With catalyzed reactions average yields of 80% were attained in 6 to 8 hours, while control reactions required 30 hours to reach similar yields.

Ethyl cyclopentanol-1,2-diacetate[4] and ethyl cyclohexanol-1-acetate[5] have been dehydrated by thionyl chloride in pyridine. In these cases the hydrogen chloride was stoichiometrically abstracted by the pyridine.

With seven of the twelve additives, small amounts (3–10%) of the isomerized product, 1,1,3-trichloro-2-methyl-1-propene, were also isolated. The five which gave no isomer were aniline, *t*-butylamine, di-*n*-butylamine, N,N-dimethylaniline and triethylamine. On the other hand, use of tetramethylammonium iodide (0.013 equiv.) as the additive yielded only the allylic isomer (88%). The iodide ion underwent exchange with the chlorine in thionyl chloride, free molecular iodine being observed. This trace of iodine apparently catalyzed the isomerization.

Gerrard[6] also reported that equimolecular quantities of pyridine with various typical alcohols and thionyl chloride react, depending upon the conditions, to form sulfites, the chlorosulfinic ester and alkyl chlorides.

The chlorosulfinic ester of 1,1,1-trichloro-2-methyl-2-propanol is produced quantitatively in one hour when purified thionyl chloride in carbon tetrachloride is allowed to react with the anhydrous alcohol in the presence of a small amount of pyridine. The uncatalyzed reaction gave a lower yield of crude product in eight hours.

Acknowledgment.—We gratefully acknowledge a grant from The Dow Chemical Co. which supported this research. We appreciate the interpretations of infrared spectral analyses by Dr. Alvin W. Baker of The Dow Chemical Co. Spectroscopy Laboratory.

Experimental[7]

General Procedure.—One mole of the 1,1,1-trichloro-2-methyl-2-propanol was mixed with 4 moles of thionyl chloride. On warming, hydrogen chloride was evolved. The catalyst (0.0124 mole) was added, and the mixture held at reflux (79°) until evolution of hydrogen chloride substantially ceased.

Each reaction mixture was fractionated through a glass helices packed column with total reflux, variable take-off head. 3,3,3-Trichloro-2-methyl-1-propene (TMP) was collected at b.p. 130–137°, the allylic propenyl chloride at b.p. 152–158°. The intermediate fraction (between the recovered thionyl chloride and the first propene fraction) contained small amounts of TMP (never above 12%). This TMP was isolated by treating the intermediate fraction with crushed ice. The organic layer was separated, washed with water and dried over potassium carbonate. Distillation gave TMP, b.p. 130–137°, $n^{20}\mathrm{D}$ 1.4790–1.4793. TMP that is pure according to infrared analysis[8] has $n^{20}\mathrm{D}$ 1.4793–1.4795. These values agree well with those of De La Mare and Vernon[9] who reported $n^{20}\mathrm{D}$ 1.4785.

Summary of Results.—Numbers in % specify the yields of TMP isolated for each of the amines or amine salts: aniline (0.06 equiv.), 79%; *t*-butylamine (0.007), 79%; *t*-octylamine (0.007), 74%; di-*n*-butylamine (0.04), 78%; piperidine (0.01), 79%; diphenylamine (0.035), 76%; N,N-dimethylaniline (0.055), 83%; triethylamine (0.05), 83%; quinoline (0.0085), 93%; pyridine (0.012), 83%; tetramethylammonium chloride (0.02), 82%; aniline hydrochloride (0.025) added as such, 78%.

Ammonia was ineffective as an additive and formed ammonium chloride, which precipitated, unlike the amine hydrochlorides.

Controls (no additive) required 30 hours reaction time to yield 81% TMP which still contained a little (5–15%) of the starting trichloromethylpropanol.[8]

Chlorosulfinic Ester of 1,1,1-Trichloro-2-methyl-2-propanol.—Purified thionyl chloride (145 ml., 2.0 mole) dissolved in 500 ml. of absolute carbon tetrachloride along with 177.5 g. (1 mole) of the anhydrous propanol and 5 ml. (0.06 mole) of pyridine was heated. At 45° hydrogen chloride came off rapidly. The temperature was slowly raised to 78° (45 minutes) when evolution of HCl slowed up markedly. One mole of HCl had come off (titration of the water absorber). The reaction mixture was cooled, and a liquefied pyridine hydrochloride which floated on the surface was removed. The remaining clear liquid was evacuated; the residue solidified as white needles of the chlorosulfinic ester, 260 g. (100%), m.p. 56.5–57.5° (sealed tube).

The chlorosulfinic ester hydrolyzes rapidly in the moisture of air to give off HCl and was found unsuitable for handling in the usual quantitative ultimate analyses. However, with extreme care, it was found possible to make a stoichiometric titration as follows. A 200-mg. sample of the dry white needles of chlorosulfinic ester was treated with 10 ml. of absolute ethyl alcohol under anhydrous conditions. The reacted sample was titrated rapidly with standard sodium hydroxide and gave neut. equiv. 257 (calcd. 260).

To simulate conditions in which the chlorosulfinic ester was formed *in situ* from the trichloromethylpropanol and excess thionyl chloride and decomposed to TMP in the presence of a trace of amine hydrochloride, the isolated chlorosulfinic ester (m.p. 56.5–57.5°) (0.49 mole) was dissolved in 108 ml. (1.5 moles) of thionyl chloride. Then, 0.03 mole equivalent of pyridine was added. The mixture was heated at 79° and required 7 hours to obtain 78% conversion to pure TMP.

Heating of the chlorosulfinic ester (65 g., 0.25 mole) alone at 79° required 23 hours to arrive at the point of very little gas evolution and a 79% yield of pure TMP.

Comparative Times Taken for Formation of the Chlorosulfinic Ester.—The purpose here was to evaluate the time necessary for conversion to the ester when pyridine hydrochloride was present and when it was not. One mole (177.5 g.) of the pure anhydrous trichloromethylpropanol, 146 ml. (2 moles) of thionyl chloride and 500 ml. of absolute carbon tetrachloride were dissolved together and the solution divided equally. To one portion was added 2.5 ml. (0.03 mole equivalent) of pyridine. The other portion was tested without any additive as a control. Both solutions were heated at 79°. When pyridine hydrochloride was present, one hour was required to complete the reaction (*i.e.*, liberation of 0.5 mole of HCl); eight hours was required by the uncatalyzed reaction. The catalyzed reaction gave 122 g. (95%) of the pure chlorosulfinic ester, m.p. 56–57°. The control gave a 73% yield of crude ester, quite impure, as it contained both TMP and unreacted 1,1,1-trichloro-2-methylpropanol which could not be satisfactorily removed from the crystals of the ester.

ORGANIC LABORATORY
DEPARTMENT OF CHEMISTRY
KANSAS STATE COLLEGE, MANHATTAN, KANSAS

---

[4] R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 942 (1934).

[5] J. W. Cook and C. A. Lawrence, *ibid.*, 1637 (1935).

[6] W. Gerrard, *ibid.*, 99 (1939).

[7] All b.p.'s and m.p.'s are uncorrected.

[8] All infrared analyses by Dr. Alvin W. Baker.

[9] P. B. D. De La Mare and C. A. Vernon, *J. Chem. Soc.*, 3629 (1952).

Preparation and Oxidation of Certain Aryl Benzhydryl Sulfides

BY D. C. GREGG, F. VARTULI AND J. W. WISNER, JR.

RECEIVED JULY 18, 1955

The comparative ease of cleavage of the benzhydryl and trityl phenyl sulfides has been investigated by Tarbell and Harnish.[1] Knoll[2] reported

---

[1] D. S. Tarbell and D. P. Harnish, THIS JOURNAL, **74**, 1862 (1952).

[2] R. Knoll, *J. prakt. Chem.*, **113**, 40 (1926).

the oxidation of benzhydryl phenyl sulfide (I) to the sulfoxide and to the sulfone. During the present work further studies were made on I, and the three isomeric benzhydryl tolyl sulfides were prepared, characterized and oxidized by using four different methods.

The benzhydryl tolyl sulfides were characterized by oxidation to their sulfoxides by using the method reported by Knoll.[2] The *m*-tolyl and *p*-tolyl sulfones were prepared by oxidation of the appropriate sulfides with hydrogen peroxide in acetic acid at 80°. When benzhydryl *o*-tolyl sulfide (II) was oxidized in this manner only a small quantity of the sulfone was obtained, but phenol and benzaldehyde were identified. Apparently the latter substances were produced by the oxidation either of free or incipient benzhydryl cation. The fate of II during this oxidation was similar to that of the aryl trityl sulfides under comparable conditions.[3] A good yield of the sulfone of II was obtained by using a reaction temperature of 35–40°.

The aryl benzhydryl sulfides were rapidly and quantitatively titrated by using the method of Siggia and Edsberg[4] and during these titrations three moles of bromine was consumed per mole of sulfide. In these titrations the source of bromine was an aqueous solution containing bromate and bromide ions. In each oxidation the major products were benzhydrol and the appropriate arylsulfonyl bromide (isolated as the sulfonamide).

Partial oxidations of the sulfides were run at 60° using 0.5 mole of bromine per mole of sulfide. When 0.5 mole of elemental bromine was added per mole of I, each in glacial acetic acid, a good yield of diphenyl disulfide (III) was obtained, and no unreacted I was isolated. However, in the presence of water this oxidation yielded less III and an appreciable amount of unreacted I. When an aqueous solution containing bromate and bromide ions was used as the source of the same quantity of bromine a comparable amount of I was isolated from the product mixture. At 60° the disulfide III appears to be the major, initial product of the oxidation of I with bromine.

Compound I was treated with equimolar amounts of bromine in aqueous acetic acid at 0°, and small amounts of III and the sulfoxide of I were isolated from the rather complex reaction mixture. Significant amounts of III were obtained at 60° using equimolar amounts of bromine and I, but unreacted I and the sulfoxide were not found. However, when sulfuric acid was used instead of hydrochloric acid during the oxidations in which bromate and bromide ions were used, a small amount of the sulfoxide of I was isolated. Apparently under certain conditions the sulfoxide is one of the initial oxidation products. This seems especially true at low temperatures, probably because I is less readily cleaved at 0° than at 60°.[1]

Apparently the sulfoxide of I is at least partially decomposed at 60–70° in solutions having the composition 90% acetic acid, 7% water and 3% hydrogen chloride, because significant yields (20%) of the disulfide III were isolated. Therefore during certain incomplete oxidations with bromine at least some III may arise as a decomposition product of the sulfoxide.

Compound I and benzhydryl *p*-tolyl sulfide (IV) were oxidized by permanganate in acetic acid. The major product of each oxidation appeared to be the sulfone. Under these conditions the analogous trityl sulfides were not oxidized to sulfones.[5]

Compound IV was refluxed for 4 hours in 4 *N* aqueous nitric acid. The major products of this oxidation were benzophenone and *p*-toluenesulfonic acid, isolated as its sodium salt.

Compound I was oxidized with iron(III) chloride in acetic acid at 80°. The product mixture was quite complex, but significant yields of III and benzophenone were obtained.

Apparently extensive cleavage occurs during the oxidations of the benzhydryl sulfides with nitric acid and iron(III) chloride. The aryl trityl sulfides behave in a similar manner.[5]

Compounds I, II and IV were refluxed with aqueous ethanolic mercury(II) chloride, and appreciable cleavage was observed in each case. These sulfides cleave much less readily than the trityl sulfides in the presence of mercury(II) chloride.[6]

Acknowledgment.—This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation, New York, N. Y.

Experimental

Preparation of the Sulfides.—The two methods used for the preparation of the sulfides were slight modifications of procedures reported previously.[6,7] Yields of the sulfides were in the range 70–85%. The melting points and elemental analyses of the sulfides are noted in Table I.

TABLE I

MELTING POINTS AND ANALYSES[a]

Ar	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
For the benzyhydryl tolyl sulfides							
o-Tolyl	44.5–45.5	82.71	83.11	6.25	6.35	11.04	10.43
m-Tolyl	60–61	82.71	82.95	6.25	6.39	11.04	10.45
p-Tolyl	66–67	82.71	82.85	6.25	6.38	11.04	10.53
For the aryl benzhydryl sulfoxides							
Phenyl[b]	134–136	78.03	77.81	5.515	5.55	10.96	10.71
o-Tolyl	131–132	78.41	78.56	5.92	6.16	10.46	10.25
m-Tolyl	112–113	78.41	78.78	5.92	6.00		
p-Tolyl	143–144	78.41	78.99	5.92	6.12		
For the benzhydryl tolyl sulfones[c]							
o-Tolyl	172–173	74.51	74.76	5.63	5.80	9.94	9.75
m-Tolyl	162–163	74.51	74.78	5.63	5.79		

[a] Melting points were uncorrected, and analyses were by Schwarzkopf Microanalytical Lab. [b] Knoll reported m.p. 139°. The present workers obtained several samples which melted at 130–132°, recrystallized from methanol, ethanol and 60% aqueous acetic acid. A specific analysis of such a sample was: C, 78.08; H, 5.51; S, 10.70. [c] The phenyl and *p*-tolyl sulfones were prepared, and each m.p. agreed with the literature.

Preparation of the Sulfoxides and Sulfones.—These preparations are noted in Table II, and melting points and analyses are given in Table I.

Oxidations of the Sulfides.—Various oxidations of the sulfides are noted in Table II. The procedures used during

---

(3) D. C. Gregg, C. A. Blood, Jr., and D. E. Weiman, THIS JOURNAL, **75**, 4344 (1953).

(4) S. Siggia and R. Edsberg, *Anal. Chem.*, **20**, 938 (1948).

(5) D. C. Gregg, K. Hazelton and T. F. McKeon, Jr., *J. Org. Chem.*, **18**, 36 (1953).

(6) D. C. Gregg, H. A. Iddles and P. W. Stearns, Jr., *ibid.*, **16**, 246 (1951).

(7) C. Finzi and V. Bellavita, *Gazz. chim. ital.*, **62**, 699 (1932).

TABLE II

OXIDATIONS OF ARYL BENZHYDRYL SULFIDES

Ar	Ref.	Oxidizing agent	Reaction conditions Solvent[a]	Temp., °C.	Time, min.	Product(s), yield, %
o-Tolyl[b]	2	Chromic acid	A	70	15	Sulfoxide, 85
m-Tolyl[c]		Hydrogen peroxide	A	80–100	60	Sulfone, 80
o-Tolyl		Hydrogen peroxide	A	80–100	60	Sulfone, 5; phenol, 10; benzaldehyde, 15
o-Tolyl	2	Hydrogen peroxide	A	35–40	24 hr.	Sulfone, 80
Phenyl[d]	4	Bromine from bromate–bromide	A	60–70	Rapid titr.	Benzhydrol, 50; benzenesulfonamide, 56
Phenyl	8	Bromine[e]	B	60	2	Diphenyl disulfide, 75
Phenyl	8	Bromine[f]	B	60	2	Diphenyl disulfide, 55
Phenyl	8	Bromine from bromate–bromide[f]	A	60	2	Diphenyl disulfide, 70
Phenyl	8	Bromine from bromate–bromide[f]	B[g]	0	20	Diphenyl disulfide, 10; sulfoxide, 12
Phenyl	5	Permanganate	B	80	60	Sulfone, 65
p-Tolyl	5	Nitric acid	H_2O	100	240	Benzophenone, 85; *p*-toluenesulfonic acid, 45[h]
Phenyl	5	Iron(III) chloride	B	80	20	Benzophenone, 30; diphenyl disulfide, 35

[a] Solvent A was aqueous acetic acid and solvent B was glacial acetic acid. [b] Oxidation of the *m*-tolyl and *p*-tolyl sulfides yielded comparable amounts of the appropriate sulfoxides. [c] Oxidation of the *p*-tolyl sulfide gave the sulfone. [d] Oxidation of the tolyl sulfides produced good yields of benzhydrol and the arylsulfonyl bromides, as sulfonamides. [e] One-half mole of bromine per mole of sulfide. [f] Equimolar amounts of bromine and sulfide. [g] Solvent also contained isopropyl ether and concd. hydrochloric acid. [h] As sodium salt.

the partial oxidation of compound I were comparable to a method reported previously.[8]

Cleavage with Mercury(II) Chloride.—Compounds I, II and IV were refluxed with a twofold molar excess of mercury(II) chloride in 90% aqueous ethanol. In order to obtain apparent maximum cleavage the time of heating was two hours. In a typical run using II a 45% yield of *o*-tolylmercaptomercuric chloride was obtained. Comparable yields of the corresponding arylmercaptomercuric chlorides were obtained during the cleavage of I and IV.

---

(8) D. C. Gregg and C. A. Blood, Jr., *J. Org. Chem.*, **16**, 1255 (1951).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF VERMONT
BURLINGTON, VERMONT

Reactions of Amines with Esters of Polyhalogenated Acids

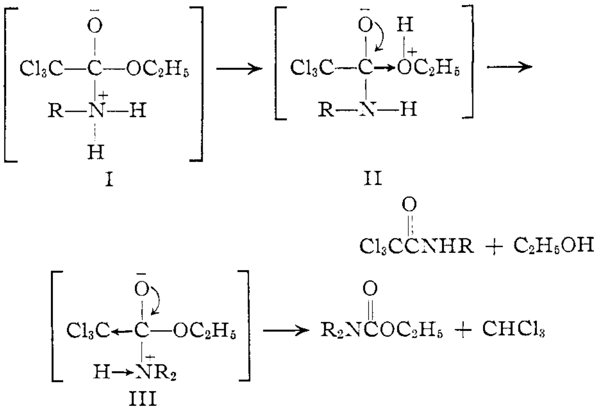
BY MADELEINE M. JOULLIÉ

RECEIVED MAY 26, 1955

An earlier investigation[1] showed that esters of trichloroacetic acid react in distinctly different ways with primary and secondary amines. The former give only amides and the latter form only urethans. It was believed at that time, because of the similarities of physical properties of the products obtained, that ethyl trifluoroacetate behaved similarly. Subsequent work on the esters of perfluoroacids shows the assumption concerning ethyl trifluoroacetate to be incorrect.

It is now shown that ethyl trifluoroacetate, ethyl perfluoropropionate, ethyl perfluoro-*n*-butyrate, ethyl difluoroacetate, ethyl chlorodifluoroacetate and ethyl dichloroacetate behave the same toward both primary and secondary amines, yielding the corresponding amides. This is in sharp contrast to the behavior of ethyl trichloroacetate. Changing the alkyl group of the ester from ethyl to *t*-butyl or trifluoroethyl did not affect the course of the reaction and amides only were formed when these esters were treated with primary and secondary amines. The infrared spectra of the esters of trifluoroacetic acid and trichloroacetic acid showed no unusual differences which could be used to explain the differences in behavior toward secondary amines.

The fact that ethyl dichloroacetate formed only amides with secondary amines, in contrast to ethyl trichloroacetate which formed urethans only, may be explained by the fact that the trichloromethyl group is more electron attracting than is the dichloromethyl group. The trichloromethyl group would therefore have a greater tendency to form a carbanion. That another effect is operating also is evidenced by the fact that ethyl trichloroacetate reacts differently with primary and secondary amines, giving amides with the first and urethans with the second. It was postulated in a previous paper[1] that this difference in behavior might be due to the relative acidities (tendency for proton transfer) of the N–H bonds in the intermediate complexes. This may be shown as



The greater acidity of the N–H bond in I could account for the oxonium intermediate pictured in II and the latter would explain the cleavage of the ethoxy-carbon bond in preference to the trichloromethyl-carbon bond. In III, however, proton transfer may be inhibited, preventing oxonium ion formation, and in this case the trichloromethyl group cleaves in preference to the less electron-attracting, unmodified ethoxy group.

Similar reasoning may be used to explain why the

---

(1) M. M. Joullié and A. R. Day, THIS JOURNAL, **76**, 2990 (1954).