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Allylic Rearrangements. XLIX. The Controlled Conversion of α - and γ -Methylallyl Alcohols to Chlorides with Thionyl Chloride¹

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Reaction of γ -methylallyl alcohol with thionyl chloride in dilute ether solution gives primarily α -methylallyl chloride, but in the presence of tri-*n*-butylamine only γ -methylallyl chloride is formed. α -Methylallyl alcohol reacts with thionyl chloride in ether to give only γ -methylallyl chloride but gives a mixture of chlorides when a tertiary amine is present. Reaction of optically active α -methylallyl alcohol with thionyl chloride proceeds with predominating retention or inversion of configuration depending on the reaction conditions. Plausible mechanisms for these reactions are discussed.

Introduction

This work is concerned with a detailed examination of the reaction of thionyl chloride with α - and α -methylallyl alcohols. Preliminary announcements were published earlier.^{3,4}

In the absence of electron-withdrawing groups on the carbinyl carbon, replacement of hydroxyl in an allylic alcohol with the usual halogenating agents, such as hydrogen halides, phosphorus halides and thionyl chloride, generally leads to a mixture of isomeric allylic halides.⁵ For preparative purposes, therefore, it was desirable to find reaction conditions which would produce a single allylic chloride. To this end a systematic investigation of the reaction of thionyl chloride with α and γ -methylallyl alcohols was undertaken.

Experimental Approach

The reactions of α - and γ -methylallyl alcohols with thionyl chloride were conducted under a wide variety of experimental conditions. The effects of different solvents, variation of temperature and order of addition of the reactants, the presence or absence of tertiary amines and their hydrochlorides, and the effect of added triphenylmethyl chloride were studied. In general, the reactions were carried out by adding one reactant slowly to an icecold solution of the other reactants. In almost all experiments, equimolar quantities were used. The reactions were considered complete one hour after mixing and the products were subsequently analyzed by careful fractional distillation. The analysis is estimated to have a precision of $\pm 4\%$ and distillation was shown to cause no rearrangement of the products. The results are summarized in Tables I-III and are discussed in more detail in the following section. Table IV lists the base strengths of the various amines used in the experiments of Table II.

Results and Discussion

Reaction in the Absence of Added Base.—The significant conclusions which can be drawn from the results in Table I are (a) without a solvent, mixtures of isomeric chlorides are always obtained (runs 1-3); and (b) in dilute ether solution, al-

(1) This work was supported in part by the National Science Foundation.

(2) Standard Oil Co. of California Predoctoral Fellow, 1952-1954.
(3) W. G. Young, F. Caserio and D. Brandon, Jr., Science, 117, 473 (1953).

(4) F. F. Caserio, G. E. Dennis, R. H. DeWolfe and W. G. Young, THIS JOURNAL, 77, 4182 (1955).

(5) R. H. DeWolfe and W. G. Young, Chem. Revs., 56, 801 (1956).

most complete allylic rearrangement occurs (run 6,8–11) such that α -methylallyl alcohol gives γ methylallyl chloride, and γ -methylallyl alcohol gives α -methylallyl chloride. Mechanisms which best explain the formation of a single rearranged chloride are the cyclic SNi^{'6} process or one involving rigidly-oriented undissociated ion-pairs.^{7a,b} The present results do not clearly differentiate between these two alternatives, but in view of recent work⁷ on the thermal decomposition of allyl chlorosulfinate-1-¹⁴C for which there is cogent evidence for reaction through an undissociated ion-pair (I), the ion-pair mechanism is favored.⁸



High reactant concentrations in ether solution reduce the specificity of reaction and a mixture of chlorides is obtained (runs 4, 5, 7). Probably, this is due to increased solvent polarity which permits some ion-pair dissociation and so leads to a mixture of products. It is suggested that previous preparations of allylic chlorides using thionyl chloride and ether as solvent led to mixtures because reactant concentrations were usually over several molar⁹⁻¹¹ (cf. also runs 4, 5 and 7, Table I of this paper).

Changing the order of addition of the reactants produced no significant change in product composition (compare runs 6 and 8, 4 and 7, 9 and 11), a result which is to be expected if the rate-determining step is decomposition of the chlorosulfinate ester. The effect of temperature on product composition appears to be very small but was not exhaustively studied (compare runs 4 and 5, 9 and 10).

(6) J. D. Roberts, W. G. Young and S. Winstein, THIS JOURNAL, $64,\,2157$ (1942).

(7) (a) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak and W. G. Young, *ibid.*, **80**, 5965 (1958); (b) E. M. Kosower, Ph.D. Thesis, U.C.L.A., 1952.

(8) For a detailed discussion of this mechanism see ref. 7.

(9) J. Meisenheimer and J. Link, Ann., 479, 211 (1930).
(10) R. T. Arnold and R. W. Liggett, THIS JOURNAL, 64, 2875

(10) R. T. Arnold and R. W. Liggert, THIS JOURNAL, **54**, 287 (1942).
 (11) D. Barnard and L. Bateman, J. Chem. Soc., 926 (1950).

	Reactants c			Products. ¢ %		
Run	Add	То	Solvent	s-RC1	p-RCI	Vield
1	p-ROH	SOC12	None	72	28	83
2	SOC12	p-ROH	None	49	51	90
3	s-ROH1	SOC12	None	33 <i>1</i>	67	77
4	p-ROH	$SOCl_2(5.6 M)$	Ether	73	22	85
5	p-ROH	$SOCl_2(5.6 M)$	Ether (-70°)	79	21	84
6 ^d	p-ROH	SOC12	Ether	98	2	70
7	SOC12	p-ROH (5.6 M)	Ether	67	33	82
8*	SOC12	p-ROH	Ether	90	10	81
9	s-ROH	SOC12	Ether	0	100	81
10	s-ROH	SOC12	Ether (34°)	5	95	90
11	SOC12	s-ROH	Ether	2	98	85
12	p-ROH	$SOCl_2(5.6 M)$	Pentane	82	18	87
13 ^d	p-ROH	SOC12	Pentane	88	12	83
14	SOC12	p-ROH (5.6 M)	Pentane	44	56	88
15	SOC12	p-ROH	Pentane	77	23	81
16	s-ROH	SOC12	Pentane	22	78	74
17ª	SOC12	s-ROH ^g	Pentane	30ª	70	89
18	p-ROH	SOC12	Dioxane	81	19	83
19	s-ROH ^h	SOC12	Dioxane	22^{h}	78	55
20	p-ROH	SOC12	$C_2H_5OC_2H_4OC_2H_5$	90	10	67
21	p-ROH	SOC12	$C_2H_5OC_2H_4OC_2H_5$ (54°)	92	8	66
22	p-ROH	$SOCl_2(2.8 M)$	CH ₃ Cl (-24°)	81	19	86
23	s-ROH	$SOCI_2(2.8 M)$	CH ₃ Cl (-24°)	26	74	77
24	p-ROH	$SOCl_2(1.4 M)$	C ₆ H ₅ Cl	83	17	89
25	SOC12	p-ROH (1.4 M)	C ₆ H ₅ Cl	72	28	80
26 ^d	p-ROH	$SOCl_2$ (2.8 M)	$SO_2(-10^{\circ})$	59	41	78
27	p-ROH	SOC12	$SO_2(-10^\circ)$	57	43	74
28	s-ROH ⁴	SOC12	$SO_2(-10^\circ)$	32'	68	66
29	s-ROH	$SOCl_2 + (C_6H_5)_3CCl (satd.)$	$SO_2(-10^{\circ})$	32^{i}	68	57
30	p-ROH	$SOC1_2 (5.6 M)$	$C_6H_5NO_2$	73	27	89

TABLE I REACTION OF THIONYL CHLORIDE WITH α - and γ -Methylallyl Alcohols^a under Controlled Conditions'

^a α -Methylallyl alcohol is racemic unless otherwise specified. γ -Methylallyl alcohol is the *trans* isomer in every case. ^a Reactants are equimolar, solutions are 0.7 M, reaction time is one hour and temperature is 5°, except where otherwise noted. ^b Reactants are equimolar, solutions are 0.7 M, reaction time is one hour and temperature is 5°, except where otherwise noted. ^c Abbreviations: p-ROH, CH₃CH=CHCH₂OH; s-ROH, CH₃CHOHCH=CH₂: p-RCl, CH₂CH=CHCH₂Cl; s-RCl, CH₃CHClCH=CH₂: d Average of two runs. ^c Average of three runs. ^f s-ROH, α^{29} D +2.22°; s-RCl, α^{25} D +1.40° = retained + 71% racemized. ^g s-ROH, α^{28} D -2.55°; s-RCl, α^{25} D +2.08° = inverted + 65% racemized. ^h s-ROH, α^{25} D +2.08°; s-RCl, α^{31} D +1.21° = retained + 75% racemized. ⁱ s-RCl, α^{29} D 1.19 = retained + 77% racemized.

In other solvents (pentane, dioxane, 1,2-diethoxyethane, methyl chloride, chlorobenzene and liquid sulfur dioxide) the nearly complete allylic rearrangement observed in diethyl ether was not realized. It may at first appear surprising that reaction should be less specific in a less polar solvent such as pentane, but the explanation may well lie in the ability of ether to form a stable undissociated complex with the hydrogen chloride^{12a,b,c} produced during reaction; this may prevent involvement of hydrogen chloride (a) by promoting an SN2-type reaction to give unrearranged chloride, and/or (b) as a polar species which may facilitate ion-pair dissociation. A combination of these two effects is seen in run 17 which used optically active α -methylallyl alcohol in pentane and gave α -methylallyl chloride with extensive racemization and inversion of configuration (SN2).

Although reaction in sulfur dioxide, dioxane and in the absence of solvent gives a mixture of products, the steric course is unusual in that racemization with *retention* of configuration is the over-all result (runs 3, 19 and 28). Involvement of solvent

(12) (a) A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, **60**, 2528 (1938); (b) D. R. Chesterman, J. Chem. Soc., 906 (1935); (c) T. Mounajed, Compt. rend., **197**, 44 (1933). with the ion-pair intermediate to prevent attack of chloride ion or its equivalent on the side opposite to the leaving group in the manner proposed by Boozer and Lewis¹³ may account for these steric results.

Liquid sulfur dioxide, of all the solvents studied, gave the most random product distribution. This is in keeping with the suggestion that the reaction proceeds by an ion-pair mechanism. The greater the ionizing power of the solvent, the larger is the degree of ion-pair dissociation and more equitable is the product mixture. However, dissociation is probably far from complete since the addition of triphenylmethyl chloride¹⁴ changes the product distribution and steric course very little (runs 28 and 29).

Reaction in the Presence of Added Base.—The entire course of reaction of γ -methylallyl alcohol

(13) C. E. Boozer and E. S. Lewis, THIS JOURNAL, 75, 3182 (1953);
 E. S. Lewis and C. E. Boozer, *ibid.*, 74, 308 (1952).

(14) In the reaction of optically active α -phenylbutanol with phosphorus pentachloride in liquid sulfur dioxide, the addition of triphenylmethyl chloride was observed to enhance greatly substitution with retention, presumably by suppressing the classical SN1 mechanism: E. D. Hughes, C. K. Ingold and I. C. Whitfield, *Nature*, **147**, 206 (1941).

TABLE	II
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Reaction of Thionyl Chloride with α - and γ -Methylallyl Alcohols ^a under Controlled Conditions ^b in the P	'RES-
ENCE OF AMINES AND AMINE HYDROCHLORIDES	

_ 		Reactants		Pr	oducts, 🦿 🥬	70
Run	Add	То	Solvent	s-RCI	∳-RCI	Yield
31	p-ROH	$SOC1_2 + Py$	None	28	72	80
32	SOC12	p-ROH + 1.2 Py	None	19	81	57
33	s-ROH	$SOCl_2 + Py$	None	45	55	67
34	SOC12	p-ROH (1.9 M) + Py (1.9 M)	Ether	32	68	89
35	SOC12	p-ROH + Py	Ether	28	72	75
36	p-ROH	$SOCl_2 + Py$	Ether	22	78	54
37	p-ROH	$SOCl_2 + Py: HCl^d$	Ether	69	31	83
38	s-ROH	$SOCl_2 + 2Py (1.4 M)$	Ether	43	57	38
39	SOCl ₂	p-ROH + Py	Pentane	23	77	84
40	p-ROH	$SOCl_2(1.4 M) + Py(1.4 M)$	C ₆ H ₅ Cl	26	74	70
41 °	SOC12	p-ROH (1.4 M) + Py (1.4 M)	C ₆ H ₅ Cl	30	70	85
42	p-ROH + Py	$SOCl_2 (1.4 M)$	C ₆ H ₅ Cl	38	62	75
43	s-ROH	$SOCl_2(1.4 M) + Py(1.4 M)$	C ₆ H ₅ Cl	39	61	80
44 ¹	SOC12	s -ROH (1.4 M) g + Py (1.4 M)	C ₆ H ₅ Cl	350	65	81
45	SOC12	p-ROH (1.4 M) + Py (1.4 M)	$C_6H_5NO_2$	20	80	79
46	SOC12	p-ROH (1.4 M) + Py (1.4 M)	$SO_2(-10^\circ)$	49	51	62
47	p-ROH + 2,6-lutidine	SOC12	Ether	6	94	53
48	SOC12	p-ROH + Bu ₃ N	Ether	0	100	93
49	1/2SOCI2	p-ROH + Bu ₃ N	Ether	0	100	74
50	p-ROH	$SOCl_2 + Bu_3N:HCl$	Ether	26	74	92
51	p-ROH	$SOCl_2 + \frac{1}{5}Bu_3N:HCl (0.14 M)$	Ether	33	67	83
52^{f}	SOC12	s-ROH ^h + Bu₃N	Ether	65^{h}	35	81
53	SOC12	s-ROH + Bu ₃ N	Ether (-50°)	72	28	83
54	SOCI2	s-ROH (0.35 M) + Bu ₃ N				
		(0.35 M)	Ether	64	36	77
55	s-ROH	$SOCl_2 + Bu_3N$	Ether	62	38	79
56	s-ROH + Bu _s N	SOC12	Ether	59	41	78
57	s-ROH + Bu₃N	SOCl ₂ + Bu ₃ N·HCl	Ether	64	36	81
58	SOC12	p-ROH + Bu₃N	Dibutyl ether	4	96	62
59	SOC12	p-ROH + Bu ₃ N	Pentane	0	100	84
60	SOC12	s-ROH + Bu ₃ N	Pentane	62	38	76
611	SOC12	p-ROH + DIPT	Ether	40	60	82
62	p-ROH	$SOCl_2 + 2DIPT (1.4 M)$	Ether	0	100	39
63	SOC12	p-ROH + DIPT	Pentane	10	90	77
64	SOCI2	s-ROH + DIPT	Pentane	44	56	70
65•	SOC12	p-ROH (1.4 M) + DIPT				
		(1.4 M)	C ₆ H ₅ Cl	5	95	85
66	SOC12	s-ROH $(1.4 M)$ + DIPT	-			
		(1.4 M)	C ₆ H ₅ Cl	69	31	70
67	SOCI2	p-ROH + (C ₆ H ₅) ₃ CN(CH ₈) ₂	C ₆ H ₅ Cl	44	56	65

^a α -Methylallyl alcohol is racemic unless otherwise specified; γ -methylallyl alcohol is the *trans* isomer in every case. ^b Reactants are equimolar, solutions are 0.7 *M*, reaction time is one hour, and temperature is 5° except where otherwise noted. ^c Abbreviations: p-ROH, CH₃CH=CHCH₂OH; *s*-ROH, CH₃CHOHCH=CH₂; *p*-RCl, CH₃CH=CHCH₂Cl; *s*-RCl, CH₃CHCHCH=CH₂; *p*y, pyridine; Py:HCl, pyridine hydrochloride; CaH₆Cl, chlorobenzene; C₆H₆NO₂, nitrobenzene; Bu₃N, tri-*n*-butylamine; Bu₃N-HCl, tri-*n*-butylamine hydrochloride; DIPT, N,N-diisopropyl-o-toluidine; (C₆H₅)₅CH-(CH₃)₅CH=CHCH₃)₅CH-(CH₃)₅, dimethyltritylamine. ^d Present as solid phase. ^e Average of two runs. ^f Average of three runs. *e s*-ROH, $\alpha^{24}D - 2.74^\circ$; *s*-RCl, $\alpha^{25}D + 2.96^\circ$ = inversion + 53% racemized. ^h *s*-ROH, $\alpha^{26}D - 4.35^\circ$; *s*-RCl, $\alpha^{26}D + 7.68^\circ$ = inversion + 22% racemized.

with thionyl chloride in ether can be changed from one of complete allylic rearrangement to one of preservation of structure by the addition of an equivalent amount of tri-*n*-butylamine. Thus γ -methylallyl alcohol gave γ -methylallyl chloride as the exclusive product (runs 48 and 49, Table II). A similar result was obtained in pentane (run 59) and in dibutyl ether solution (run 58), and in the presence of the other tertiary amines, 2,6-lutidine (run 47) and N,N-diisopropyl-o-toluidine (runs 62, 63 and 65). Pyridine, on the other hand, always led to a mixture of chlorides whether or not ether was used as solvent (runs 31, 32, 34, 35, 36, 39-42, 45 and 46). A mixture of products was also obtained if the hydrochlorides were used in place of the free amines (runs 37, 50 and 51).

In contrast to the behavior of γ -methylallyl alcohol in the presence of a molar equivalent of tri*n*-butylamine, α -methylallyl alcohol under similar conditions always gave mixed chlorides (runs 52– 56 and 60). However, the α -methylallyl chloride derived from optically active alcohol was found to be only 22% racemized and of *inverted* configuration (run 52). These results can be explained by the already well established SN2 mechanism¹⁵ for reaction of aliphatic alcohols with thionyl

(15) W. A. Cowdry, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, J. Chem. Soc., 1252 (1937).

Reaction of Thionyl Chloride with Di- α - and Di- γ -methylallyl Sulfites^a under Controlled Conditions^b

Reactants c				Products & %		
Add	To	Solvent	s-RC1	p-RC1	Yield	
SOC12	$(p-RO)_2SO$	Ether	72	28	73	
$(p-RO)_2SO$	SOC12	Ether	71	29	79	
$(p-RO)_2SO$	Bu ₃ N:HC1	Ether	0	100	100	
$(s-RO)_2SO^f$	$Bu_3N:HCl$	Ether (25°, 10 hr.)	100 ^f	0	15	
$(s-RO)_2SO^g$	$Bu_2N:HCl$	Ether (34°, 50 hr.)	100%	0	20	
SOC12	$(p-RO)_2SO$	Pentane	72	28	63	
$(p-RO)_2SO$	SOC1 ₂	Pentane	70	30	79	
$(p-RO)_2SO + Bu_3N$	2SOCl ₂ (1.4 M)	Pentane	0	100	60	
$(p-RO)_2SO$	SOC12	$HCON(CH_3)_2$	15	85	67	
$(p-RO)_2SO$	$SOCl_2 + LiCl$	$HCON(CH_3)_2$	-1	96	75	
$(p-RO)_2SO$	LiCl	$HCON(CH_3)_2$	0	100	37	
	Add SOC1 ₂ $(p-RO)_2SO$ $(p-RO)_2SO^{-1}$ $(s-RO)_2SO^{-1}$ $(s-RO)_2SO^{-1}$ $(s-RO)_2SO^{-1}$ $(p-RO)_2SO$ $(p-RO)_2SO + Bu_5N$ $(p-RO)_2SO$ $(p-RO)_2SO$ $(p-RO)_2SO$ $(p-RO)_2SO$ $(p-RO)_2SO$	Add To SOCl2 $(p\text{-RO})_2\text{SO}$ $(p\text{-RO})_2\text{SO}$ SOCl2 $(p\text{-RO})_2\text{SO}$ SOCl2 $(p\text{-RO})_2\text{SO}$ Bu ₃ N:HCl $(s\text{-RO})_2\text{SO}'$ Bu ₂ N:HCl $(s\text{-RO})_2\text{SO}'$ Bu ₂ N:HCl SOCl2 $(p\text{-RO})_2\text{SO}$ $(p\text{-RO})_2\text{SO}$ SOCl2	AddToSolventSOCl2 $(p-RO)_2SO$ Ether $(p-RO)_2SO$ SOCl2Ether $(p-RO)_2SO$ SOCl2Ether $(p-RO)_2SO$ Bu_3N:HClEther $(s-RO)_2SO'$ Bu_3N:HClEther (25°, 10 hr.) $(s-RO)_2SO'$ Bu_2N:HClEther (34°, 50 hr.)SOCl2 $(p-RO)_2SO$ Peutane $(p-RO)_2SO$ SOCl2Pentane $(p-RO)_2SO$ SOCl2HCON(CH_3)2 $(p-RO)_2SO$ SOCl2HCON(CH_3)2 $(p-RO)_2SO$ SOCl2HCON(CH_3)2 $(p-RO)_2SO$ SOCl2HCON(CH_3)2 $(p-RO)_2SO$ LiClHCON(CH_3)2	AddToSolvents-RCl $SOCl_2$ $(p-RO)_2SO$ Ether72 $(p-RO)_2SO$ $SOCl_2$ Ether71 $(p-RO)_2SO$ $SOCl_2$ Ether71 $(p-RO)_2SO$ $Bu_3N:HCl$ Ether0 $(s-RO)_2SO'$ $Bu_3N:HCl$ Ether0 $(s-RO)_2SO'$ $Bu_2N:HCl$ Ether (25°, 10 hr.)100' $(s-RO)_2SO'$ $Bu_2N:HCl$ Ether (34°, 50 hr.)100' $SOCl_2$ $(p-RO)_2SO$ Peutane72 $(p-RO)_2SO$ $SOCl_2$ Pentane70 $(p-RO)_2SO + Bu_5N$ $2SOCl_2(1.4 M)$ Pentane0 $(p-RO)_2SO$ $SOCl_2$ $HCON(CH_3)_2$ 15 $(p-RO)_2SO$ $SOCl_2 + LiCl$ $HCON(CH_3)_2$ 4 $(p-RO)_2SO$ $LiCl$ $HCON(CH_3)_2$ 0	AddToSolvent s -RCI p -RCISOCl2 $(p$ -RO)2SOEther 72 28 $(p$ -RO)2SOSOCl2Ether 71 29 $(p$ -RO)2SOBu3N:HCIEther 0 100 $(s$ -RO)2SO'Bu3N:HCIEther 0 100 $(s$ -RO)2SO'Bu2N:HCIEther (25° , 10 hr.)100' 0 $(s$ -RO)2SO'Bu2N:HCIEther (34° , 50 hr.)100'' 0 SOCl2 $(p$ -RO)2SOPeutane 72 28 $(p$ -RO)2SOSOCl2Pentane 70 30 $(p$ -RO)2SOSOCl2Pentane 0 100 $(p$ -RO)2SOSOCl2HCON(CH3)2 15 85 $(p$ -RO)2SOSOCl2 + LiCIHCON(CH3)2 4 96 $(p$ -RO)2SOLiCIHCON(CH3)2 0 100	

^a Di- α -methylallyl sulfite is racenic unless otherwise specified; di- γ -methylallyl sulfite is the di-*trans* isomer in every case. ^b Reactants are equimolar, solutions are 0.7 *M*, temperature is 5° and reaction time is 1 hour unless otherwise noted. ^c Abbreviations: (*p*-RO)₂SO, (CH₃CH=CHCHO)₂SO; (*s*-RO)₂SO, [(CH₃)(CH₂=CH)CHO]₂SO; *p*-RCl, CH₃CH=CHCH2Cl; *s*-RCl, CH₃CHClCH=CH₂; Bu₃N, *n*-tributylamine; Bu₃N·HCl, *n*-tributylamine hydrochloride. ^d Average of two runs. ^e Extent of racemization uncertain because product contained ether. ^f (*s*-RO)₂SO, $\alpha^{25}D - 10.72^{\circ}$; *s*-RCl, $\alpha^{24}D - 2.93^{\circ} =$ inversion.^e

TABLE IV

 pK_{*} Values of Tertiary Amines in 75% Ethanol-Water Solution at 30°

Amine	$\phi K_{ m a}~(\pm 0.03)$
Pyridine	3.91
2,6-Lutidine	5.25
Tri-n-butylamine	8.48
N,N-Diisopropyl-o-toluidine	5.75
$N, N-Dimethyltriphenylmethylamine^a$	ca. 4.9
N,N-Diisopropyl- <i>o</i> -toluidine N,N-Dimethyltriphenylmethylamine ^a	5,75 ca. 4,9

^a This amine was found to evolve dimethylamine in solution and its pK_a value may be somewhat high.

chloride along with some contribution from the SN1 ion-pair mechanism to account for both the rearranged chloride and the racemization observed. However, intermediates other than the first formed chlorosulfinate ester may be involved in the ratedeterimining step. In addition to attack of chloride ion on the chlorosulfinate ester (eq. 1), the base present may react with the ester to form a quaternary salt which could lead to products by an SN2 attack on the quaternary cation (eq. 2). Alternatively, the chlorosulfinate ester may combine with unreacted alcohol to form a disulfinate ester which then reacts with chloride ion to give the products (eq. 3). Indeed, the disulfinate esters of both α - and γ -methylallyl alcohols have been shown to react with chloride ions by an SN2-type mechanism. The results of Table III show that if the disulfinate ester is isolated and subsequently

$$ROSOCI \xrightarrow{Cl \oplus} RCl + SO_2 \tag{1}$$

$$ROSOCI \xrightarrow{\mathbf{R'}_{3}\mathbf{N}} ROSO\overset{\leftrightarrow}{\mathsf{NR'}_{3}\mathbf{Cl}} \longrightarrow RCl + SO_{2} + NR'_{3}$$
(2)

$$\begin{array}{c} \text{ROSOCI} \xrightarrow{\text{ROH}} \text{ROSOOR} + \text{HCI} \\ & \stackrel{\oplus}{\underset{| R'_{3} \text{NHCI}}{\overset{\oplus}{\underset{| R'_{3} \text{NHCI}}}{\overset{\oplus}{\underset{| R'_{3} \text{NHCI}}{\overset{\oplus}{\underset{| R'_{3} \text{NHCI}}{\overset{\oplus}{\underset{N}'_{3} N'}}{\overset{\oplus}{\underset{N'_{3} N'_{3} N'}}{\overset{&}}}}}}}}}}}}}}}}}}}}}}}}}}}$$

added to a source of chloride ion (tri-*n*-butylamine hydrochloride or lithium chloride) dissolved in an appropriate solvent, unrearranged chloride is the exclusive product. This is the only method by which α -methylallyl chloride could be prepared free of the γ -isomer from α -methylallyl alcohol. Furthermore, the over-all steric result at the carbinol carbon atom was *inversion* of configuration. However, since the reaction of di- α -methylallyl sulfinate was found to be very slow (runs 77 and 78), this intermediate can hardly be important in the reactions listed in Table II. In contrast, di- γ -methylallyl sulfinate reacted rapidly and quantitatively with chloride ion and its participation cannot be ruled out (runs 76, 81 and 84). This latter intermediate would clearly be favored in the experiments of Table II where thionyl chloride was added to the alcohol (runs 32, 34, 35, 39, 41, 58, 59, 61, 63 and 65), but since no starting alcohol was ever observed in the products exclusive reaction by equation 3 is certainly ruled out.

Little positive evidence has been obtained to substantiate a quaternary salt intermediate (eq. 2) except that less rearrangement is generally observed in the presence of the more basic amines even when the amine hydrochlorides are quite insoluble (cf. compare results in Table II with pK_a 's of the tertiary amines in Table IV). Early in this work the interesting speculation was made that the use of a sufficiently hindered amine might reveal the importance of the quaternary salt as an intermediate. It was argued that a hindered amine would deter the formation of the salt and so force the reaction to take an alternative course. This should alter drastically the product composition relative to that found in the presence of an unhindered amine. Inspection of models showed the nitrogen atom of N,N-diisopropyl-o-toluidine to be virtually buried in a cage of carbon and hydrogen atoms and seemingly unavailable for quaternization. However, no obvious influence of this hindered amine was observed (compare the results of run 63 with 59 and 64 with 60). It seems improbable, therefore, that the quaternary salt plays any important role in the formation of products.

Several other processes which conceivably could have produced chlorides have been shown inoperative by suitable blanks. Thus, interaction of hydrogen chloride with α - and γ -methylallyl alcohols was tested under the standard experimental conditions and only trace amounts of chlorides were formed along with material which was probably a mixture of the various possible ethers.

When pyridine was present, only pyridine hydrochloride and the starting alcohol were isolated. $Di-\gamma$ -methylallyl sulfinate when treated with hydrogen chloride in ether produced α -methylallyl chloride in about 50% yield together with a complex mixture of ethers and a trace of γ -methyl-allyl chloride. The chlorides may have arisen from the decomposition of γ -methylallyl chlorosulfinate formed by the reaction of the disulfinate with hydrogen chloride.¹⁶

Experimental

trans- γ -Methylallyl alcohol was prepared by the method of Nystrom and Brown¹⁷ using lithium aluminum hydride to reduce crotonaldehyde; b.p. 119-121°, n^{25} D 1.4296. dl- α -Methylallyl alcohol was prepared by the method of Delaby¹⁸ as modified by Prevost.¹⁹ The desired product had b.p. 96-97° and n^{25} D 1.4125. **Personution** of the Methylallyl Alloched Desired Product had

Resolution of α -Methylallyl Alcohol.—Partially resolved α -methylallyl alcohol was obtained by the procedure of Kenyon and Snellgrove²⁰ by 12 recrystallizations of the brucine salt of α -methylallyl acid phthalate from acetone. The purified alcohol had b.p. 97°, n^{25} D 1.4121 and α^{27} D +20.09 ± 0.02° (l 1, neat), $[\alpha]^{27}$ D +24.15° (72% of optical purity). The mether liquers wielded α small α -methylallyl acid phthalate from acetone. purity). The mother liquors yielded a small amount of (-)- α -methylallyl alcohol, α^{25} -8.45° (l 1, neat).

Di- γ -methylallyl Sulfinate.—A solution of 86 g. (0.72 mole) of thionyl chloride in 100 ml. of ether was added dropwise in 1 hr. to a solution of 104 g. (1.44 moles) of γ -methylallyl alcohol and 114 g. (1.44 moles) of pyridine in 400 ml. of ether maintained at -78° . The reaction mixture was warmed to room temperature and 1 N hydrochloric acid was added until the precipitate of pyridine hydrochloride dissolved. The layers were separated and the ether solution was washed with water and dilute potassium carbonate solution and dried over anhydrous potassium carbonate. The ether was removed by distillation and the residue was distilled to give 84 g. (61%) of di- γ -methylallyl sulfinate, b.p. 92.5–94° (2–3 mm.), n^{25} p 1.4632.

Anal. Calcd. for C₈H₁₄O₃S: C, 50.50; H, 7.41. Found: С, 50.85; Н, 7.57.

 $Di-\alpha$ -methylallyl sulfinate was prepared in the manner described for di- γ -methylallyl sulfinate except that pentane was used as solvent in place of ether. The purified product had b.p. 60° (3 mm.) and n²⁵D 1.4450.

Anal. Caled. for $C_8H_{14}O_3S$: C, 50.50; H, 7.41. Found: C, 50.73; H, 7.33.

Optically active di-a-methylallyl sulfinate was prepared from (+)- α -methylallyl alcohol $(\alpha^{24}D + 4.41^{\circ}, l 1, neat,$ 15.6% of optical purity). The optically active di- α -methyl-allyl sulfinate obtained had $\alpha^{24}D - 18.44^{\circ}$ (l 1, neat). Thionyl Chloride.—Eastman Kodak Co. white label

thionyl chloride was purified according to the procedure of Cottle.²¹

Pyridine .-- Technical grade pyridine was purified by allowing it to stand over solid potassium hydroxide for about 1 week after which it was distilled from barium oxide through a 25-cm. glass helices column. The constant boiling portion was retained and stored over barium oxide.

Tri-n-butylamine.-Eastman Kodak Co. white or yellow Label material was heated 3 hours on a steam-bath with acetic anhydride. The anhydride was destroyed with potassium carbonate solution and the amine was separated and distilled under reduced pressure.

2,6-Lutidine was purified in the same manner as described for pyridine.

N,N-Dimethyltriphenylmethylamine was prepared from triphenylmethyl bromide and dimethylamine according to the procedure of Hemilian and Silberstein.22

N,N-Diisopropyl-o-toluidine.-To a refluxing mixture of 68.5 g. (0.41 mole) of isopropyl iodide and 28 g. (0.5 mole)

(16) W. E. Bissinger and F. E. Kung, THIS JOURNAL, 69, 2158 (1947)

(17) R. F. Nystrom and W. G. Brown, ibid., 69, 1197 (1947).

(18) R. Delaby, Compt. rend., 175, 967 (1922)

(19) C. Prevost, Ann. chim., 10, 113, 147 (1928).

(20) J. Kenyon and D. Snellgrove, J. Chem. Soc., 127, 1174 (1925).

(21) D. L. Cottle, THIS JOURNAL, 68, 1380 (1946).

(22) W. Hemilian and H. Silberstein, Ber., 17, 746 (1884)

of powdered potassium hydroxide was added slowly 20 g. (0.2 mole) of *o*-toluidine. After the mixture had been refluxed overnight, water was added and the layers were separated. The organic layer was dried over potassium hydroxide and was distilled to yield 28 g. (92%) of N-iso-propyl-o-toluidine, b.p. 216° (atm.), 113° (25 mm.) and n^{25} D 1.5291. The picrate, m.p. 154°d.; N-benzoyl, m.p. $50-51^{\circ}$; N-acetyl-, m.p. *ca*. room temp., b.p. 150° (25 mm.), $n^{25}p$ 1.5164; and hydrochloride, m.p. $162-163^{\circ}$ were prepared. The hydrochloride gave equiv. wt. 187.2 (theor. 185.7) upon titration with standard base. Next, 36 g. (0.24 mole) of N-isopropyl-o-toluidine was added dropwise to 0.24 mole of stirred methyllithium in about 300 ml. of ether and after a 2-hr. reflux period was followed by dropwise addition of 70 g. (0.41 mole) of isopropyl iodide. The mixture was refluxed 3 days after which excess methyllithium was destroyed with methanol and water. The organic solution was separated, dried over anhydrous potassium carbonate and concentrated on a steam-bath after addition of 40 ml. of acetic anhydride. The concentrate was treated with potassium carbonate solution, dried and distilled through a 30-cm. concentric tube column to yield 34.5 g. (73.5%) of N,N-diisopropyl-o-toluidine, b.p. 114° (20 mm.), n^{25} D 1.4975, d^{24} 0.8932.

Anal. Caled. for C13H21N: C, 81.62; H, 11.1. Found: C, 81.16; H, 11.2.

The picrate was formed in ether, m.p. 126-128°; the hydrochloride was formed in ether and recrystallized from benzene, m.p. 173-174°.

Anal. Caled. for C₁₃H₂₂NCl: C, 68.54; H, 9.74; equiv. wt., 227.77. Found: C, 68.20; H, 9.66; equiv. wt., 227.4.

Solvents .--- Ethyl ether was Mallinckrodt A.R. grade and was stored over sodium hydride. *n*-Pentane was Phillips Pure grade further purified by passage through a 90-cm. silica gel column then distillation through a 2.5 imes91 cm. column packed with Podbielniak Heli-Pak and was stored over sodium hydride. **Chlorobenzene** was Eastman Kodak Co. white label grade purified by distillation through a 100-cm. glass helices packed column. Technical grade dioxane was purified according to the directions of Fieser²³ followed by fractionation through the Heli-Pak column and was stored over sodium hydride. Eastman Kodak Co. yellow label 1,2-diethoxyethane was purified in the same manner as described for dioxane, and was freshly distilled from sodium immediately before use. Union Carbide and carbon di-n-butyl ether was purified and stored sulfur diox de was obtained from Dow Chemical Co. and was used without purification. Dimethylformamide was obtained from Matheson and was used without purification.

General Procedure for the Reaction of Thionyl Chloride with α - and γ -Methylallyl Alcohols. A. Table I Experiments .--- One pure reactant was added dropwise to the other dissolved in a solvent or neat and contained in a 300-ml., 3-neck flask fitted with a pressure equalizing dropping funnel, cold finger condenser, protected by a Drierite drying tube, glass or Tefion stirrer and a thermometer well. reaction flask was immersed in an ice-bath during combination of the reactants and the cold finger condenser was maintained at -10 to 0° . Combination of the reactants generally was accomplished in about 40 min. after which the ice-bath was removed and the reactant mixture was stirred for 1 hr. longer. In runs not having a solvent or which used solvents boiling lower than α -methylallyl chloride, the reaction solution was fractionated directly to obtain the product composition. In runs which used solvents boiling higher than γ -methylallyl chloride, the volatile materials were flash distilled into a Dry Ice trap from the bulk of the solvent and then fractionated. The reaction quantities used were 10.0 g. (0.139 mole) of α - or γ -methylallyl alcohol, 16.5 g. (0.139 mole) of thionyl chloride and 200 ml. (0.7 M), 100 ml. (1.4 M), 50 ml. (2.8 M) or 25 ml. (5.6 M), or no ml. of solvent. Exceptions are noted in Table I. The theoretical total yield of α - or γ -methylallyl chlorides was 12.6 g.

B. Table II experiments .- The same apparatus and addition procedure was used as described in A. Addition times averaged about 60 minutes owing to a more exothermic reaction than encountered with the experiments of Table I.

⁽²³⁾ L. F. Fieser, "Experiments in Organic Chemistry," second edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

Amine hydrochloride precipitated immediately upon addition of the reactants except when tri-n-butylamine was used in ether. In the latter case no precipitate was noticed until almost all of the reactants had been combined when a second liquid phase sometimes appeared. After being stirred for 1 hr. with the ice-bath removed, the volatile products and solvents more volatile than α -methylallyl chloride were flash distilled into a Dry Ice trap and then fractionated. The reaction quantities were as in A with 11.0 g. (0.139 mole) of pyridine, 26.5 g. (0.139 mole) of N,N-diisopropyl-toluidine, 25.7 g. (0.139 mole) of tri-*n*-butylamine or 14.9 g. (0.139 mole) of 2,6-lutidine. Exceptions are noted in Table ÍI.

C. Table III Experiments were done as described in A and B above and were on the same scale. Exceptions are noted in Table III.

Distillation Analysis of α - and γ -Methylallyl Chlorides.-The reaction mixtures after treatment as described above were carefully fractionated through a concentric tube vacuum jacketed column, the fractionating section of which consisted of a 30 cm. long, 6.5-mm. Truebore rod within an 8-mm. Trubore tube. The column was equipped with a solenoid operated, total condensation, partial takeoff head and was determined to have 35-plate efficiency at total Holdup was about 1.5 ml. About 10 fractions reflux. were collected in the course of an analysis in such a way that only a binary mixture was present in any specific fraction with the exception of runs which yielded less than 10% of one of the chlorides. Toward the end of each distillation, a small amount of chlorobenzene was added as a pusher to ensure isolation of the entire yield of chlorides. The boiling range, weight and refractive index of each fraction was recorded and the composition was obtained from calibration curves of refractive index plotted against weight per cent. of the components of the various binary mixtures encountered. The analysis was shown to be accurate within 4% by distillation of known synthetic mixtures of α - and γ -methylallyl chlorides in various solvents containing

hydrogen chloride and sulfur dioxide as contaminants. Small amounts of these contaminants were frequently present in the first few fractions along with traces of thionyl chloride and were destroyed by treatment of these fractions with several drops of water followed by addition of a small with several drops of water followed by addition of a small amount of anhydrous potassium carbonate. The blanks showed that little, if any, isomerization of α - and γ -methyl-allyl chlorides occurred during the distillation analyses within the accuracy stated. That α - and γ -methylallyl chlorides are relatively stable has also been demonstrated by Catchpole and Hughes.²⁴ Optically active α -methylallyl chloride racemized 12% when isolated from liquid sulfur dioxide. The values reported in Table I are uncorrected dioxide. The values reported in Table I are uncorrected for this racemization. In one experiment, the absence of cis-y-methylallyl chloride in the product was established by infrared spectroscopy.

The possibility that reaction between thionyl chloride and the butenols in the absence of a tertiary amine was not completed in the times described but was still proceeding during distillation analysis must be considered; however, unpublished results²⁵ pertaining to attempted isolation of γ methylallyl chlorosulfinate indicate that the reactions were essentially completed before fractionation was begun.

Determination of $pK_{\rm B}$ of the tertiary amines used in this work employed the method of Thompson²⁶ in which the pHvalue of a solution of a tertiary amine in the presence of an excess of standard hydrochloric acid was measured and used directly for calculation of pK_a . For preparation of 75% alcohol-water solutions, an accurately weighed sample of tertiary amine was dissolved in 25 ml. of standard aqueous hydrochloric acid and made up to 100 ml. with 96.5%ethanol which had been distilled from potassium carbonate. The results are summarized in Table IV.

(24) A. G. Catchpole and E. D. Hughes, J. Chem. Soc., 4 (1948).

- (25) F. F. Caserio, Jr., Ph.D. Thesis, U.C.L.A., 1954. (26) G. Thompson, J. Chem. Soc., 1113 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

The Thermal Decomposition of Thiolsulfonates. II

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Study of the thermal decomposition of a series of diphenylmethanethiolsulfonates, $(C_6H_5)_2CHSO_2SR'$, reveals the following pronounced dependence of the relative rate of decomposition on R': C_6H_5 -, 25; $C_6H_5CH_2$ -, 1; CH_3 -, 0.3; *n*- C_1H_9 , 0.2. The principal products of the decompositions [$(C_6H_5)_2CHSR' + SO_2$] and the variation in rate with solvent establish the mechanistic kinship of these and the previously studied² decompositions of $(C_6H_5)_2CHSO_2SCH_2C_6H_5$ and $C_6H_5CH_2SO_2-C_6H_5$. $SCH_2C_6H_5$. When taken together with these previous results the present data require a mechanism involving heterolytic cleavage of both the C-SO2 and SO2-S bonds in the transition state of the rate-determining step. One acceptable mechanism is an initial equilibrium followed by a rate-determining decomposition of the first-formed ion-pair, $RSO_2SR' \rightleftharpoons [RSO_2\oplus \dots \oplus SR'] \rightarrow [R\oplus \dots \oplus SR'] + SO_2$. The possible general significance of these data in view of the previously noted² similarities between the thiolsulfonate decomposition and such Sxi reactions as the decomposition of chlorocarbonates and chlorosulfites is discussed. The extent of deuteration of the diphenylmethane and tetraphenylethane formed in the decomposition of $(C_6H_5)_2CHSO_2SCD_2C_6H_5$ has been determined; the results permit some further conclusions to be drawn concerning the origin of these products in the decomposition of the diphenylmethanethiolsulfonates.

Recent work² has shown that the thiolsulfonates $RSO_2SCH_2C_6H_5$, where $R = (C_6H_5)_2CH$ - or C₆H₅CH₂-, undergo thermal decomposition in inert solvents in the temperature range 130-200° with essentially quantitative evolution of sulfur dioxide and the formation of varying amounts of $RSCH_2C_6H_5$, RH, stilbene, R-R and dibenzyl disulfide. Investigation of the kinetics of the decomposition has shown that for both thiolsulfonates the reaction is a simple first-order process whose rate is notably dependent on solvent, being faster in relatively polar solvents (nitrobenzene,

benzonitrile) than in non-polar solvents (bromobenzene, methylnaphthalene, etc.). Under comparable conditions the benzhydryl compound decomposes about 150 times more rapidly than the α -toluenethiolsulfonate. These facts, together with the failure of added diphenylmethanethiolsulfonate to accelerate the polymerization of styrene in bromobenzene, led to the proposal of a mechanism for the thiolsulfonate decomposition (eq. 1) involving a rate-determining heterolytic fission of the C-SO₂ bond followed by recombination of the fragments with loss of sulfur dioxide in either of two ways. The minor products of the decomposition, tetraphenylethane and the disulfide, were believed to result from either subsequent

⁽¹⁾ To whom inquiries should be addressed: Department of Chemistry, Oregon State College, Corvallis, Ore.
(2) J. L. Kice, F. M. Parham and R. M. Simons, THIS JOURNAL, 82,

^{834 (1960).}