethylenetriamine; XDN, p-xylylenediamine. [b] $(C_4H_9)_2S_x$ ($x = 1, x \geqq 4$) not isolated.

Isolation of Hydropolysulfides of Amines. A. $EN \cdot H_2S_3$.—A solution of 7.8 g of sulfur in 30 ml of EN was heated for about 2 hr at 50° under nitrogen until evolution of ammonia gas ceased, cooled, and diluted with 100 ml of ethanol to yield yellow, crystalline solid, which is soluble in DMF. The crystals were collected by filtration, washed with ethanol and benzene, and then dried in a desiccator: 98% yield (12.6 g) based on sulfur. The yield of the product recrystallized from EN–ethanol (1:3) was 92% (11.8 g); decomposition temperature, 116–120°; ir (KBr) SH–H_2N at 3000–3700 cm^{-1}, S–S at 480 cm^{-1}.

Anal. Calcd for $EN \cdot H_2S_3$: C, 15.17; H, 6.37; N, 17.70; S, 60.76. Found: C, 15.44; H, 5.57; N, 17.33; S, 61.06.

B. $HN \cdot H_2S_5$.—A solution of 7.8 g of sulfur in 30 ml of HN was heated for about 2 hr at 80° under nitrogen, and then treated in a similar manner as above. The yield of the product recrystallized from HN–ethanol (1:3) was 75% (9.1 g); decomposition temperature, 140–145°.

Anal. Calcd for $HN \cdot H_2S_5$: C, 25.87; H, 6.51; N, 10.06; S, 57.56. Found: C, 25.59; H, 6.27; N, 9.67; S, 57.45.

C. Other Hydropolysulfides.—By adding 100 ml of ethanol to the reaction mixture of 7.8 g of sulfur with 30 ml of 1,3-PN or DETN, no crystalline products were obtained but a dark red oil deposited. The oily products were unable to be purified, as thermal decomposition was noted on distillation *in vacuo*. From the reaction mixtures of sulfur with BN, tributylamine, and morpholine, no reaction products were separated.

Dibutylpolysulfides from Amine Hydropolysulfides and Butyl Chloride.—Ten grams of n-butyl chloride was added dropwise to the solution of 7.9 g of $EN \cdot H_2S_3$ in 50 ml of the solvent indicated in Table I. The mixture was stirred for 2 hr at the indicated temperature under nitrogen and then poured into ice–water containing an excess of sulfuric acid. The solution was extracted with benzene, and the extracts were washed with water and dried over anhydrous sodium sulfate. It was then evaporated to recover the crude product, which was distilled under a reduced pressure in a current of nitrogen. Dibutyl disulfide [bp 113–115° (15 mm),[4] ir S–S at 480 cm^{-1}] and dibutyl trisulfide [bp 73–75° (0.1 mm),[4] ir S–S at 480 cm^{-1}] were obtained, as shown in Table I.

Anal. Calcd for $(C_4H_9)_2S_2$: S, 35.95. Found: S, 35.48. Calcd. for $(C_4H_9)_2S_3$: S, 45.71; S, 45.71. Found: S, 45.29.

Similarly, dibutyl polysulfides were obtained from the hydropolysulfides of other primary diamines as summarized in Table I. Some of the dibutyl polysulfides were detected by the proton nmr spectrum analyses as previously reported.[5]

Dibutyl Polysulfides from Butyl Chloride and Amine Solutions of Sulfur.—To the solution of 5.2 g of sulfur in 50 ml of various amines, 12.5 g of n-butyl chloride was added dropwise with stirring at the temperature indicated in Table II. The mixture was cooked in a nitrogen atmosphere. The reaction mixture was treated similarly as described in the previous section and dibutyl polysulfides were isolated which are summarized in Table II.

Desulfurization of Dibutyl Trisulfide in EN.—To 20 ml of EN, 15.8 g of dibutyl trisulfide was added and the mixture was stirred for 2 hr at 30° under nitrogen. The reaction mixture was treated similarly as described previously and 9.6 g of dibutyl disulfide was obtained.

Isolation of $H_2NCH_2CH_2N{=}CHCH_2NH_2 \cdot 3HCl$.—The cooled filtrate from $EN \cdot H_2S_3$ described before was neutralized with concentrated hydrochloric acid and allowed to settle the precipitates of $EN \cdot 2HCl$. The filtrate was then evaporated to dryness under reduced pressure, and the residue was extracted with the mixture of C_2H_5OH–H_2O (1:1). Removal of the solvent of the extracts left 2 g of colorless, crystalline product in needles which began to decompose on heating, ir (KBr) 1660 cm^{-1} (C=N).

Anal. Calcd for $H_2NCH_2CH_2N{=}CHCH_2NH_2 \cdot 3HCl$: C, 22.82; H, 6.70; N, 19.96; Cl, 50.52. Found: C, 22.56; H, 6.95; N, 20.29; Cl, 50.48.

Determination of Ammonia from Amine Solution of Sulfur.—Ammonia, generated from the mixture of 30 ml of amine and 9.6 g of sulfur at 50–80°, was determined by alkalimetry after separating amine through a trap at −10°.

Registry No.—S_8, 10544-50-0; $EN \cdot H_2S_3$, 31044-74-3; $HN \cdot H_2S_5$, 31044-75-4; ethylenediamine, 107-15-3; 1,3-propanediamine, 109-76-2; hexamethylenediamine, 124-09-4; diethylenetriamine, 111-40-0; p-xylylenediamine, 539-48-0; n-butylamine, 109-73-9; n-butyl chloride, 109-69-3; $H_2N(CH_2)_2N{=}CHCH_2NH_2 \cdot 3HCl$, 31044-76-5.

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Conversion of Aliphatic and Alicyclic Polyalcohols to the Corresponding Primary Polyamines

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Received February 5, 1971

As part of a study of complexes of transition metal ions which is presently being conducted in this laboratory,[1] it was found necessary to synthesize several aliphatic and alicyclic primary polyamines. Examples of four such polyamines are shown in Table I. These compounds have been synthesized previously (**1**,[2,3] **3**,[4] **5**,[5,6] and **7**[7-9]), but, unfortunately, the yields obtained were often quite low (see Table I) and the conditions used are inconvenient for laboratory syntheses of large quantities of material. Since the polyalcohols (**2**, **4**, **6**, and **8**) corresponding to the required polyamines are readily available (**2**, **4**, **6**,[10] and **8**[11]), it seemed desirable to design a synthetic route which would allow smooth conversion of alcohol groups to primary amine groups.

TABLE I

SOME ALIPHATIC AND ALICYCLIC PRIMARY POLYAMINES. A SUMMARY OF SYNTHETIC DETAILS

Polyamine	No.	Starting material	No.	Overall yields, % This work	Overall yields, % Previously
$(CH_3)_2C(CH_2NH_2)_2$	**1**	$(CH_3)_2C(CH_2OH)_2$	**2**	64	*a*
$(CH_3)C(CH_2NH_2)_3$	**3**	$(CH_3)C(CH_2OH)_3$	**4**	76	31[b]
$C(CH_2NH_2)_4$	**5**	$C(CH_2OH)_4$	**6**	62	<23[c]
$(-CH_2CHNH_2-)_3$ (*cis,cis*)	**7**	$(-CH_2CHOH-)_3$ (*cis,cis*)	**8**	50	11[d]

[a] **2** → $(CH_3)_2C(CH)_2C(CH_2Br)_2$ (ref 2) → $(CH_3)_2C(CH_2N(CO)_2C_6H_4)_2$ (ref 2) → $(CH_3)_2C(CH_2NH_2 \cdot HCl)_2$ (ref 2) → **1** (ref 3). No yields quoted. [b] **4** → $CH_3C(CH_2OSO_2C_6H_4$-*p*-$CH_3)_3$ (ref 4) → $CH_3C(CH_2N(CO)_2C_6H_4)_3$ (ref 4) → $CH_3C(CH_2NH_2 \cdot HCl)_3$ (ref 4) → **3** (ref 4). [c] **6** → $C(CH_2Br)_4$ (ref *e*) → $C(CH_2NHSO_2C_6H_4$-*p*-$CH_3)_4$ (ref 5) → $C(CH_2NH_3^+)_4(SO_4^{2-})_2$ (ref 5) → **5** (ref 6). No yields quoted for last two steps. [d] $C_6H_3(OH)_3$ → $(-CH_2CNOH-)_3$ (ref *f*) → $(-CH_2CHNH_2-)_3$ *cis,trans* and *cis,cis* (ref 8) → **7** *cis,cis* (ref 9). Yield for first step = 39% (this work). [e] H. L. Herzog, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 753. [f] A. Baeyer, *Ber.*, **19**, 159 (1886).

The low-yield step in the earlier syntheses of the polyamines **1**, **3**, **5**, and **7** is the introduction of a nitrogen residue, generally by nucleophilic displacement; *e.g.*, the substitution by the phthalimide moiety in these reactions requires high temperatures[2,4] for only partial conversion. Similar conditions result in only partial substitution by the *p*-toluenesulfonamido group.[5] Since the azide ion is a good nucelophile[12] and is much less bulky than either the phthalimido or *p*-toluenesulfonamido group it suggests itself as a better substrate for the introduction of nitrogen into the molecule. Also, since reduction of aliphatic azides with lithium aluminum hydride has been shown[13] to yield primary amines, we decided to test the scheme $ROH \rightarrow ROSO_2C_6H_5 \rightarrow RN_3 \rightarrow RNH_2$ for conversion of alcohol groups into primary amines by applying it to the syntheses of compounds **1**, **3**, **5**, and **7**.

The experimental details are given below. Because of the potential hazards associated with the polyazide intermediates, they were characterized only by their ir and nmr spectra, and were used immediately in the reduction step to obtain the polyamines. Under these circumstances, no difficulties were encountered with the polyazides.

The yields resulting from this synthetic scheme are summarized in Table I, and show a marked improvement over those of earlier methods. The method is particularly useful for the cyclohexanetriamine, since it proceeds stereospecifically to yield the cis,cis isomer, as identified by the nmr of the trihydrochloride.[14] Additionally, the nmr spectrum of the tribenzenesulfonyloxy and of the triazido precursors are similar to those of the starting *cis,cis*-triol[15] and final *cis,cis*-triamine[16] and resemble those obtained for other *cis,cis*-1,3,5-trisubstituted cyclohexane compounds[16-18] (Table II).

TABLE II

COUPLING CONSTANTS FOR *cis,cis*-1,3,5-TRISUBSTITUTED CYCLOHEXANE COMPOUNDS

Compd	J_{gem}[a]	J_{aa}[a]	J_{ae}[a]	Ref
cis,cis-1,3,5-Trimethylcyclohexane	13	11	3	17
cis,cis-1,3,5-Tris(4-pyridyl)-cyclohexane	12.5	12.5	2	16
cis,cis-1,3,5-Cyclohexanetriol	11.5	11.5	4.5	14
cis,cis-1,3,5-Trichlorocyclohexane	12.7	12.4	4.3	18
cis,cis-1,3,5-Tris(benzenesulfonyloxy)cyclohexane	11	11	4.5	
cis,cis-1,3,5-Triazidocyclohexane	11	11	4	
cis,cis-1,3,5-Triaminocyclohexane	12	12	4	15

[a] In hertz.

Experimental Section

(1) **Benzenesulfonate Esters of 2, 4, 6, and 8. 1,1,1-Tris(benzenesulfonyloxymethyl)ethane (9).**—Benzenesulfonyl chloride (480 ml) was added slowly (3 hr) to a solution of **4** (126 g) in pyridine (550 ml) at 10°. After stirring for 24 hr at room temperature the product was added slowly to a mixture of water (1 l.), CH_3OH (2 l.), and concentrated HCl (800 ml). The resulting granular white precipitate was collected, washed with water and a little CH_3OH, and dried. The crude **9** (541 g, 96%) (mp 103–103.5°) on recrystallization (acetone) gave colorless needles: mp 105–106°; nmr ($CDCl_3$–TMS) τ 2.0–2.6 (m, 5, aromatics), 6.15 (s, 2, methylene), and 9.10 (s, 1, methyl).

Anal. Calcd for $C_{23}H_{24}S_3O_9$: C, 51.10; H, 4.47. Found: C, 51.04; H, 4.49.

The following were prepared in a similar manner.

2,2-Bis(benzenesulfonyloxymethyl)propane) (yield 96%) had mp 62–63°. Recrystallization (CH_3OH + little $CHCl_3$) gave colorless needles: mp 62–63°; nmr ($CDCl_3$–TMS) τ 2.0–2.6 (m, 5, aromatics), 6.20 (s, 2, methylene), and 9.12 (s, 3, methyl).

Anal. Calcd for $C_{17}H_{20}S_2O_6$: C, 53.11; H, 5.24. Found: C, 53.46; H, 5.25.

cis,cis-**1,3,5-Tris(benzenesulfonyloxy)cyclohexane** (yield 95%) had mp 183–185°. Recrystallization (CH_3OH + little $CHCl_3$) gave fine white needles: mp 190–191°; nmr (pyridine-d_5–TMS) τ 2.0–2.8 (m, 5, aromatics), 5.12 [m, 1, methine, (axial), J_{aa}^{vic} = 11, J_{ae}^{vic} = 4.5 Hz], 7.58 [m, 1, methylene (equatorial proton), J_{ae}^{gem} = 11, J_{ae}^{vic} = 4.5 Hz] and 8.58 [m, 1, methylene (axial proton), J_{ae}^{gem} = 11, J_{aa}^{vic} = 11 Hz).

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Anal. Calcd for $C_{24}H_{24}S_3O_9$: 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.

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]

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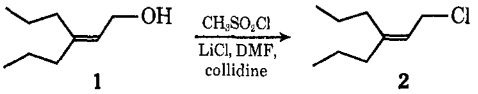
Received March 9, 1971

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 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 **2**

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[19] Footnote *e*, Table I.

[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.

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