Extreme caution must be exercised in distilling N-chlorocyclohexylimine.

The infrared spectrum of a film of N-chlorocyclohexylimine has absorption bands (μ) and relative intensities (absorbancies) as follows: 3.44 (vs), 5.78 (w), 6.20 (m), 6.91 (vs), 7.00 (s), 7.45 (m), 7.65 (m), 8.03 (m), 8.30 (m), 8.89 (m), 9.13 (w), 9.25 (w), 9.86 (w), 10.19 (s), 10.95 (w), 11.10 (w), 11.69 (m), 11.90 (w), 13.10 (m), and ~14.9 μ (s) cut-off of spectrum. Shoulders are not reported.

Oxidation of *n*-Butylamine to Butyronitrile.—The procedure of Jackson, Smart, and Wright[15] was used to synthesize N,N-dichlorobutylamine in greater than 90% yield. The dichloroamine was dehydrochlorinated and worked up in a manner similar to the procedure described for N-chlorocyclohexylimine. Butyronitrile was obtained in greater than 90% yield and identified by its infrared spectrum and by its identical gas chromatographic retention time with that of authentic butyronitrile.

Registry No.—N,N-Difluorocyclohexylamine, 14182-78-6; N-fluorocyclohexylimine, 15645-66-6; N,N,N′,N′-tetrafluorohexamethylenediamine, 15645-67-7; N,N-difluoro-*n*-butylamine, 10524-16-0; N,N-difluoro-*t*-butylamine, 646-55-9; N,N-difluorocyclopentylamine, 14182-80-0; N-chlorocyclohexylimine, 6681-70-5.

The Trichloromethylation Reaction. III. Reaction with Benzoic Anhydride and Participation by the Solvent 1,2-Dimethoxyethane[1]

ANTHONY WINSTON, RONALD E. THOMAS, AND DALE E. BATTIN

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

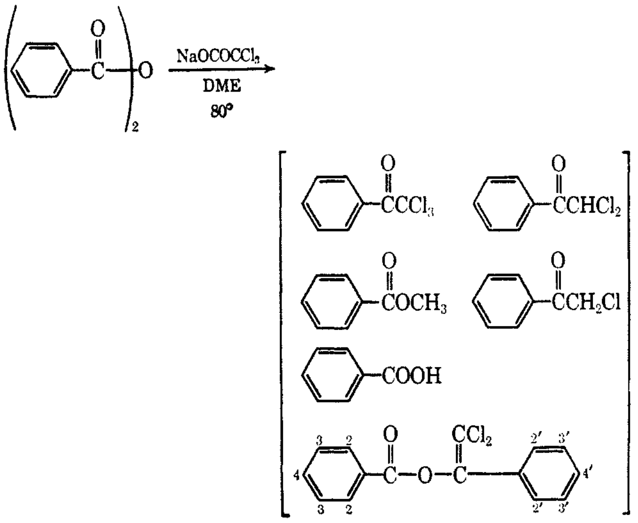
Received October 9, 1967

Reaction of sodium trichloroacetate with benzoic anhydride in dimethoxyethane (DME) solution yields $C_6H_5COOC(=CCl_2)C_6H_5$ (**1**, 79%), benzoic acid, some methyl benzoate, and minor amounts of α,α,α-trichloro-, α,α-dichloro-, and α-chloroacetophenone. A similar reaction with p,p'-dichlorobenzoic anhydride gives the corresponding p,p'-dichloro analog (**2**) of **1**, methyl p-chlorobenzoate, and the p-chloro analogs of the other minor components. The reaction of sodium trichloroacetate with α,α,α-trichloroacetophenone and p,p'-dichlorobenzoic anhydride in DME produces $p\text{-}ClC_6H_4COOC(=CCl_2)C_6H_5$ (**3**). The proposed mechanism for the formation of **1**, **2**, and **3** involves the abstraction of chlorine from α,α,α-trichloroacetophenone, initially produced by a normal trichloromethylation reaction, followed by a condensation of the enolate anion with the parent anhydride. The methyl benzoate originates from the DME solvent. Reaction of sodium trichloroacetate, α,α,α-trichloroacetophenone, and DME also gives methyl benzoate. Reaction of DME with various bases produces formaldehyde and ethylene. These results are accounted for by a mechanism involving the abstraction of a proton from the methyl group of DME and a resulting decomposition of the DME. The methoxide ion produced in the decomposition then attacks the trichloroacetophenone to give methyl benzoate.

Sodium trichloroacetate has been shown to be a useful reagent for the trichloromethylation of anhydrides.[2,3] The success of this reaction is greatly dependent upon the nature of the anhydride and the reactivity of the resulting product. High yields (70–90%) of trichloromethylation products are obtained in several instances, but in others the yields are moderate to very low. One factor which definitely affects the yield is the ease by which the primary trichloromethylation product reacts with sodium trichloroacetate to provide additional reaction products. In the case of succinic anhydride, the initially formed 5,5,5-trichlorolevulinic acid reacts further with the trichloromethyl anion to give dichloroprotoanemonin, apparently by α-proton abstraction followed by cyclization and elimination of hydrogen chloride.[4] The reaction of sodium trichloroacetate with benzoic anhydride, which was previously reported to give a 13% yield of α,α,α-trichloroacetophenone,[2] has now been found to be another case in which further reactions of the product occur. In this paper a detailed account of this reaction will be presented along with studies which have provided reasonable mechanisms to account for most of the observed products. An unusual participation by the solvent, dimethoxyethane, is included.

The reaction of sodium trichloroacetate with benzoic anhydride in dimethoxyethane (DME) solution results in a complex mixture of products (Scheme I). After removal of the benzoic acid, the residue was separated by distillation into three fractions. The low boiling fraction was fairly pure methyl benzoate. The second fraction was a mixture of α,α,α-trichloro-, α,α-dichloro-, and α-chloroacetophenone in 1.4, 2.8, and 1.0% yield, respectively, as determined by vpc analysis. The

SCHEME I



1

---

(1) Taken in part from the M. S. Thesis of R. E. Thomas, West Virginia University, Morgantown, W. Va., 1967, and the M. S. Thesis of D. E. Battin, Kanawha Valley Graduate Center of West Virginia University, Morgantown, W. Va., 1965. Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, and at the 42nd Annual Meeting of the West Virginia Academy of Science, Morgantown, West Virginia, April, 1967.

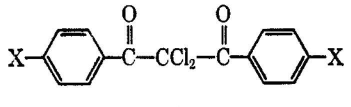
(2) A. Winston, J. P. M. Bederka, W. G. Isner, P. C. Juliano, and J. C. Sharp, *J. Org. Chem.*, **30**, 2784 (1965).

(3) A. Winston, J. C. Sharp, K. E. Atkins, and D. E. Battin, *ibid.*, **32**, 2166 (1967).

(4) A. Winston and J. C. Sharp, *J. Amer. Chem. Soc.*, **88**, 4196 (1966).

high boiling fraction was identified as the dichloromethylene compound **1**, and was the major reaction product, obtained in 79% yield based on 2 moles of anhydride required per mole of compound **1**.

The structural assignment of compound **1** is consistent with the elemental analysis, the carbonyl peak at 1750 cm^{-1} in the infrared spectrum, and the fact that on acidic hydrolysis both benzoic acid and dichloroacetophenone were obtained. The unsymmetrical structure **1**, as opposed to the symmetrical structure A, is supported by the appearance of two aromatic multiplets in the nmr spectrum in the area ratio of 1:4 (Table I).



A, X=H
B, X=Cl

The downfield multiplet is assigned to the two H_2 protons *ortho* to the carbonyl group, while the upfield multiplet includes the eight other protons.

TABLE I

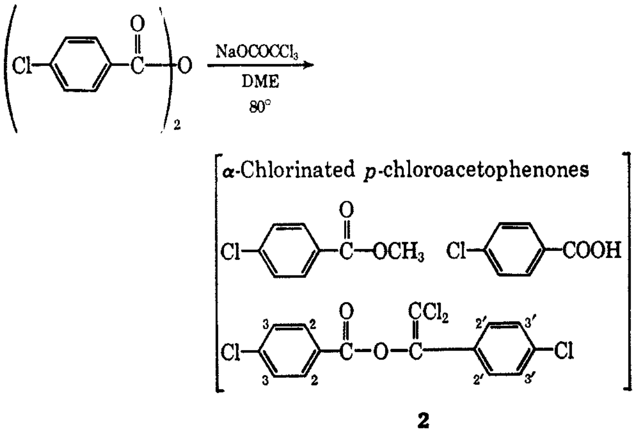
NMR AND INFRARED DATA

	Nmr^a					
Compd	Proton assignment	Chemical shift, τ	Multiplicity	Area ratio	Coupling constants, cps	Infrared,^{b} ν_{C-C}, cm^{-1}
1	H_2	2.0	m	1		1750
	H_3,H_4,H_2' H_3',H_4'	2.6	m	4		
2	H_2	1.99	q^c	1	$J_{2,3} = 8$	1747
	H_3	2.56		3	$J_{2',3'} = 9$	
	H_2'	2.49	q^c			
	H_3'	2.76				
3	H_2	2.03	q^c	2	$J_{2,3} = 8$	1747
	H_3	2.66				
	H_2',H_3',H_4'	2.7	m	7		

^{a} Carbon tetrachloride solution. ^{b} Neat. ^{c} The basic pattern is a quartet. Fine splitting due to AA′, AB′, and BB′ coupling was observed, but was not analyzed in detail.

The *p,p*′-dichloro analog of **1** (compound **2**) was prepared in 30% yield by the reaction of sodium trichloroacetate with *p,p*′-dichlorobenzoic anhydride in DME solution. Methyl *p*-chlorobenzoate, *p*-chlorobenzoic acid, and a small amount of a mixture of α-chlorinated *p*-chloroacetophenones were also obtained (Scheme II).

SCHEME II



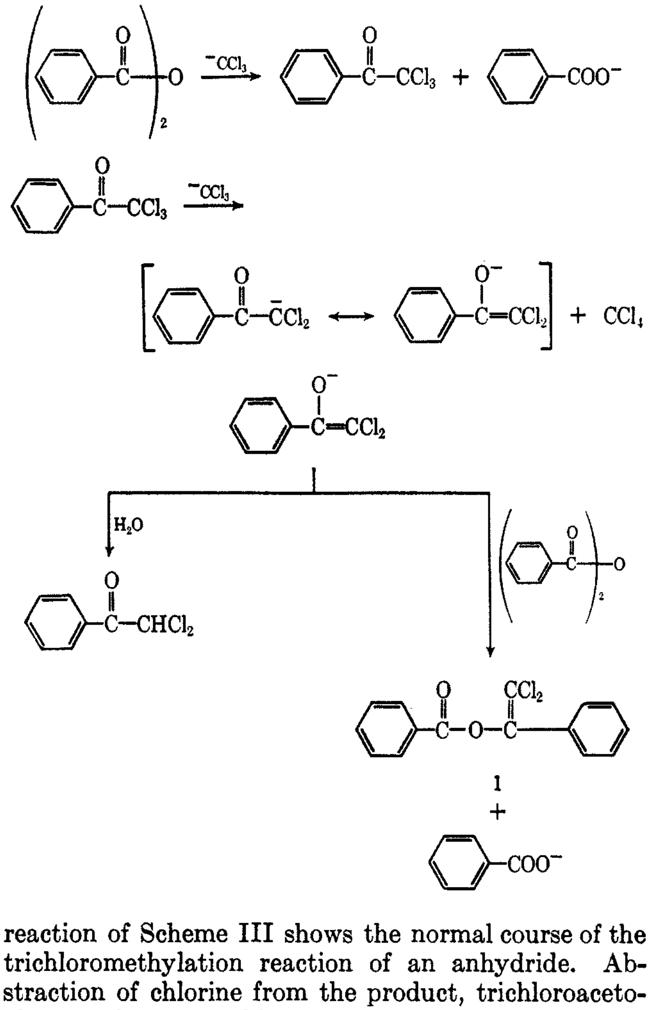
2

The presence of the two primary A_2B_2 quartets in the nmr spectrum of **2**, Table I, clearly reveals the presence of the two nonequivalent *p*-chlorophenyl groups and completely rules out the alternate symmetrical structure B, which would possess only a single quartet. The downfield doublet at τ 1.99 is assigned to the H_2 protons, consistent with the usual downfield shift of aromatic protons *ortho* to a carbonyl substituent.

The study of the mechanism of the reaction of sodium trichloroacetate with benzoic anhydride involved two areas of investigation: (a) reactions leading to the dichloromethylene compounds **1** and **2** and (b) reactions leading to the rather surprising formation of methyl benzoate.

The mechanism shown in Scheme III accounts for the products indicated in Scheme I with the exception of methyl benzoate and α-chloroacetophenone. The first reaction of Scheme III shows the normal course of the trichloromethylation reaction of an anhydride. Abstraction of chlorine from the product, trichloroacetophenone, by the trichloromethyl anion would give rise to the enolate anion, which on condensation with unreacted benzoic anhydride would give **1**, or on addition of water to the reaction mixture would give dichloroacetophenone. Chlorine abstraction is a typical reaction of the trichloromethyl ion and is known to lead to complex condensation products.[5]

SCHEME III



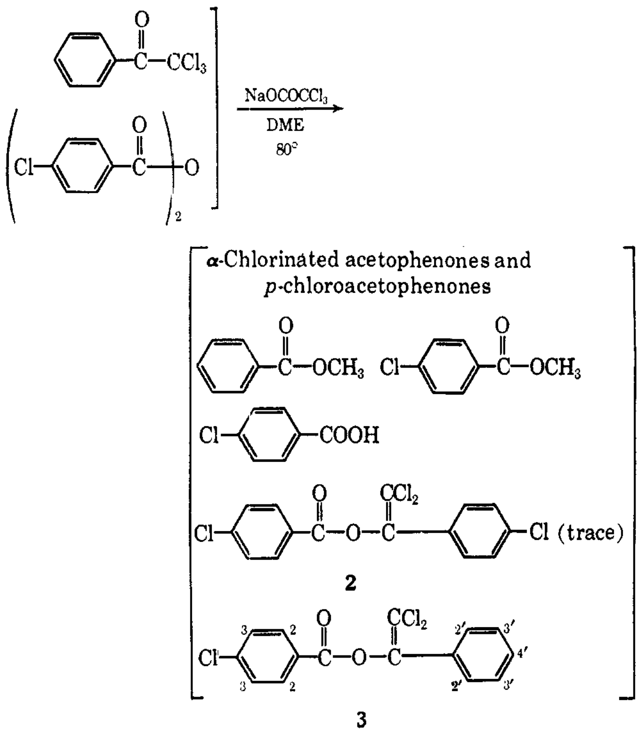
In order to determine if **1** is indeed formed through a reaction involving both trichloroacetophenone and the anhydride, a mixed reaction was carried out between

---

[5] W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 933 (1962).

α,α,α-trichloroacetophenone, *p,p′*-dichlorobenzoic anhydride, and sodium trichloroacetate in DME solution (Scheme IV). Compound **3** was obtained in 25% yield. A trace of **2**, but no **1**, was indicated by vpc. The position of the *p*-chloro substituent was established through the nmr spectrum (Table I), which exhibited the A_2B_2 pattern of a *para*-substituted phenyl ring with the A_2 protons *ortho* to a carbonyl substituent and the B_2 protons *ortho* to the chlorine. Confirmation of the structural assignment was obtained through acid methanolysis of **3**, which produced methyl *p*-chlorobenzoate and α,α-dichloroacetophenone.

SCHEME IV



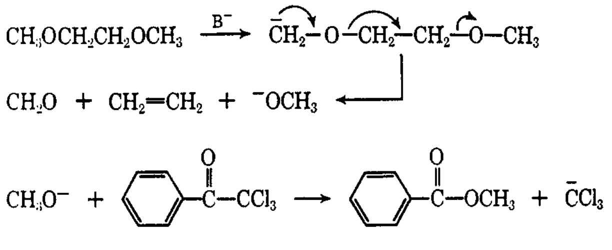
The isolation of **3** as the major product of this reaction is entirely consistent with the mechanism proposed in Scheme III, and confirms the proposal that formation of dichloromethylene compounds **1**, **2**, and **3**, requires the condensation of the trichloroacetophenone with the anhydride. A direct route, as proposed by Villieras and Normant[6] to explain the formation of similar dichloromethylene compounds from the reaction of trichloromethyl magnesium chloride with anhydrides, thus cannot apply to these sodium trichloroacetate reactions. The failure to detect **1** in the reaction shown in Scheme IV and the fact that from a reaction between sodium trichloroacetate and trichloroacetophenone in DME no **1** was obtained indicate that the condensation is not between the enolate anion and trichloroacetophenone. The origin of the α-chloroacetophenone (Scheme I) is still under investigation.

The origin of methyl benzoate produced in the reaction of sodium trichloroacetate with benzoic anhydride in DME must be through solvent participation. Not only is DME the only reasonable source of the methoxide ion, but, when other solvents such as dioxane or tetrahydrofuran were used, no methyl benzoate was observed. The reaction between sodium trichloroacetate, α,α,α-trichloroacetophenone, and DME also produces methyl benzoate, which suggests that the trichloromethyl anion reacts with DME to produce methoxide ion, which then reacts with trichloroacetophenone to form methyl benzoate by displacement of the trichloromethyl group. Other bases may be used to generate the methoxide ion from DME. Reaction of α,α,α-trichloroacetophenone with DME in the presence of either calcium hydride or phenyl(trichloromethyl)mercury provided small amounts of methyl benzoate.

In determining the mechanism by which the base reacts with DME to produce methoxide ion, two paths should be considered. Abstraction of a methyl proton, followed by decomposition of the DME anion, would produce formaldehyde, ethylene, and methoxide ion. On the other hand, abstraction of a methylene proton would lead to methyl vinyl ether and methoxide ion. In order to distinguish between these two possible paths, the volatile products of the reactions were analyzed. The gases evolved in the reaction between sodium trichloroacetate, α,α,α-trichloroacetophenone, and DME were condensed in a Dry Ice cold trap. Infrared analysis of the products collected revealed formaldehyde. Formaldehyde was also evolved on heating DME with sodium trichloroacetate, calcium hydride, or lithium aluminum hydride. The vapors from these reactions were also passed through a solution of bromine in carbon tetrachloride. On vpc analysis of the products isolated from the carbon tetrachloride, 1,2-dibromoethane was found, thus indicating ethylene as one of the products from the decomposition of DME. In the absence of base, refluxing DME still produced a trace of formaldehyde, but no ethylene could be found. Although methyl vinyl ether was sought in the cold trap as was the dibromide from the carbon tetrachloride solution, none was found.

The generation of methoxide ion, ethylene, and formaldehyde from DME by the action of base indicates that the mechanism of the reaction most likely proceeds through an initial abstraction of a proton from the methyl group by the base, followed, or accompanied, by a decomposition to give the observed products. The methoxide ion then attacks the trichloroacetophenone to give methyl benzoate (Scheme V). This decomposition of DME is an example of the "fragmentation reaction" recently reviewed by Grob and Schiess.[7]

SCHEME V



These results clearly reveal that DME is not nearly so inert as is generally thought, but under basic conditions is rather reactive, and this reactivity should be considered when DME is employed as a reaction medium.

Two reasons can now be provided to account for the low yields of trichloromethylation products occurring in

---

[6] J. Villieras and H. Normant, *Compt. Rend.*, **264**, 593 (1967).

[7] C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1 (1967).

certain cases. First, the trichloromethylation product may, through loss of chlorine or an active proton,[4] undergo condensation reactions which consume not only the trichloromethylation product itself, but the parent anhydride as well. Second, additional losses of the trichloromethylation products occur through reaction with methoxide ion from the DME solvent. It is significant that the yield of trichloromethylation product is quite high when the product happens to precipitate from the reaction mixture, and is thereby removed from the site of further reaction. The cyclic anhydrides, generally providing high yields, are of this class and precipitate during the reaction as the sodium salt of the trichloromethyl keto acids.[2,3]

The role of the solvent in determining product ratios is not fully understood. In tetrahydrofuran and dioxane the yields of α,α,α-trichloroacetophenone were markedly improved, increasing to 40 and 57%, respectively, while the yield of condensation product **1** decreased to about 40%. Apparently, in these solvents the relative rates of the various competing reactions do not favor the formation of the condensation product as they do in the case of DME.

The reaction of sodium trichloroacetate with DME suggests that the mechanism of dichlorocarbene insertion reactions may well proceed by way of an initial proton abstraction, followed by the successive addition of dichlorocarbene and a proton, as originally proposed in 1961 by Parham and Koncos.[8] Other proposed mechanisms include ylide intermediates,[8] direct insertion,[9] and hydride ion abstraction.[10] In the case of DME, if proton abstraction by base is rapidly followed by decomposition, dichlorocarbene addition would not be observed. In our work as well as that of Wagner, *et al.*,[5,11] no dichlorocarbene insertion products of DME have been found. In other cases, such as tetrahydrofuran,[10] where α insertion of dichlorocarbene readily occurs, fragmentation of the intermediate anion would not be expected.

Experimental Section

Melting points (determined on a Mel-Temp block) and boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on the Perkin-Elmer 137 and Beckman IR-8 spectrophotometers. The nmr spectra were recorded on the Varian Associates, HA-60, high resolution spectrometer using TMS as the internal standard. Vapor phase chromatography was performed on a Perkin-Elmer 154 vapor fractometer with thermal conductivity detector without correction for molar response. The following columns, constructed from 0.25-in. copper tubing, were used: column A, 20% SE-30 on firebrick (60–80 mesh), 6 ft, 170°, with 30 psi of helium for methyl benzoate, methyl-*p*-chlorobenzoate, and α-chlorinated acetophenones and *p*-chloroacetophenones; column B, 2% SE-30 on Chromosorb W, 2 ft, 182°, with 10 psi of helium for **1**, **2**, and **3**; column C, 15% SF-96 on firebrick (60–80 mesh), 12 ft, 130°, with 21 psi of helium for 1,2-dibromoethane and methyl 1,2-dibromoethyl ether; column D, 5% diisodecylphthalate on Fluoropak 80 (20-80 mesh), 2 ft, 132°, with 13 psi helium for methyl benzoate. Compounds were identified by peak enhancement on admixture of the unknown mixture with authentic samples of the known compounds.

Materials.—Dimethoxyethane (DME) and dioxane were stored over calcium hydride and distilled over calcium hydride before use. Tetrahydrofuran was treated with potassium hydroxide and distilled over calcium hydride. Sodium trichloroacetate was prepared from trichloroacetic acid and sodium hydride in ether, as described in an earlier communication.[3] *p,p'*-Dichlorobenzoic anhydride was prepared by the reaction of the acid chloride with pyridine.[12] Phenyl(trichloromethyl)mercury was prepared by the method of Logan.[13]

Reaction of Sodium Trichloroacetate with Benzoic Anhydride. A. DME Solvent.—A solution of 50 g (0.22 mol) of benzoic anhydride and 135 g (0.727 mol) of sodium trichloroacetate in 300 ml of DME was stirred at 85°. After 10 min a gelatinous solid separated. An additional 100 ml of DME was added and heating was continued for 2 hr. The reaction mixture was diluted with 500 ml of water and the solution was then extracted with ether. The ether solution was washed with two 150-ml portions of sodium bicarbonate solution and two 150-ml portions of water, dried over anhydrous magnesium sulfate, and evaporated to a small volume. Distillation gave 1.0 g (0.0073 mol, 3.3%) of methyl benzoate, bp 35–43° (2 mm), 2.2 g of a second fraction, bp 40–60° (0.3 mm), and 25.6 g (0.0873 mol, 79%) of **1**, a heavy oil, bp 140–165° (0.33 mm). The methyl benzoate was identified by comparison of the infrared spectrum with that of an authentic sample and by vpc. Vpc of the second fraction, using column A, showed that it was a mixture containing α-chloroacetophenone, α,α-dichloroacetophenone, and α,α,α-trichloroacetophenone in a molar ratio of 1.0:2.7:1.3, which is equivalent to 1.0, 2.8, and 1.4% yields, respectively. The third fraction, bp 140–165° (0.3 mm), was redistilled and analyzed.

Anal. Calcd for $C_{15}H_{10}Cl_2O_2$: C, 61.45; H, 3.44; Cl, 24.19. Found: C, 61.14; H, 3.39; Cl, 24.29.

B. Dioxane Solvent.—A mixture of 100 g (0.443 mol) of benzoic anhydride, 120 g (0.65 mol) of sodium trichloroacetate, and 1000 ml of dioxane was stirred at 110° for 5.5 days. The solution was cooled and filtered, and the bulk of the dioxane was removed by evaporation. The residue was dissolved in ether and washed twice with saturated sodium bicarbonate solution and twice with water. The solution was dried over anhydrous magnesium sulfate and evaporated. The residue was fractionally distilled to yield as a first fraction 63.5 g of an oil, bp 98.0–99.5° (3.2 mm). Vpc analysis of the oil, using column A, showed that it was a mixture of α,α,α-trichloroacetophenone and α,α-dichloroacetophenone in a 5.8:1.0 ratio, which is equivalent to a 57 and a 9% yield, respectively. A second fraction, 26 g (0.088 mol, 40%) of **1**, bp 150–164° (0.5 mm), was obtained.

C. Tetrahydrofuran Solvent.—A mixture of 40.0 g (0.18 mol) of benzoic anhydride, 100 g (0.54 mol) of sodium trichloroacetate, and 800 ml of tetrahydrofuran was stirred for 20 hr at 65° and then for 10 hr at room temperature. About 450 ml of tetrahydrofuran was removed by distillation. The residue was dissolved in ether and washed four times with a saturated solution of sodium bicarbonate and once with water. The solution was dried over anhydrous magnesium sulfate and evaporated. The residue was fractionally distilled to yield 4.0 g of 2-(dichloromethyl)tetrahydrofuran,[10] bp 54–56° (3.5 mm), bp 181° (1 atm), 19.4 g of an oil, bp 88° (0.6 mm), and 11.6 g (0.040 mol, 44%) of **1**, bp 165–168° (0.7 mm). Identification of 2-(dichloromethyl)tetrahydrofuran was made by spectral comparison with an authentic sample synthesized according to the method of Anderson.[10] Vpc of the oil, bp 88° (0.6 mm), using column A, showed that it was a mixture of α,α,α-trichloroacetophenone and α,α-dichloroacetophenone in 5:1 molar ratio, which is equivalent to 40 and 8% yields, respectively.

Acid Hydrolysis of Compound 1.—A solution of 1.0 g (0.0034 mol) of **1** in 25 ml of methanol was heated under reflux for 16 hr in the presence of a slow stream of anhydrous hydrogen chloride. The reaction mixture was taken up in ether and washed with dilute hydrochloric acid, 20% sodium hydroxide, and water. Evaporation of the ether gave 0.6 g of an oil, which was shown by its infrared spectrum to contain α,α-dichloroacetophenone. Acidification of the basic washings gave 0.3 g (0.002 mol) of benzoic acid, mp 121–122°.

The α,α-dichloroacetophenone fraction was dissolved in 25 ml of methanol. To the stirred solution was added 2 g of sodium

---

[8] W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961).

[9] E. K. Fields, *ibid.*, **84**, 1744 (1962).

[10] J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 4874 (1964).

[11] W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961); W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *ibid.*, **81**, 925 (1962); W. M. Wagner, private communication.

[12] C. F. H. Allen, C. J. Kibler, D. M. McLachlin, and C. V. Wilson in "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 29.

[13] T. J. Logan, *J. Org. Chem.*, **28**, 1129 (1963).

borohydride over a 5-min period. Stirring was continued for an additional 15 min. The reaction mixture was diluted with 100 ml of water and extracted with ether. Evaporation of the ether gave 0.5 g of an oil, which on crystallization from hexane gave 0.3 g of 2,2-dichloro-1-phenylethanol, mp 53.0–53.5° (lit.[14] mp 54°).

Reaction of Sodium Trichloroacetate with *p,p'*-Dichlorobenzoic Anhydride in DME.—A mixture of 25 g (0.085 mol) of *p,p'*-dichlorobenzoic anhydride in 400 ml of DME was stirred at 85° for 2 hr in order to fully dissolve the anhydride. Sodium trichloroacetate, 60 g, was added and the mixture was stirred at 85° for 5 hr. After 2 and 4 hr, additional 15-g portions of sodium trichloroacetate were added for a total of 90 g (0.49 mol). About 150 ml of DME was removed by distillation. The residue was dissolved in ether and the ether solution was washed with sodium bicarbonate, sodium carbonate, and water and dried over magnesium sulfate. Evaporation of the ether followed by fractional distillation of the residue yielded 0.5 g of methyl *p*-chlorobenzoate, bp 80° (1.1 mm), mp 40–42° (lit.[15] mp 43°), 1.3 g of a second fraction of oil, bp 103–110° (0.5 mm), and 18.4 g of residue. The second fraction of oil was shown by vpc, using column A, to be a mixture of *α,α,α*-trichloro-*p*-chloroacetophenone and *α,α*-dichloro-*p*-chloroacetophenone in a molar ratio of 3.5:1, respectively. On standing for several weeks a brown solid crystallized from the dark residue. The solid was removed by filtration and sublimed to give 3.92 g (0.013 mol, 30%) of **2**. Recrystallization from petroleum ether (bp 65–67°) gave white crystals, mp 79.0–80.5°.

Anal. Calcd for $C_{15}H_8Cl_4O_2$: C, 49.76; H, 2.23; Cl, 39.18. Found: C, 49.56; H, 2.41; Cl, 39.27.

Methyl-*p*-chlorobenzoate was identified by comparison of the infrared and nmr spectra with those of an authentic sample and by vpc, using column A.

Reaction of Sodium Trichloroacetate with *p,p'*-Dichlorobenzoic Anhydride and *α,α,α*-Trichloroacetophenone in DME.—A mixture of 21 g (0.093 mol) of *α,α,α*-trichloroacetophenone, 15 g (0.051 mol) of *p,p'*-dichlorobenzoic anhydride, and 75 g (0.40 mol) of sodium trichloroacetate in 400 ml of dimethoxyethane was stirred at 85° for 2 hr. About 200 ml of DME was removed by distillation. The residue was dissolved in ether and the solution was washed with saturated sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and evaporated. The residue was fractionally distilled to give 8.1 g of a clear oil, bp 60–160° (1.0 mm), and 4.1 g (0.013 mol, 25%) of **3**, a heavy oil, bp 160–178° (0.7 mm). The first fraction was shown by vpc analysis, using column A, to be a mixture of methyl benzoate, methyl-*p*-chlorobenzoate, and various *α*-chlorinated acetophenones and *p*-chloroacetophenones. Acidification of the basic washings yielded 1.6 g (0.010 mol) of *p*-chlorobenzoic acid, mp 232–239° (lit.[16] mp 239–240°). On further purification by distillation, **3** crystallized. The solid was recrystallized twice from petroleum ether (bp 65–67°) to give fine white crystals, mp 49.0–49.5°.

Anal. Calcd for $C_{15}H_9Cl_3O_2$: C, 55.00; H, 2.77; Cl, 32.47. Found: C, 55.18; H, 2.84; Cl, 32.68.

The vpc retention time for **3** was midway between those of **1** and **2**. Vpc analyses of **3** before purification revealed a trace of **2**.

Acid Methanolysis of Compound 3.—A 1.25-g (0.0038 mol) portion of **3** was dissolved in 25 ml of methanol and heated under reflux for 19 hr in the presence of a slow stream of anhydrous hydrogen chloride. The solution was cooled and diluted with ether. The ether solution was washed with dilute hydrochloric acid, water, and sodium hydroxide solution. Acidification of the basic washings yielded 0.05 g of *p*-chlorobenzoic acid, mp 230–240° (lit.[16] mp 239–240°). The ether solution was dried over anhydrous magnesium sulfate and evaporated. Vpc of the residue, using column B, showed that the primary constituents of the mixture were *α,α*-dichloroacetophenone and methyl-*p*-chlorobenzoate.

Reaction of Sodium Trichloroacetate with *α,α,α*-Trichloroacetophenone in DME.—A mixture of 19.0 g (0.085 mol) of *α,α,α*-trichloroacetophenone, prepared by the reaction of sodium trichloroacetate with benzoic anhydride in dioxane, 40.0 g (0.216 mol) of sodium trichloroacetate, and 170 ml of DME was stirred at 85° for 20 min. Water was added and the mixture was extracted with ether. The ether solution was washed with sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and evaporated. The residue was fractionally distilled to yield 0.98 g (0.007 mol, 8.2%) of methyl benzoate, bp 70–73° (2.5 mm), and 7.0 g of a second fraction, bp 83–86° (0.6 mm). Vpc of the second fraction, using column A, revealed a mixture of *α,α*-dichloroacetophenone (31% yield) and *α,α,α*-trichloroacetophenone in a molar ratio of 3:1. Identification of methyl benzoate was based on comparison of its infrared spectrum with that of an authentic sample and by vpc using column A. Vpc, using column B, of the distillation residue revealed no trace of **1**.

In another experiment a mixture of 300 ml of DME and 23.5 g (0.104 mol) of *α,α,α*-trichloroacetophenone was stirred at 80° for 39 hr. Analysis of the reaction products by vpc failed to indicate the presence of any methyl benzoate or *α,α*-dichloroacetophenone. Only starting materials and a small amount of benzoic acid were obtained.

Reaction of Calcium Hydride with *α,α,α*-Trichloroacetophenone and DME.—A mixture of 20 g (0.088 mol) of *α,α,α*-trichloroacetophenone, 20 g (0.48 mol) of calcium hydride, and 450 ml of DME was stirred at 85° for 30 hr. The volatile vapors were swept into a Dry Ice trap. Infrared analysis of the contents of the trap revealed the presence of formaldehyde. The reaction mixture was evaporated and the residue was fractionally distilled to give 1.16 g (0.0085 mol, 9.7%) of methyl benzoate, bp 80–92° (5.0 mm), and 16.0 g (0.071 mol) of *α,α,α*-trichloroacetophenone, bp 83–87° (0.80 mm). The identification of the methyl benzoate fraction was confirmed by vpc using column A and by the infrared spectrum.

Reaction of Phenyl(trichloromethyl)mercury with *α,α,α*-Trichloroacetophenone and DME.—A mixture of 100 g (0.252 mol) of phenyl(trichloromethyl)mercury, 75 g (0.33 mol) of *α,α,α*-trichloroacetophenone, prepared by the reaction of sodium trichloroacetate with benzoic anhydride in dioxane, and 600 ml of dimethoxyethane was stirred at 85° for 3.5 hr. The solution was evaporated to a small volume. The residue was fractionally distilled to give 3.5 g of an oil, bp 40–85° (2.2 mm), and 2.8 g of an oil, bp 86–96° (2.2 mm). The first fraction was shown by vpc, using columns A and D, to be a mixture largely made up of trichloroacetophenone with smaller amounts of methyl benzoate and several unidentified compounds. The second fraction was shown by its infrared spectrum and by vpc, using column A, to be essentially trichloroacetophenone. The residue, 53 g, decomposed on standing and was not analyzed.

Analysis of the Volatile Gases Produced on Heating DME, A. With Sodium Trichloroacetate.—A solution of 25 g of sodium trichloroacetate in 500 ml DME was heated slowly with stirring to 85° over a 3-hr period. The solution was cooled and another 25-g portion of sodium trichloroacetate was added. The mixture was again heated slowly to 85° over a 5-hr period. The evolved vapors were bubbled through a solution of 10% bromine in carbon tetrachloride. Excess bromine was reduced by washing the carbon tetrachloride solution with a saturated solution of sodium sulfite. The carbon tetrachloride fraction was dried over anhydrous magnesium sulfate and evaporated. Vpc of the residue, using column C, showed that 1,2-dibromoethane was present.

In another reaction, the vapors were passed into a Dry Ice trap for 7 hr. The infrared spectrum of the trapped gases revealed the presence of carbon dioxide, DME, and formaldehyde. The spectrum also indicated the absence of methyl vinyl ether.

B. With Calcium Hydride.—A mixture of 1000 ml of DME and 20 g of calcium hydride was heated at 85° for 72 hr. The volatile gases were flushed out of the system with a stream of dry nitrogen. For the first 3 hr the volatile products were collected in a trap cooled in Dry Ice. Infrared analysis of the trapped contents revealed the presence of formaldehyde. During the remainder of the period the vapors were passed through a solution of bromine in carbon tetrachloride. Vpc of the products from the carbon tetrachloride solution revealed the presence of 1,2-dibromoethane.

C. With Lithium Aluminum Hydride.—A mixture of 600 ml of DME and 16 g of lithium aluminum hydride was heated at 85° for 60 hr. The volatile gases were flushed with a stream of dry nitrogen into a solution of 10% bromine in carbon tetrachloride. Vpc of the products from the carbon tetrachloride solution revealed the presence of 1,2-dibromoethane.

D. In the Absence of Added Bases.—Dimethoxyethane (350 ml) was heated under reflux for 53 hr. The volatile products

---

(14) T. Bergkvist, *Svensk Kem. Tidskr.*, **59**, 24 (1947); *Chem. Abstr.*, **41**, 5119 (1947).

(15) W. I. Jones, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, **123**, 2688 (1923).

(16) P. A. S. Smith and B. Ashby, *J. Amer. Chem. Soc.*, **72**, 2503 (1950).

were swept with a stream of dry nitrogen into a trap cooled in Dry Ice. A sample of the volatile products was collected during the first 3 hr and another during the last 3 hr. In each case, the infrared spectrum of the trapped products indicated a trace of formaldehyde. In another reaction, 300 ml of DME was heated under reflux for 2.5 days. The vapors were passed through a 10% solution of bromine in carbon tetrachloride. Vpc of the products from the carbon tetrachloride failed to reveal any 1,2-dibromomethane.

Registry No.—**1**, 15649-35-1; **2**, 15649-36-2; **3**, 15649-37-3; benzoic anhydride, 93-97-0; 1,2-dimethoxyethane, 110-71-4; sodium trichloroacetate, 650-51-1.

Acknowledgment.—The use of the research facilities of Union Carbide Corp., South Charleston, W. Va., by D. E. B. is gratefully appreciated. We thank Mr. Robert R. Smith for recording the nmr spectra.

A Synthesis of Perfluoroalkyl Trifluorovinyl Ketones

B. C. ANDERSON

Contribution No. 1313 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

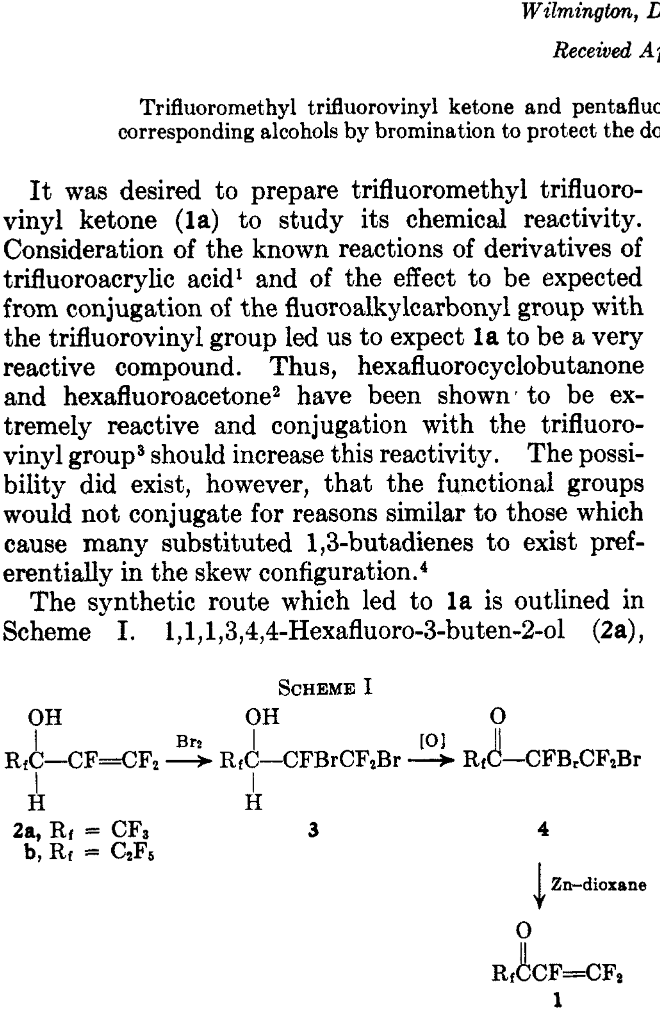
Received April 29, 1967

Trifluoromethyl trifluorovinyl ketone and pentafluoroethyl trifluorovinyl ketone have been prepared from corresponding alcohols by bromination to protect the double bond, oxidation, and debromination.

It was desired to prepare trifluoromethyl trifluorovinyl ketone (**1a**) to study its chemical reactivity. Consideration of the known reactions of derivatives of trifluoroacrylic acid[1] and of the effect to be expected from conjugation of the fluoroalkylcarbonyl group with the trifluorovinyl group led us to expect **1a** to be a very reactive compound. Thus, hexafluorocyclobutanone and hexafluoroacetone[2] have been shown to be extremely reactive and conjugation with the trifluorovinyl group[3] should increase this reactivity. The possibility did exist, however, that the functional groups would not conjugate for reasons similar to those which cause many substituted 1,3-butadienes to exist preferentially in the skew configuration.[4]

The synthetic route which led to **1a** is outlined in Scheme I. 1,1,1,3,4,4-Hexafluoro-3-buten-2-ol (**2a**), prepared by a route similar to that used for other perfluoroalkyl trifluorovinyl carbinols,[5] was brominated to form 3,4-dibromo-1,1,1,3,4,4-hexafluoro-2-butanol (**3a**), obtained as a mixture of diastereomeric forms. The secondary alcohol was oxidized with acid dichromate[6] to form 3,4-dibromo-1,1,1,3,4,4-hexafluoro-2-butanone (**4a**) in good yield. When the dibromo ketone was debrominated with zinc in boiling dioxane[7] under carefully controlled conditions, a mixture of ketone **1a** and solvent distilled which contained only small amounts of other components according to gas chromatographic analysis on several columns. Large scale chromatography was used to separate **1a**, a colorless, volatile liquid boiling near room temperature.

SCHEME I



The unsaturated ketone was very sensitive to nucleophilic attack; it decomposed rapidly in protonic solvents with formation of fluoride ion. Purified samples were stable to storage at room temperature if sealed in ampoules with careful exclusion of moisture.

The observed reactivity of **1a** undoubtedly explains the failure of direct oxidation of **2a** to **1a** with a number of oxidizing agents. Even if **2a** is preferentially attacked by an oxidizing agent at the proton on carbon, the double bond of any **1a** formed is probably attacked immediately by the same reagent. Among oxidizing agents which destroyed **2a** without evidence of formation of **1a** were manganese dioxide, N-bromosuccinimide in acetone, and chromic acid in pyridine.

The structure of **1a** is confirmed by spectral data. The ultraviolet spectrum of **1a** shows that it is similar to methyl vinyl ketone. The peaks are λ_{max} 237 mμ (ϵ_{max} 6340), λ_{max} 316 mμ (ϵ_{max} 19), compared with λ_{max} 212 (ϵ 7100), λ_{max} 320 mμ (ϵ_{max} 27), for methyl vinyl ketone.[8] These data appear to indicate that the functional groups are coplanar. F^{19} nmr spectrum at 56.4 Mc showed four peaks centered at +703, +724, +1424, and +7028 cps from symmetrical difluorotetrachloroethane in the ratio of 1:3:1:1. Coupling constants were first order and of the expected magnitudes. The infrared spectrum showed strong bands at 5.6 and 5.9 μ for carbonyl and trifluorovinyl groups, but specific bands could not be assigned to each functional group.

The synthetic route was repeated starting from 1,1,2,4,4,5,5,5-octafluoro-1-penten-3-ol (**2b**) and pentafluoroethyl trifluorovinyl ketone (**1b**) was obtained. Compound **1b**, a colorless volatile liquid, bp 62°, was somewhat less reactive than **1a**, possibly owing to re-

---

[1] (a) J. D. Lazerte, D. A. Rausch, R. J. Koshar, J. D. Park, W. H. Pearlson, and J. R. Lacher, *J. Amer. Chem. Soc.*, **78**, 5639 (1956). (b) A. L. Henne and C. J. Fox, *ibid.*, **76**, 479 (1954).

[2] (a) D. C. England, *ibid.*, **83**, 2205 (1961). (b) H. E. Simmons and D. W. Wiley, *ibid.*, **82**, 2288 (1960).

[3] R. D. Chambers and R. H. Mobbs in "Advances in Fluorine Chemistry," Vol. 4, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth, Inc., Washington, D. C., 1965, pp 50–112.

[4] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3445 (1965).

[5] P. Tarrant, P. Johncock, and J. Savory, *J. Org. Chem.*, **28**, 839 (1963).

[6] A. M. Lovelace, D. A. Rausch, W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Co., New York, N. Y., 1958, p 185.

[7] See ref 6, p 105.

[8] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 100.