

TABLE II
 OXIDATIONS OF ARYL BENZHYDRYL SULFIDES

| Ar | Ref. | Oxidizing agent | Reaction conditions | | | Product(s), yield, % |
|------------------------------|------|---|----------------------|------------|-------------|---|
| | | | Solvent ^a | Temp., °C. | Time, min. | |
| <i>o</i> -Tolyl ^b | 2 | Chromic acid | A | 70 | 15 | Sulfoxide, 85 |
| <i>m</i> -Tolyl ^c | | Hydrogen peroxide | A | 80-100 | 60 | Sulfone, 80 |
| <i>o</i> -Tolyl | | Hydrogen peroxide | A | 80-100 | 60 | Sulfone, 5; phenol, 10; benzaldehyde, 15 |
| <i>o</i> -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 |
| <i>p</i> -Tolyl | 5 | Nitric acid | H ₂ O | 100 | 240 | Benzophenone, 85; <i>p</i> -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

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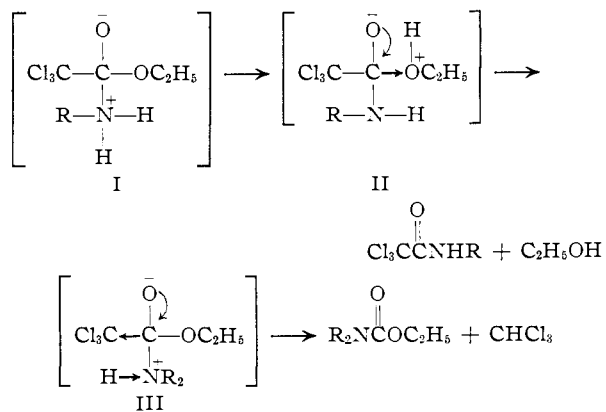
An earlier investigation¹ showed that esters of trichloroacetic acid react in distinctly different ways with primary and secondary amines. The former give only amides and the latter form only urethans. It was believed at that time, because of the similarities of physical properties of the products obtained, 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

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

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 paper¹ 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

TABLE I

| | M.p. or b.p. (mm.), °C. | Yield, % | n_D^{25} | Carbon, % | | Hydrogen, % | | Nitrogen, % | | Infrared absorption bands in μ^c , d | |
|---|-------------------------|----------|------------|-----------|-------|-------------|-------|-------------|-------|--|------|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found | | |
| N-Substituted trifluoroacetamides | | | | | | | | | | | |
| $\text{CF}_3\text{CON}(\text{C}_2\text{H}_5)_2^a$ | 30(2) | 60 | 1.3780 | 42.60 | 42.48 | 5.96 | 6.03 | 8.27 | 8.48 | .. | .. |
| $\text{CF}_3\text{CON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{CH}_2$ | 44(1) | 84 | 1.4153 | 46.41 | 46.46 | 5.56 | 5.66 | 7.73 | 7.74 | 5.90 | .. |
| $\text{CF}_3\text{CON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{O}$ | 47(1) | 87 | 1.4177 | 39.38 | 39.35 | 4.56 | 4.40 | 7.46 | 7.64 | .. | .. |
| N-Substituted perfluoropropionamides | | | | | | | | | | | |
| $\text{CF}_3\text{CF}_2\text{CONHC}_4\text{H}_9$ | 48(1) | 80 | 1.3642 | 38.39 | 38.37 | 4.60 | 4.67 | 6.38 | 6.52 | .. | .. |
| $\text{CF}_3\text{CF}_2\text{CON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{O}$ | 59(1) 46-47 | 85 | | 36.06 | 35.99 | 3.45 | 3.58 | 6.00 | 6.16 | .. | .. |
| N-Substituted perfluorobutyramides | | | | | | | | | | | |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{CONHC}_4\text{H}_9$ | 56(2) | 80 | 1.3568 | 35.70 | 35.88 | 3.74 | 3.84 | .. | .. | 5.85 | 6.40 |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{CON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{CH}_2$ | 57(2) | 85 | 1.3846 | 38.45 | 38.39 | 3.58 | 3.58 | 4.98 | 4.99 | 5.95 | .. |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{CON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array}$ | 65(2) | 76 | 1.3755 | 35.97 | 35.92 | 3.01 | 3.19 | 5.24 | 5.31 | 5.95 | .. |
| $\text{CF}_3\text{CF}_2\text{CF}_2\text{CON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{O}$ | 72(2) | 89 | 1.3850 | 33.94 | 33.85 | 2.84 | 2.94 | 4.94 | 4.95 | 5.95 | .. |
| N-Substituted difluoroacetamide | | | | | | | | | | | |
| $\text{CF}_2\text{HCON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{CH}_2$ | 66(3) | 85 | 1.4500 | 51.55 | 51.36 | 6.79 | 6.92 | 8.58 | 8.35 | .. | .. |
| N-Substituted chlorodifluoroacetamide | | | | | | | | | | | |
| $\text{CF}_2\text{ClCON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array} \text{CH}_2$ | 98(10) | 90 | 1.4520 | 42.55 | 42.55 | 5.10 | 4.92 | 7.09 | 7.12 | .. | .. |
| N-Substituted dichloroacetamide ^b | | | | | | | | | | | |
| $\text{CCl}_2\text{HCON} \begin{array}{l} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{array}$ | 120(2) | 75 | 1.5182 | 39.59 | 39.54 | 4.98 | 5.06 | 7.69 | 7.85 | .. | .. |

^a N,N-Diethyltrifluoroacetamide has been prepared recently by a different method; J. H. Robson and T. Reinhart, *THIS JOURNAL*, **77**, 498 (1955). ^b Calcd.: Cl, 38.95. Found: Cl, 38.84. ^c Infrared data are included only for those amides not previously reported. ^d *t*-Butyl trifluoroacetate and β -trifluoroethyl trifluoroacetate absorbed at 5.65 μ and 5.55 μ respectively.

esters of trifluoroacetic acid form amides with both primary and secondary amines. In this case it is assumed that the strongly electron-attracting trifluoromethyl group increases the ease of proton transfer so that the reactions proceed by way of the oxonium intermediate with both primary and secondary amines.²

Infrared data for compounds used in this investigation which have not been reported previously and the physical data and analyses for all of the new compounds are included in Table I.

Acknowledgment.—The author wishes to thank Dr. Allan R. Day for his interest and support in this study.

Experimental

The esters used in this work, with the exception of *t*-butyl trifluoroacetate, were either purchased or prepared by known methods.

Preparation of *t*-Butyl Trifluoroacetate.—Isobutylene was passed into trifluoroacetic acid (37 g., 0.33 mole) at 50° for one hour. The solution was allowed to stand overnight. More isobutylene was then passed into the solution until no more evolution of heat was noticed. The mixture was

fractionally distilled *in vacuo*; yield 75%, b.p. 30° at 60 mm. and 83° at 760 mm., n_D^{25} 1.3300.

Anal. Calcd. for $\text{C}_6\text{H}_9\text{O}_2\text{F}_3$: C, 42.36; H, 5.33. Found: C, 42.39; H, 5.48.

Preparation of Amides.—In general, the appropriate amine was added gradually to the cooled ester. The reactions were highly exothermic. After standing overnight, the mixtures were fractionally distilled *in vacuo*. In the case of the reactions of *t*-butyl trifluoroacetate with amines, the reaction mixtures were allowed to stand for four days before fractionating.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA 4, PENNA.

Isolation and Characterization Studies on Muscarine

BY FREDERICK A. KUEHL, JR., NORMAN LEBEL AND JOHN W. RICHTER

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As a result of the work of Kogl, Duisberg and Erxleben,¹ muscarine has been considered to be represented by either structure I or II. These structures were advanced on the basis of analyses

(1) F. Kogl, H. Duisberg and H. Erxleben, *Ann.*, **489**, 156 (1931).

(2) The study is being extended to esters having other electron-attracting groups in place of the trihalomethyl group in order to obtain more conclusive evidence for the mechanism involved.