Halomethyl–Metal Compounds. VII.[1] The Reaction of Phenyl(bromodichloromethyl)mercury with Carboxylic Acids[2]

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Abstract: Phenyl(bromodichloromethyl)mercury reacts with carboxylic acids in benzene at 80° to give high yields of phenylmercuric bromide and dichloromethyl esters, $RCOOCCl_2H$. With trichloroacetic acid phenyl-mercury cleavage becomes an important side reaction. Evidence is presented that it is the monomeric RCOOH (not the hydrogen-bonded dimer) which is the reactive species. A mechanism in which the carboxylic acid reacts with dichlorocarbene released by mercurial decomposition is favored.

A. Nature and Scope of the Reaction

In our studies of phenyl(trihalomethyl)mercury compounds we have used brominolysis as a degradative procedure in the assessment of $C_6H_5HgCX_3$ purity and in the analysis of mixtures of phenyl(trihalomethyl)mercurials,[4] and we were interested in examining alternate procedures for the cleavage of such mercury compounds. The cleavage of the mercury–carbon linkage of organomercury compounds by acids, *e.g.*, by HCl[5] or by carboxylic acids,[6] is well documented, and more recently it was reported by Russian workers[7] that phenyl(trichloromethyl)mercury reacts with methanolic HCl to give chloroform and phenylmercuric chloride. These reports suggested to us that the reaction of acetic acid with phenyl(trihalomethyl)mercury compounds might be worth studying, with possible application to mercurial analysis.

When a benzene solution of phenyl(bromodichloromethyl)mercury and acetic acid (1:3 molar ratio) was heated at reflux for 1 hr, phenylmercuric bromide precipitated rapidly, and thin layer chromatography after the heating period showed that the starting mercurial had been consumed completely. Phenylmercuric bromide was isolated in 96% yield. Gas–liquid partition chromatography (glpc) of the filtrate showed the presence of dichloromethyl acetate (92%) as sole product. Further work showed that this unexpected reaction was a general one for carboxylic acids, and that dichloromethyl esters could be prepared in generally high (60–95%) yields by this procedure (eq 1). The

$$C_6H_5HgCCl_2Br + RCOOH \longrightarrow RCOOCCl_2H + C_6H_5HgBr \quad (1)$$

esters thus prepared, their yields, and their physical data are given in Table I. Their nmr spectra showed a characteristic resonance peak due to the $-OCCl_2H$ proton at 7.6–8 ppm downfield from tetramethylsilane. Their infrared spectra showed C=O stretching frequencies *ca.* 50–100 cm^{-1} higher than those of the free acids.

Table I. Dichloromethyl Esters of Carboxylic Acids, $RCOOCCl_2H$, Physical and Spectroscopic Properties

R	Bp, °C (mm)	$n^{25}D$	δ_{OCCl_2H}[a]	$\nu_{C=O}$,[b] cm^{-1}
CH_3	121–122 (atm)	1.4272	7.67	1780
C_2H_5	54–55 (21)	1.4290	7.80	1770
$(CH_3)_3C$	64–65 (26)	1.4223	7.68	1770
CH_3OCH_2	67–69 (7.8)	1.4414	7.88	1785
C_6H_5	58–60 (0.2)	1.5335	8.05	1750
$CH_2{=}CH$	*c*	1.4526	7.84	1770
$CH_3CH{=}CH$	*c*	1.4637	7.86	1760
$CH_2{=}CHCH_2$	*c*	1.4481	7.83	1780
$(CH_3)_3SiCH_2$	*c*	1.4436	7.74	1760
$ClCH_2$	55–56 (6)	1.4653	7.72	1775
$BrCH_2$	57–58 (2.4)	1.4910	7.81	1775, 1790 sh
CH_3CHBr	43–44 (2.1)	1.4789	7.76	1775
$CHCl_2$	50–51 (2.3)	1.4696	7.80	1790, 1770
CCl_3	45–46 (1.4)	1.4750	7.83	1780

[a] In ppm downfield from tetramethylsilane; obtained in carbon tetrachloride solution. [b] In carbon tetrachloride solution. [c] Isolated by glpc.

The first attempted preparation of dichloromethyl acetate was reported in 1839 by Malaguti,[8] who claimed to have prepared $CH_3COOCCl_2H$ by chlorination of methyl acetate. In our hands, however, this reaction gave CH_3COOCH_2Cl, but none of the dichlorinated ester. Furthermore, Malaguti's physical constants (bp 145° and d 1.25) were not in agreement with those (bp 121–122°, d^{23} 1.34) of the product of the $C_6H_5HgCCl_2Br$ + CH_3COOH reaction. Laato[9] has recently reported that chlorination of chloromethyl acetate with sulfuryl chloride in the presence of benzoyl peroxide gives $CH_3COOCCl_2H$ (13%) and $ClCH_2COOCH_2Cl$ (17%). The refractive index of the former, $n^{20}D$ 1.4290, and density, d^{20} 1.3264, are in good agreement with our density and refractive index ($n^{22}D$ 1.4284). With the exception of dichloromethyl acetate, none of the dichloromethyl esters listed in Table I have been reported previously. It may be noted that chlorination of methyl esters of aliphatic carboxylic acids above acetic acid does not result in chlorination of the OCH_3 group; rather chlorination of the acyl portion takes place.[10] Also, dichloromethanol does not appear to

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(1) Part VI: D. Seyferth and H. D. Simmons, Jr., *J. Organometal. Chem.*, 6, 306 (1966).

(2) Preliminary communication: D. Seyferth, J. Y.-P. Mui, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 2961 (1964).

(3) Alfred P. Sloan Foundation Fellow, 1962–1966.

(4) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

(5) M. S. Kharasch and M. W. Graffin, *J. Am. Chem. Soc.*, **47**, 1948 (1925); M. S. Kharasch and R. Marker, *ibid.*, **48**, 3130 (1926); M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

(6) A. A. Bol'shakova, *Zh. Obshch. Khim.*, **24**, 266 (1954).

(7) A. N. Nesmeyanov, R. Kh. Freidlina, and F. K. Velichko, *Dokl. Akad. Nauk SSSR*, **114**, 557 (1957).

(8) F. Malaguti, *Ann. Pharm.*, **32**, 47 (1839).

(9) H. Laato, *Suomen Kemistilehti*, **37B**, 11 (1964).

(10) A. Bruylants, M. Tits, and R. Danby, *Bull. Soc. Chim. Belges*, **58**, 310 (1949).

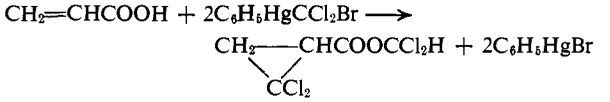
be stable. Thus the reaction of $C_6H_5HgCCl_2Br$ with carboxylic acids has unique preparative applicability.

Our studies of reaction 1 showed that highly acidic carboxylic acids such as trichloroacetic acid cause cleavage of the C_6H_5–Hg bond to a major extent. Thus in an experiment in which 0.013 mole each of phenyl(bromodichloromethyl)mercury and trichloroacetic acid were allowed to react in benzene at 80°, the yield of $CCl_3COOCCl_2H$ was only 19%, and the residue apparently was a mixture of solids. In the reaction of this mercurial with hydrogen chloride it had been found that dihalomethylenation (to give chloroform) was favored over C_6H_5–Hg cleavage as the reaction temperature was raised.[11] Accordingly, the reaction between $C_6H_5HgCCl_2Br$ and trichloroacetic acid was carried out in toluene at 100°, a toluene solution of mercurial being added to the heated acid solution. The yield of dichloromethyl trichloroacetate rose to 59% and phenylmercuric bromide was isolated in 79% yield.

The dichloromethyl esters thus prepared are colorless liquids which are readily hydrolyzed. They decompose on being heated above 130°. Unlike ordinary esters, they exhibit a pungent, unpleasant odor. The dichloromethyl esters derived from some carboxylic acids were unstable under the experimental conditions used. This appeared to be the case with cyanoacetic acid, *p*-methoxybenzoic acid, and trimethylsilylacetic acid. In the latter example, $(CH_3)_3SiCH_2COOCCl_2H$ could be characterized spectroscopically, but the pure ester could not be obtained.

Attempts to prepare dibromomethyl and bromochloromethyl esters of carboxylic acids were unsuccessful. The reaction of $C_6H_5HgCBr_3$ with acetic acid gave a solid residue whose weight exceeded that expected for phenylmercuric bromide. Hydrogen bromide was evolved when the reaction mixture was exposed to air. Analysis of the distilled filtrate showed the presence of bromoform (25%), which presumably was formed by the reaction of $C_6H_5HgCBr_3$ with HBr formed in the decomposition of the original product. No $CH_3COOCBr_2H$ could be detected. Similar results were obtained in the $C_6H_5HgCClBr_2$ + CH_3COOH reaction.

That the reaction between $C_6H_5HgCCl_2Br$ and carboxylic acids is very rapid was shown in a competition reaction in which 0.036 mole each of acetic acid and cyclohexene were allowed to compete for 0.012 mole of $C_6H_5HgCCl_2Br$ in benzene solution at 80°. Phenylmercuric bromide was obtained in 96% yield. The expected products, dichloromethyl acetate and 7,7-dichloronorcarane, were found to be present in 64 and 28% yield, respectively. Furthermore, reactions of $C_6H_5HgCCl_2Br$ with $CH_2{=}CHCOOH$, $CH_3CH{=}CHCOOH$, and $CH_2{=}CHCH_2COOH$ in 1:1 molar ratio gave the corresponding dichloromethyl esters in yields of 85% or better to the complete exclusion of CCl_2 addition to the C=C bonds. When mercurial and unsaturated acid were used in 2:1 molar ratio, dichloromethyl *gem*-dichlorocyclopropyl-substituted carboxylates were obtained, *e.g.*[12]


(2)

B. Concerning the Mechanism of the Reaction

Competition reactions in which two olefins were allowed to compete for a deficiency of various dihalocarbene sources have provided valuable information concerning the nature of the dihalocarbene–olefin reactions.[13–15] Also competition reactions of this type provide a convenient means of comparing relative reactivities of two radically different substrates, provided the kinetic orders of the reagent + substrate (1) and reagent + substrate (2) reactions are the same. In order to obtain further information concerning the $C_6H_5HgCCl_2Br$ + carboxylic acid reaction, a series of reactions in which acetic acid and cyclohexene computed for mercurial was carried out. The reactions were effected in *ca.* 25–30 ml of benzene solvent at 80° for 25 min, and the mercurial:cyclohexene:acetic acid ratio was varied roughly as 1:3:12, 1:3:6, 1:3:3, 1:6:3, and 1:12:3. The yields of dichloromethyl acetate and 7,7-dichloronorcarane were determined by glpc, and the relative reactivity of acid *vs.* cyclohexene, k_a/k_c, was calculated by the formula:[13] $k_a/k_c = P_aO_c/P_cO_a$, where P_a and P_c are the moles of products derived from acetic acid (a) and cyclohexene (c), and O_a and O_c the initial moles of acetic acid and cyclohexene. The results are summarized in Table II. While k_a/k_c remained roughly constant in the 1:3:3, 1:6:3, and 1:12:3 experiments, it decreased markedly when the concentration of acetic acid became very high. Such behavior might find an explanation in the fact that acetic acid is known to exist as an equilibrium mixture of monomer and hydrogen-bonded dimer in hydrocarbon solution, and therefore another series of experiments was carried out with the effective mole fraction (mf)[16] of acetic acid kept constant at a value of 0.1. The results of these experiments are given in Table III. Under these conditions, k_a/k_c thus remained effectively constant even at high acid:mercurial ratios. This suggests, but does not prove conclusively, that the mercurial + acetic acid reaction, like the mercurial + olefin reaction,[17] is first order in mercurial and zero order in substrate, and that a reaction of acetic acid with free or complexed dichlorocarbene is involved. The results of Tables II and III can be explained on the assumption that monomeric CH_3COOH reacts much more rapidly than the hydrogen-bonded dimer. As the proportion of acetic acid in the reaction mixture increases, the monomer–dimer equilibrium (3) is driven to the right, thus leaving a smaller concentration of monomeric CH_3COOH for the reaction.

$$2CH_3COOH \overset{K}{\rightleftharpoons} (CH_3COOH)_2$$

$$K = \frac{[(CH_3COOH)_2]}{[CH_3COOH]^2} \qquad (3)$$

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[11] D. Seyferth and J. Y.-P. Mui, *J. Organometal. Chem.*, in press.

[12] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

[13] W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

[14] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

[15] D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

[16] Effective mole fraction = (moles of acetic acid)/(moles of benzene + moles of cyclohexene + moles of acetic acid).

[17] D. Seyferth, in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," Robert A. Welch Foundation, Houston, Texas, 1966, in press.

Table II. Competition Reactions of Cyclohexene and Acetic Acid for Phenyl(bromodichloromethyl)mercury in 25–30 ml of Benzene at 80°

Molar ratio Mercurial: C_6H_{10}: CH_3COOH	CH_3COO-CCl_2H yield, %	Dichloro-norcarane yield, %	k_u/k_c
1:3.07:12.53	66.0	19.3	0.837
1:3.05:6.21	60.0	27.0	1.09
1:3.08:3.12	59.9	31.0	1.91
1:6.38:3.08	40.8	48.0	1.76
1:12.48:3.12	28.8	58.4	1.97

Table III. Competition Reactions of Cyclohexene and Acetic Acid for Phenyl(bromodichloromethyl)mercury at Constant Mole Fraction[16] of Acetic Acid = 0.1

Molar ratio Mercurial: C_6H_{10}: CH_3COOH	CH_3COO-CCl_2H yield, %	Dichloro-norcarane yield, %	k_a/k_c
1:3.05:12.20	80.1	9.9	2.02
1:2.96:6.01	71.6	18.4	1.92
1:2.98:3.00	59.6	30.0	1.97
1:6.00:2.98	44.8	44.0	2.05
1:11.93:3.00	27.9	57.5	1.93

Since the mole per cent of acetic acid was shown to be an important factor in the competition reactions, the effect of dilution on the value of k_a/k_c was examined in greater detail. Experiments were carried out using 5, 10, 20, and 30 mole % of acetic acid, with a constant 1:1 acetic acid:cyclohexene ratio. Table IV lists the results obtained; a marked effect of dilution on k_a/k_c is apparent. This is explained readily in terms of the monomer–dimer equilibrium (3). Since acetic acid exists mainly as dimeric species, the concentration of acid monomer is only a small fraction of the total acid concentration.[18] Thus the relative effect of dilution on the concentration of dimer (in terms of percentage of the total acetic acid concentration) would be small, while the effect of dilution on the concentration of the monomer would be larger. Assuming, as we do, that the monomer is the reactive species, an increase of monomer concentration would result in a higher yield of $CH_3COOCCl_2H$. This idea is supported by the following considerations. If the assumptions that under the experimental conditions acetic acid exists mainly in the dimeric form[19] and that the equilibrium constant K remains constant within a small variation of acid concentration are correct, then the concentration of acetic acid monomer would be directly proportional to the square root of the total acid concentration: $(CH_3COOH) = \sqrt{[(CH_3COOH)_2]/K}$, but the total acid concentration $(A) \cong [(CH_3COOH)_2]$, so $(CH_3COOH) \cong \sqrt{(A)/K}$. Taking the experiment with 10 mole % of acetic acid as a reference standard, dilution of the reaction mixture by a factor of 2 (*i.e.*, the reaction with 5 mole % of acetic acid) resulted in a decrease of monomer concentration by a factor of $1/\sqrt{2}$ (not $^1/_2$).

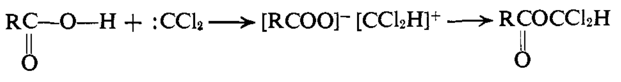
$$\frac{(CH_3COOH)_{5\%}}{(CH_3COOH)_{10\%}} = \sqrt{\frac{(A)_{5\%}}{(A)_{10\%}}} = \sqrt{\frac{^1/_2(A)_{10\%}}{(A)_{10\%}}} = \frac{1}{\sqrt{2}}$$

On the other hand, the concentration of cyclohexene in the 5 mole % acetic acid reaction was one-half of the cyclohexene concentration in the 10 mole % reaction. The term O_c/O_a thus is changed by a factor of $1/\sqrt{2}$ as the reaction mixture was diluted by a factor of 2: $O_c/O_a = {}^1/_2/(1/\sqrt{2}) = 1/\sqrt{2}$ (correction factor, CF). Thus, on the basis of these assumptions, the relative rate constants (k_a/k_c) of the 5 mole % reaction differed from that of the 10 mole % reaction by a factor of $1/\sqrt{2}$. When the observed k_a/k_c values in the fifth column of Table IV each were multiplied by the appropriate correction factor, the corrected k_a/k_c (last column) remained approximately constant. Thus it appears that these assumptions have merit, and it appears established that it is the monomeric RCOOH which is the reactive species in the dichloromethylenation reaction.

The effect of temperature on k_a/k_c was examined briefly. A reaction was carried out in benzene at 61–63° for 2 hr with 10 mole % acetic acid (mercurial: acid ratio *ca.* 1); k_a/k_c was found to be 1.50 (*vs.* 1.97 at 80–82°). This is in line with expectation, since the association constant K should increase and the monomer concentration decrease as the temperature is lowered.

Further insight into the $C_6H_5HgCCl_2Br$ + RCOOH reaction was sought by determining relative reactivities toward this mercurial of some ten different carboxylic acids *vs.* acetic acid as reference. The results are summarized in Table V. The relative reactivities k'/k_a of the stronger acids (mono- and dichloroacetic, bromoacetic, bromopropionic) appeared to increase with increasing acid strength, but this did not hold for the other acids examined. As mentioned above, the acid monomer–dimer equilibrium is of importance in the mercurial–carboxylic acid reaction. Unfortunately, the equilibrium constants for this equilibrium under the reaction conditions for the various acids used are not known. These have been determined at low acid concentration in benzene (*ca.* 0.1–0.001 *M*) at 25°.[18] In general, the association constant K decreased with increasing acid strength: pivalic, 690; acetic, 370; benzoic, 190; chloroacetic, 102. Thus it is conceivable that the increase of k'/k_a in Table V may be due primarily to an increase in the concentration of RCOOH monomer relative to acetic acid. However, in the absence of any knowledge concerning association constants of carboxylic acids in benzene at 80°, further discussion of the data in Table V is not warranted.

Noteworthy in this study is the very high reactivity of carboxylic acids toward the mercurial–CCl_2 transfer system. Even though the RCOOH monomer concentration is very low, the acid competes very successfully against cyclohexene for CCl_2. The exact nature of the RCOOH–CCl_2 interaction remains unknown. Some possibilities may be mentioned. (i) Nucleophilic attack by CCl_2 (which is in the singlet state, according to all available evidence, and thus has a lone pair of electrons in an sp² orbital) at the proton.



$$R\underset{\underset{O}{\|}}{C}—O—H + :CCl_2 \longrightarrow [RCOO]^- [CCl_2H]^+ \longrightarrow R\underset{\underset{O}{\|}}{C}OCCl_2H$$

(ii) Electrophilic attack by CCl_2 at an oxygen atom

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(18) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960. For example, the association constant K for acetic acid in a 0.01 mf (mole fraction) benzene solution at 30° is 370. The monomer represents *ca.* 2% of the total acid concentration.

(19) K for equilibrium 3 under our experimental conditions is not known. The increase in temperature to 80° from 30° should decrease the value of K, but the relatively high acid concentrations used (1–3 *M*) in our experiments should favor association to dimer.

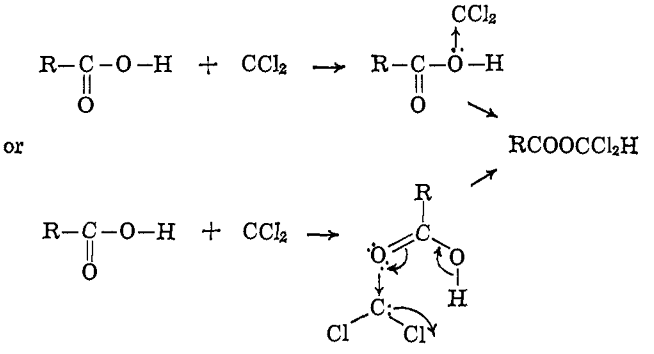
Table IV. Competition Reactions of Cyclohexene and Acetic Acid for Phenyl(bromodichloromethyl)mercury with Variation of the Effective Mole Fraction of Acetic Acid

Molar ratio Mercurial: C_6H_{10}: CH_3COOH	$CH_3COOCCl_2H$ yield, %	Dichloronorcarane yield, %	k_a/k_c	Mole % of acetic acid[16]	CF	k_a/k_c × CF
1:2.98:3.00	66.6	24.2	2.74	5	$1/\sqrt{2}$	1.94
1:2.98:3.00	59.6	30.0	1.97	10	1	1.97
1:5.95:5.94	53.2	37.0	1.44	20	$\sqrt{2}$	2.05
1:12.0:12.0	43.2	40.4	1.07	30	$\sqrt{3}$	1.85

Table V. Relative Reactivities of Carboxylic Acids toward Phenyl(bromodichloromethyl)mercury *vs.* Acetic Acid = 1

Acid, RCOOH, R =	$K_a \times 10^5$ in water at 25°	$RCOOCCl_2H$ yield, %	$CH_3COOCCl_2H$ yield, %	Total yield, %	Rel. reactivity k'/k_a
$(CH_3)_3C$	0.94	45.5	34.8	80.3	1.31
CH_3CH_2	1.34	42.8	46.0	88.8	0.93
CH_3OCH_2	2.7	34.6	44.3	78.9	0.78
$CH_2{=}CH$	5.66	36.6	46.4	83.0	0.79
C_6H_5	6.64	37.8	45.0	82.8	0.84
CH_2Cl	140	57.3	27.4	84.7	2.09
CH_2Br	205	48.8	28.9	77.7	1.66
CH_3CHBr		51.7	35.9	87.6	1.44
$CHCl_2$	3320	48.7	8.0	56.7	6.1
CCl_3	20000	32.9	2.4	35.3	13.7

of an un-ionized RCOOH molecule, followed by proton migration to carbon.



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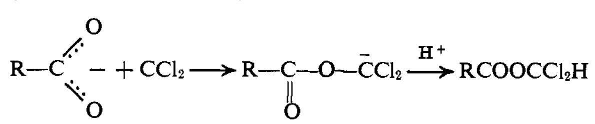
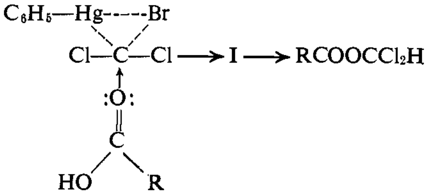
(iii) Electrophilic attack by CCl_2 at a carboxylate anion (which could be present in these systems in only very low concentration).



These possibilities assume a rate-determining decomposition of $C_6H_5HgCCl_2Br$ followed by rapid reaction of the reactive intermediate formed, CCl_2 (free or complexed), with the acid. We feel that such a process most likely prevails, since these mercurial–acid reactions are rapid at temperatures at which CCl_2 transfer to olefins from phenyl(bromodichloromethyl)mercury is rapid and also because of the results of the study of the relative reactivity of cyclohexene and acetic acid toward this mercurial. A bimolecular mechanism is, however, not completely excluded by this study, and a transition state such as II could be written for such a process. Further investigation, including a kinetic study, are required before the question concerning the mechanism of the mercurial–carboxylic acid reaction can be answered.



II

In conclusion, we must mention the report by Mitsch and Robertson[20] (which was published after our initial disclosure[2] of this dichloromethyl ester synthesis) that difluorocarbene generated by photolysis of difluorodiazirine reacts with carboxylic acids to give difluoromethyl esters, $RCOOCF_2H$. It was conjectured that this reaction occurs in a "concerted manner," but further amplication of this idea was not made. It is noteworthy, in any case, that difluorodiazirine was found to be stable to acids under conditions which did not lead to CF_2 generation.

Experimental Section

General Comments. Elemental analyses were performed by Dr. S. M. Nagy, MIT Microchemical Laboratory, the Schwarzkopf Microanalytical Laboratory, and the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using a Perkin-Elmer 337 infrared spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Associates A-60 nmr spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane. All reactions were carried out under an atmosphere of prepurified nitrogen. Reactions involving phenyl(trihalomethyl)mercurials could be followed conveniently by thin layer chromatography.[4] For gas–liquid partition chromatography (glpc) two types of instruments were used. Most frequently used was the MIT isothermal unit with a preparative size glass column 8 ft × 12 mm o.d. packed with 20–25% General Electric Co. SE-30 silicone rubber gum on 80–100 mesh Johns-Mansville Chromosorb P or an analytical size column 7 ft × 8 mm o.d. In the analysis of high-boiling materials and of compounds of limited thermal stability a short 3 ft or 4 ft × 10 mm o.d. glass column was found

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[20] R. A. Mitsch and J. E. Robertson, *J. Heterocyclic Chem.*, **2**, 152 (1965).

Table VI. Dichloromethyl Esters, $RCOOCCl_2H$, Yields and Analytical Data

R	Yield, %	Carbon, % Found	Carbon, % Calcd	Hydrogen, % Found	Hydrogen, % Calcd	Chlorine % Found	Chlorine % Calcd
CH_3	92	25.33	25.20	2.87	2.82	50.09	49.60
C_2H_5	87	30.27	30.60	3.87	3.85		
$(CH_3)_3C$	84	39.37	38.90	5.78	5.45	38.23	38.33
CH_3OCH_2	84	27.59	27.77	3.79	3.50	40.30	40.99
C_6H_5	95	47.19	46.85	2.85	2.95	34.02	34.57
$CH_2{=}CH$[a]	83						
$CH_3CH{=}CH$[a]	87						
$CH_2{=}CHCH_2$[a]	83						
$ClCH_2$	86	20.79	20.31	1.92	1.70	59.73	59.98
$BrCH_2$	92	15.95	16.24	1.45	1.36		
CH_3CHBr	88	19.94	20.38	2.15	2.14		
$CHCl_2$	76	17.30	17.00	0.60	0.95	66.02	66.93
CCl_3	59	14.62	14.63	0.54	0.41	71.02	71.98

[a] Analytical data are given in ref 12.

useful. Also used was an F & M Model 700 gas chromatograph. A 6 ft or 12 ft × 0.25 in. o.d. aluminum column was used.

Phenyl(trihalomethyl)mercury compounds were prepared as described in a previous paper of this series.[4] Nearly all carboxylic acids used were commercial products and were purified by distillation or vacuum sublimation if necessary.

Reaction of Phenyl(bromodichloromethyl)mercury with Carboxylic Acids. The reaction of $C_6H_5HgCCl_2Br$ with acetic acid is described as an example of the procedure used.

In a 100-ml three-necked flask equipped with a condenser, a thermometer, a nitrogen inlet tube, and a magnetic stirring unit was placed 13.2 g (30 mmoles) of phenyl(bromodichloromethyl)mercury, 5.40 g (90 mmoles) of acetic acid, and 50 ml of dry benzene. The reaction mixture was heated to reflux (81°) for 1 hr with stirring under an atmosphere of prepurified nitrogen. Precipitation of phenylmercuric bromide began at 74°. Thin layer chromatographic analysis of the reaction mixture showed that the starting mercurial had been consumed. Flakelike, crystalline phenylmercuric bromide (10.3 g, 96%), mp 284–287°, was filtered off. In view of the high yield of the latter, the filtrate could be analyzed by glpc prior to distillation in order to minimize decomposition of the air-sensitive product. Glpc analysis at 103°, chlorobenzene internal standard, showed 27.6 mmoles (92%) of dichloromethyl acetate to be present. Fractional distillation of the filtrate (45-cm, platinum spinning band column) gave 3.66 g (80%) of this product, bp 121–122°.

Yield data for similar reactions of $C_6H_5HgCCl_2Br$ and other carboxylic acids are given in Table VI, together with analytical data for the product dichloromethyl esters.

Reaction of Phenyl(bromodichloromethyl)mercury with Trichloroacetic Acid. A solution of 13 moles of $C_6H_5HgCCl_2Br$ and 12.3 mmoles of trichloroacetic acid in 25 ml of benzene was heated at reflux (83°) for 5.5 min. The solid residue, 2.52 g (mp 256–276°, turned black *ca.* 250°), was filtered. The clear filtrate was distilled at 0.02 mm (to 90° pot temperature) into a receiver at −78°. White, solid residue (3.8 g, mp 149–153° dec) remained. The distillate was analyzed by glpc at 118° to establish that $CCl_3COOCCl_2H$ had been produced in 19% yield. The impure solids apparently resulted from by-products introduced *via* Hg–C cleavage.

In a second experiment, 1.92 g (11.7 mmoles) of trichloroacetic acid was dissolved in 20 ml of toluene in a 50-ml flask. The contents were heated under nitrogen to *ca.* 100° and then 11.8 mmoles of $C_6H_5HgCCl_2Br$ dissolved in 10 ml of toluene in a heated dropping funnel was added slowly with vigorous stirring over a 2.5-min period. The light brown reaction mixture was cooled rapidly to room temperature after a total of 4 min of heating. Phenylmercuric bromide, 3.29 g, 79% yield, mp 274–281°, was filtered. Glpc analysis of the filtrate at 108° (bromobenzene standard) showed that the expected ester had been formed in 59% yield. Glpc analysis at 80° showed benzene to be present in 15% yield. The filtrate was trap-to-trap distilled (pot temperature to 90°) at 0.01 mm and concentrated. Analytical samples of $CCl_3COOCCl_2H$ were isolated by glpc.

Reaction of Phenyl(bromodichloromethyl)mercury with Trimethylsilylacetic Acid. The mercurial (10.5 mmoles) and 10 mmoles of $(CH_3)_3SiCH_2COOH$ (prepared by the method of Sommer, *et al.*[21]) were allowed to react in benzene at 81° for 20 min. Phenylmercuric bromide (93%) was filtered off. The filtrate was trap-to-trap distilled at reduced pressure. A white, powdery solid (1.2 g) settled out toward the end of the distillation. Glpc analysis at 104° of both the original filtrate and the distillate showed only a poor yield (*ca.* 35%) of product. The ester, $(CH_3)_3SiCH_2COOCCl_2H$, appeared to be unstable and no accurate elemental analysis could be obtained. Fairly pure samples were isolated by glpc and characterized spectroscopically. The nmr spectrum (in CCl_4) showed singlets at 7.74 (1 H), 1.91 (2 H), and 0.11 ppm (9 H), in good agreement with expected structure. The infrared spectrum (CCl_4–CS_2 composite) showed absorption at 2960 (w), 2890 (w), 1760 (s), 1690 (w), 1410 (w), 1315 (w), 1258 (m), 1210 (m), 1128 (m), 1070 (s), 1032 (s), 908 (m), 850 (s), 810 (w), 788 (w), 742 (m), 716 (w), 658 (w), and 620 (w) cm^{-1}.

Reaction of Phenyl(tribromomethyl)mercury with Acetic Acid. The mercurial (5.71 g, 10.8 mmoles) and 10.3 mmoles of acetic acid were heated in 30 ml of benzene at 81° under nitrogen for 50 min. Phenylmercuric bromide precipitated after 5 min of heating. The reaction mixture turned light yellow, and white, powdery solid separated out as the contents cooled to room temperature. The solid residue was filtered (3.99 g, partially melting at *ca.* 150°, followed by vigorous decomposition); 0.8 g of solid residue was recovered after trap-to-trap distillation in vacuum of the filtrate. [The total weight of solids (4.79 g) exceeded that of the expected C_6H_5HgBr (3.86 g)]. The distillate was analyzed by glpc at 122°. Only one major peak was detected and identified as bromoform (25% yield) by comparison of its infrared spectrum and glpc retention time with those of an authentic sample. A fuming gas which turned moist blue litmus paper red was observed when the reaction mixture was exposed to the air.

Relative Reactivities of Carboxylic Acids toward Phenyl(bromodichloromethyl)mercury. The competition reaction between acetic and pivalic acids is described. Into a dry, 50-ml, three-necked flask, equipped with a thermometer, condenser, nitrogen inlet tube, and magnetic stirring assembly, was distilled *ca.* 25 ml of benzene. The mercurial (10.1 mmoles), acetic acid (30.2 mmoles), and pivalic acid (30.2 mmoles) were added under an atmosphere of prepurified nitrogen. The contents were stirred until all mercurial had dissolved. The resulting solution was heated with an oil bath to reflux while stirring gently. The reaction was discontinued after 25 min of heating at 81–82°. White, crystalline C_6H_5HgBr (92%) was filtered; it had mp 283–286°. Glpc analysis of the filtrate was carried out directly using the MIT isothermal gas chromatograph (8-ft glass column containing 25% General Electric SE-30 on Chromosorb P, jacket at 105°, 17.5 psi helium). Chlorobenzene was used as internal standard. Empirical response factors were used in the yield calculations. The yields of dichloromethyl acetate and pivalate were found to be 3.51 and 4.60 mmoles (34.8 and 45.5%), respectively. k_{rel} was calculated to be 1.31. A duplicate experiment gave a value of 1.30.

This procedure also was used in the competition experiments involving cyclohexene and acetic acid.

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