Reactions of Bismuth Triacetate with Organic Compounds

ANNE L. REESE, KENNETH MCMARTIN, DIANE MILLER, AND PETER P. WICKHAM*

Department of Chemistry, Coe College, Cedar Rapids, Iowa 52402

Received August 15, 1972

Reaction of bismuth triacetate (1) with amines and alcohols at ~150° usually affords the respective N- and O-acetylated derivatives. Formates and formamides undergo reaction when heated with 1 at 200°; bismuth metal and the respective acetate or acetamide result. For example, formanilide is converted to acetanilide in 71% yield by this method. On the other hand, the reaction of 1 with propionanilide under these conditions does not lead to production of bismuth metal, and a mixture of amides results. Some variations of reactivity with structure are presented, and a possible reaction pathway is suggested.

In view of the elaborate elucidation of the utility of such heavy metal salts as lead tetraacetate, mercuric acetate, and thallium acetate in organic synthesis,[1] there seems a notable paucity of reports concerning the corresponding chemistry of salts of bismuth. This deficiency prompted us to study the reactions of bismuth triacetate (**1**) with some representative amines, alcohols, amides, and esters.

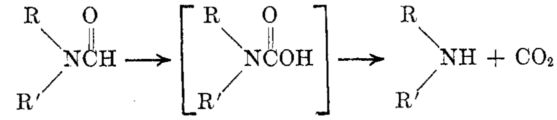
Bismuth triacetate has been a well-known compound for some 50 years. Early reports[2] were primarily concerned with its preparation and stability. More recently, it has been reported useful as a catalyst in industrial applications such as the vapor-phase conversion of acetylene to vinyl acetate,[3] a high-temperature preparation of phthalate esters,[4] and in the high-pressure air oxidation of various aliphatic hydrocarbons.[5] In 1951, Rigby reported[6] that acyloins were readily oxidized to 1,2 diketones with **1** in acetic acid (or with bismuth oxide in acetic acid) at about 100°, and suggested its general use as a mild oxidant for acyloins. Bismuth was the reduction product resulting from the bismuth(III) salt. On the other hand, refluxing solutions of other readily oxidizable substances such as hydrazine, formaldehyde, catechol, *p*-phenylenediamine, and glucose with bismuth oxide in acetic acid was claimed to give "negative results," although no effort apparently was made to isolate the products from these reactions. No other reactions of bismuth triacetate with organic substances have been reported which seem of general synthetic interest.

We initially observed that **1** reacts with formamides such as dimethylformamide (**2**) and formanilide (**3**) at bath temperatures of about 200° to produce the corresponding acetamides, with concomitant deposition of metallic bismuth. In most cases, the reaction seems complete within 24 hr. Generally, these reactions are carried out by heating an equimolar mixture of the two reactants without solvent, extracting the organic products, and purifying the organic residue after concentration of these extracts. A summary of the reactions of **1** with various formamides is shown in Table I.

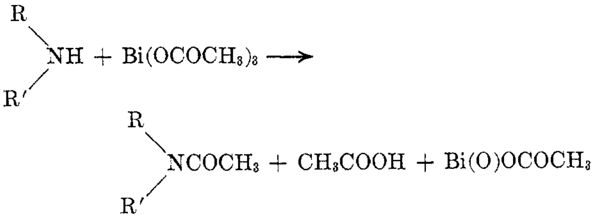
In these examples, it appears that the speed with which this reaction occurs is not a function of steric hindrance about nitrogen, since tertiary and secondary amines (*e.g.*, **4** and **3**) appear to react equally readily. We believe that the slow rate of reaction of **1** with **2** is due to the fact that **2** boils at temperatures well below those we used to effect these reactions. Consequently, the temperature of the reaction mixture and the concentration of the amide in it were certainly lower than in the case of any of the other higher boiling amides shown; this would then lead to the lower apparent rate. On the other hand, the slow rate of conversion of diphenylformamide (**7**) does appear to be a true indication of the unreactive nature of **7** in the present reaction.

In order to test the applicability of this reaction to amides other than formamides, the interaction of **1** and propionanilide (**8**) was investigated. Following reaction of equimolar amounts of **1** and **8** at a bath temperature of 200° for 24 hr, formation of metallic bismuth could not be detected; the organic portion of the mixture appeared to be a mixture of starting material and acetanilide in roughly equal amounts. It thus appears that oxidation does not occur with typical amides other than formamides, although some acyl interchange clearly does result.

One likely hypothesis for the pathway of this reaction seemed to be the possibility that it proceeds *via* an amine intermediate, perhaps as shown below. In



(1)



(2)

this scheme, the carbamic acid, formed by oxidation of the formamide by bismuth(III), would be expected to decarboxylate readily, affording an amine which might then be acetylated by **1** *in situ*.

To test the viability of this hypothesis, several amines were treated with **1**. Amines with appreciable nucleophilic character were found to react readily with **1** at temperatures at or below 150°, as shown in Table II.

Amines which were very reactive (such as **10** and **14**) exhibited evidence of extensive decomposition when heated at 150°, and consequently these reactions

---

[1] See, for example, L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967.

[2] (a) E. Salkowski, *Biochem. Z.*, **79**, 96 (1917); (b) M. O. Kharmandar'yan, *J. Russ. Phys. Chem. Soc.*, **60**, 1477 (1928); (c) L. Cuny, *Bull. Sci. Pharmacol.*, **34**, 65 (1927).

[3] I. B. Vasil'eva, A. I. Gel'bshtein, I. N. Tolstikova, and W.-T. Tao, *Kinet. Katal.*, **5**, 144 (1964).

[4] J. R. Leebrick, W. J. Considine, and N. Kudisch, British Patent 1,010,175 (1965); *Chem. Abstr.*, **64**, 9645*e* (1966).

[5] C. S. Morgan, Jr., and N. C. Robertson, U. S. Patent 2,659,746 (1953); *Chem. Abstr.*, **49**, 1099*e* (1955).

[6] W. Rigby, *J. Chem. Soc.*, 794 (1951).

Table I

Reactions of Formamides with Bismuth Triacetate[a]

Compd	Name	Reactant ratio (1:amide)	Time, hr	Product	Yield, %[b]
2	Dimethylformamide	1:1	90[c]	Dimethylacetamide	69
3	*N*-Phenylformamide	1:1	24	*N*-Phenylacetamide	71
	N-Phenylformamide	1:2	24	*N*-Phenylacetamide	83
	N-Phenylformamide	1:3	24	*N*-Phenylacetamide	47.5
4	*N*-Methyl-*N*-phenylformamide	1:1	24	*N*-Methyl-*N*-phenylacetamide	80
5	*N*-Cyclohexylformamide	1:1	24	*N*-Cyclohexylacetamide	76
6	*N*-Formylpiperidine	1:1	30	*N*-Acetylpiperidine	69
7	*N*,*N*-Diphenylformamide	1:2	130[d]	*N*,*N*-Diphenylacetamide Diphenylamine	4.5[e]

[a] Reactions carried out at 200° unless otherwise noted. [b] Isolated yield of product after purification by distillation or recrystallization. [c] Reaction incomplete at 18, 40, and 60 hr. [d] Reaction carried out at 210–220°. [e] A 20% yield of sublimed diphenylamine was obtained prior to recrystallization.

Table II

Reactions of Amines with Bismuth Triacetate[a]

Compd	Name	Temp, °C	Time, hr	Product	Yield, %[b]
9	Aniline	150	3	Acetanilide	86
10	*p*-Anisidine	105	24	*p*-Acetaniside	34
11	*p*-Bromoaniline	170	3.5	*p*-Bromoacetanilide	38
12	Benzylamine	150	2.5	*N*-Benzylacetamide	70
13	*p*-Nitroaniline	150	5	*c*	
14	Phenylhydrazine	80	24	Hydracetin	27
15	Hydrazobenzene	130[d]	3	Azobenzene	60

[a] Approximately equimolar amounts of reactants employed in all reactions. [b] After recrystallization of the product. [c] No obvious reaction; starting material recovered. [d] Carried out under nitrogen.

Table III

Reaction of Bismuth Triacetate with Formates and Alcohols[a]

Compd	Name	Temp, °C	Time, hr	Product	Yield, %[b]
16	Dodecanol	150	24	Dodecyl acetate	60
17	Benzyl alcohol	185	24	Benzyl acetate	58
18	Cholesterol	160	25	Cholesteryl acetate	48
19	Dodecyl formate	190	24	Dodecyl acetate	58
20	Benzyl formate	190	25	Benzyl acetate	72
21	Cholesteryl formate	190	48	Cholesteryl acetate	87

[a] Equimolar ratios of 1 to substrate employed. [b] After recrystallization or distillation of the product.

had to be run at lower temperatures. Reactivity appeared to be directly related to the nucleophilicity of the amine, and the very poor nucleophile **13** did not react at all. Not unexpectedly, oxidation rather than acetylation occurred with **15**, and azobenzene was the only observable product. The development of extensive color in many of these reactions and the highly variable yields of amides obtained contrasted with the results from the reaction of **1** with formamides.

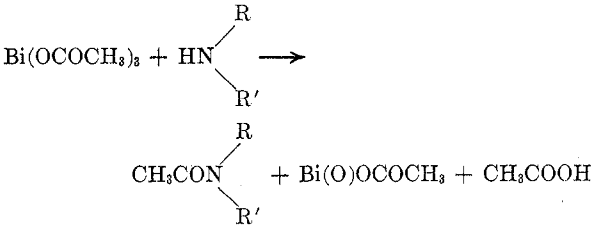
Inasmuch as the formyl group was implicated as the oxidized moiety in the reactions of formamides with **1**, we then extended our investigation to consider the reactivity of **1** with alcohols and formate esters. The results of these experiments are summarized in Table III.

In these experiments, we found that bismuth metal was produced in the reaction of **1** with formates at temperatures of 190° with concomitant formation of the corresponding acetates, paralleling the results obtained in the reactions of **1** with formamides. Although we investigated only a few examples, there seems no reason why yields of 70–80% of the analogous acetate should not normally be expected in this reaction.

Alcohols reacted with **1** to form the respective acetates. The yields obtained from the reaction of **1** with various alcohols are generally lower than those from its reactions with the corresponding formates, although they do not appear to be variable in the way that yields from reactions of **1** with amines of different types are.

Discussion

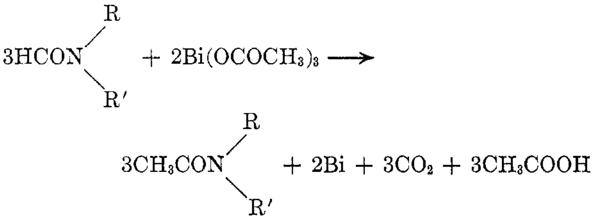
The inorganic residue isolated from the reactions of **1** with the amines and alcohols was identified as bismuthyl acetate. This enables us to propose the following overall representations for these two reactions.



$$\mathrm{Bi(OCOCH_3)_3} + \mathrm{HN}\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix} \longrightarrow \mathrm{CH_3CON}\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix} + \mathrm{Bi(O)OCOCH_3} + \mathrm{CH_3COOH} \quad (3)$$

$$\mathrm{Bi(OCOCH_3)_3} + \mathrm{HOR} \longrightarrow \mathrm{CH_3COOR} + \mathrm{Bi(O)OCOCH_3} + \mathrm{CH_3COOH} \quad (4)$$

Although carbon dioxide was not identified among the products of the reaction of **1** with formates and formamides, this seems the most reasonable result from the oxidation–reduction reaction involved. Hence, these two overall reactions may be written as follows.



$$3HCON(R)(R') + 2Bi(OCOCH_3)_3 \longrightarrow 3CH_3CON(R)(R') + 2Bi + 3CO_2 + 3CH_3COOH \quad (5)$$

$$3HCOOR + 2Bi(OCOCH_3)_3 \longrightarrow 3CH_3COOR + 2Bi + 3CO_2 + 3CH_3COOH \quad (6)$$

Because reactions 3 and 4 seem to be examples of one type of reaction of **1**, whereas 5 and 6 are examples of a different type, each type of reaction is discussed separately below.

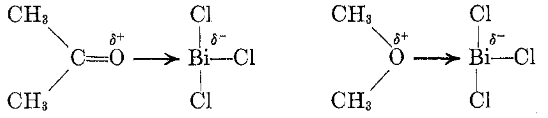
Reactions of 1 with Amines and Alcohols.—Inasmuch as it had been previously reported that **1** decomposes into bismuthyl acetate upon heating,[2a] it seemed attractive initially to postulate a two-step procedure in which acetic anhydride was produced from the decomposition of **1**, and that the anhydride subsequently acetylated the amine or alcohol in the reaction mixture, as shown (for a primary amine).

$$Bi(OCOCH_3)_3 \xrightarrow{\Delta} Bi(O)OCOCH_3 + (CH_3CO)_2O \quad (7)$$

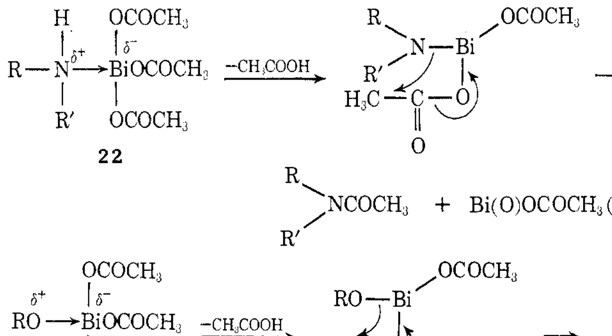
$$(CH_3CO)_2O + RNH_2 \longrightarrow CH_3CONHR + CH_3COOH \quad (8)$$

However, in our hands, bismuth acetate, when heated to temperatures as high as 190° under nitrogen (*i.e.*, in the absence of water), does not decompose. No acetic anhydride can be detected, and the ir spectrum of the salt remains unchanged. This makes this hypothesis seem improbable at best.

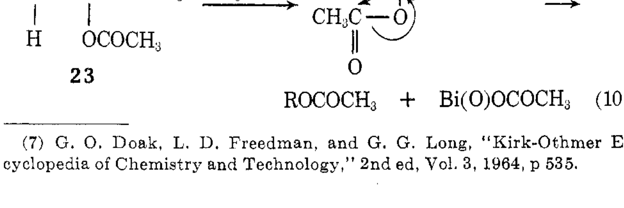
Recently, a number of complexes formed by reaction of organic substances with bismuth(III) salts have been reported.[7-10] These reflect the ability of the latter to function as Lewis acids; two examples may be represented as follows.[7]



It seems reasonable to believe that reaction of amines and alcohols with **1** would afford initially the structures **22** and **23** analogous to the complexes shown above.



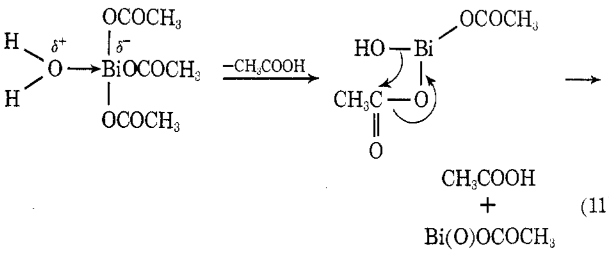
(9)



(10)

By elimination of the elements of acetic acid, followed by a four-centered reaction, these could then decompose to the observed products.

These reactions appear to be completely analogous to the reaction of **1** with water, which may be formulated in a similar way.

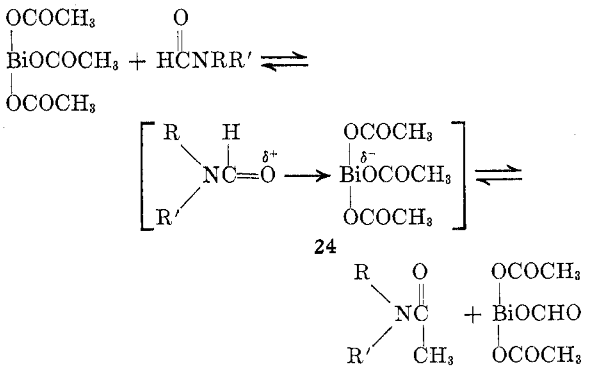


(11)

Reactions of 1 with Formamides and Formates.—A hypothesis for the sequence of reactions involved in these transformations which initially appeared attractive involved initial oxidation of the formyl moiety to a carboxylic acid function, affording either a carbamate or a carbonate. These products would then be expected to readily lose carbon dioxide to afford the corresponding amine or alcohol; the latter could then be acetylated by additional **1** in the mixture, or perhaps by the acetic acid formed, as shown in eq 1 and 2, for a formamide example.

This sequence, however, predicts that no more than 3 mol of a formamide can react with 2 mol of bismuth triacetate, even if the latter does not itself acylate the amine. Additional excesses of the formamide should remain unattacked. However, in the reaction of **1** with formanilide (**3**), it was observed that a 2:1 ratio of **3** to **1** afforded an 83% yield of recrystallized acetanilide, even though, by this mechanism, a 75% yield is the maximum possible. The inescapable conclusion is that oxidation of the formyl group is *not* a necessary prerequisite to its replacement by an acetyl function. The additional observation that propionanilide also reacts with **1** to form substantial amounts of acetanilide in the product mixture, even though in this case no formyl group is present and no bismuth metal can be detected in the product mixture, also suggests that two different, unrelated reactions are being observed.

We believe, therefore, that **1**, through a reversible reaction with acyl groups (see eq 12), can effect acyl interchanges on amides and esters. In contrast with most such interchanges, the decomposition of the formyl group through its oxidation by bismuth(III) drives



(12)

---

[7] G. O. Doak, L. D. Freedman, and G. G. Long, "Kirk-Othmer Encyclopedia of Chemistry and Technology," 2nd ed, Vol. 3, 1964, p 535.

[8] B. V. Tronov, A. A. Zhelnov, and G. V. Gavrilin, *Zh. Obshch. Khim.*, **37**, 576 (1967).

[9] S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1965).

[10] A. K. Mishra and K. N. Tandon, *Inorg. Chem.*, **10**, 1896 (1971).

this reaction to completion of exchange and the resultant relatively high yields observed in such cases.

A crystalline addition product directly analogous to the proposed intermediate **24** has been isolated from the reaction of dimethylformamide with bismuth(III) chloride at room temperature.[10] However, acyl interchanges of the type proposed have not previously been reported for bismuth salts.

This analysis does not preclude the possibility that *some* of the reaction takes place through initial oxidation of the formamide or formate. The fact that the acetylations of various amines by **1** which we investigated led to extremely variable yields and to highly colored by-products—in contrast to reactions of the latter with a variety of formamides—leads us to believe (in conjunction with our earlier reasoning) that this sequence is not likely to account for a very large portion of the reaction.

Continuing studies in these laboratories are directed toward investigating the nature of these reactions when other bismuth(III) salts are used. Our expectation is that such studies may clearly delineate the scope and allow more definitive mechanistic formulations for the reactions of bismuth(III) salts with various organic substances.

Experimental Section

Materials and Equipment.—Melting points were determined using a Hoover capillary melting point apparatus, and are corrected. Boiling points are uncorrected. Infrared spectra were obtained with a Beckman Model IR-8 spectrophotometer and absorptions are reported in inverse centimeters. Gas–liquid chromatography (glc) was carried out on a Bendix Model 2200 gas chromatograph equipped with an 8 ft × 0.125 in. stainless steel column packed with 10% Carbowax 20M, h.p., on Chromosorb W, 60–80 mesh, unless otherwise noted. Nuclear magnetic resonance spectra were obtained using a Varian Associates A-60A nuclear magnetic resonance spectrometer. All spectra are reported in parts per million relative to tetramethylsilane (δ).

Bismuth triacetate (1) was prepared from bismuth oxide following the procedure of Rigby,[6] and identified as authentic by comparison of its infrared spectrum[11] with that reported by Donaldson, *et al.*[12] The white crystals thus obtained were filtered, washed with ethyl acetate, and sucked dry. Prolonged passage of air through the crystals or heating of the crystals in a humid atmosphere led to loss of characteristic infrared absorption at 1550, 1030, and 950 cm^{-1}. A sample heated in this manner at 75° for 15 hr appeared to be bismuthyl acetate, $Bi(O)OCOCH_3$. *Anal.* Calcd for $C_2H_3BiO_3$: C, 8.45; H, 1.06. Found: C, 8.31; H, 0.98. Presumably this change is due to its reaction with moisture present in the air, since a sample of 1 appeared unchanged in its physical appearance and infrared spectrum after having been heated at 150° under a nitrogen atmosphere for 6.5 hr, contrary to a previous report of its thermal instability.[2a]

Reactions of 1 with Formamides. A. General Procedure.—An intimate mixture of 5.00 g (0.0143 mol) of formanilide and 15.94 g (0.0413 mol) of 1 was heated for 24 hr in a bath maintained at 200°. After the formanilide melted, the solution became mushy. After a few hours, an amber liquid began to form above a gray, mushy solid which gradually darkened and became more metallic. At the end of the reaction, this solid was almost wholly metallic.

The mixture was allowed to cool and was then triturated with two 50-ml portions of chloroform. The organic extracts were washed with saturated aqueous $NaHCO_3$ and evaporated to dryness, and the solid residue was then recrystallized from carbon tetrachloride. A second crop was obtained by concentration of the mother liquors, total yield, 3.96 g (71%), mp 111–113.5° (reported[13] mp 113.9–114.4°). The ir ($CHCl_3$) and nmr ($CDCl_3$) spectra of the product were identical with those of authentic acetanilide.

B. With Dimethylformamide (DMF).—A mixture of 10.0 g (0.137 mol) of DMF and 47.9 g (0.124 mol) of 1 was heated in a bath maintained at 200°. The mixture refluxed vigorously; gradually a yellowish liquid formed above a grayish solid mush. Prior studies of this reaction, employing equimolar amounts of 1 and DMF under the same conditions, had shown (based on glc analysis of the crude reaction mixture[14] and comparison of peak areas due to DMF and dimethyl acetamide) that conversion of DMF to dimethyl acetamide after 18, 40, 60, and 90 hr was, respectively, 22, 46, 70, and 100%. Consequently, the reaction mixture was allowed to cool after 90 hr and then extracted with two 75-ml portions of ether. The combined extracts were carefully concentrated to an oil, 500 ml of benzene was added, and any residual acetic acid was then removed by azeotropic distillation at atmospheric pressure. The residue was then fractionally distilled at a pressure of 19 mm to afford 2.2 g of pure dimethylacetamide, bp 60–69°, identical by ir spectrum (CCl_4) and glc retention time[14] with an authentic sample of dimethylacetamide. Two slightly higher boiling fractions, bp 69–71° (19 mm), showed, by glc analysis,[14] a peak identical in retention time with dimethylacetamide and a much smaller second peak with a longer retention time. Redistillation of these combined fractions afforded additional dimethylacetamide, bp 59–68° (18 mm), and, again, a fraction, bp 68–69° (18 mm), which exhibited two peaks on glc analysis.[14] This second peak was shown clearly not to be acetic acid, DMF, or acetic anhydride; attempted collection, however, failed and it was not conclusively identified. Total yield of distilled dimethylacetamide, including amounts calculated from the glc analysis of the high-boiling mixture isolated from the second distillation, was 8.25 g (69%).

C. With Diphenylformamide.—A mixture of 5.00 g (0.0254 mol) of *N,N*-diphenylformamide and 4.90 g (0.0127 mol) of 1 was heated in a bath maintained at 210–220° for 130 hr. The resultant solution was black; in addition, some bismuth metal had precipitated. The mixture was triturated with four 25-ml portions of chloroform; these extracts were decanted, filtered, combined, and concentrated to a black oily residue. This residue was then extracted with small portions of hot hexane. Further separation by decantation from oily residues which appeared on slight cooling was necessary; additional cooling of these hexane extracts afforded 0.51 g of brownish, flaky crystals in two crops, mp 96–100°.

The residues from this purification were again combined and reconcentrated. Hot petroleum ether (bp 30–60°) was added to the residue. Cooling afforded another crop of brownish crystals, mp 99.5–101°, and subsequent concentration of the mother liquors yielded still another crop, mp 99–101°. The total yield of these two crops of crystals was 0.69 g.

The crystals obtained from hexane showed no depression of melting point when mixed with those obtained from petroleum ether. The ir spectra ($CHCl_3$) of all of these crops of crystals were superimposable, and confirmed the identity of the samples as somewhat impure diphenylacetamide (reported[15] mp 101–102°). These spectra were similar to that of diphenylformamide, but differed in that a peak near 2900 cm^{-1} typical of formyl CH absorption was absent and a peak at 1375 cm^{-1} indicative of the new CCH_3 linkage was now present. The total yield of diphenylacetamide, mp 96–101°, was 1.20 g (22.4%).

The brown mother liquors from these crystallizations were placed in a small sublimation apparatus and sublimed at 0.5 mm (bath temperature 130°). A crystalline, whitish substance containing some brown specks, weight 0.875 g, mp 35–50°, sublimed from the residue and was collected. An ir spectrum ($CHCl_3$) of this sublimate showed only very weak absorption at 1665 cm^{-1}; in all other respects, the spectrum was identical with that of an authentic sample of diphenylamine. Recrystallization of the sublimate from hexane afforded a low yield of white crystals, mp 45.5–49°, with an ir spectrum identical with that of authentic diphenylamine, mp 53–55°.

Reaction of 1 with Propionanilide.—An intimate mixture of

---

[11] Obtained as a mull in Nujol.

[12] J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, **21**, 275 (1965).

[13] L. W. Winkler, *Arch. Pharm. (Weinheim)*, **266**, 45 (1928).

[14] Carried out on a Carbowax 20M column programmed at 100° for 7 min, then to 130° in 1 min, and 130° subsequently.

[15] O. Wallach and I. Kamensky, *Justus Liebigs Ann. Chem.*, **214**, 234 (1882).

5.00 g (0.0335 mol) of propionanilide and 12.96 g (0.0336 mol) of **1** was heated for 24 hr in an oil bath maintained at 200°. At the conclusion of this period, there was no evidence of bismuth metal in the reaction mixture. The mixture was allowed to cool, and was then extracted with three 50-ml portions of chloroform. The organic extracts were filtered, combined, washed with saturated aqueous $NaHCO_3$, and concentrated to afford a black, oily residue (4.99 g).

This residue was dissolved in hot carbon tetrachloride. Cooling of this solution afforded a brown, flocculent precipitate (1.52 g) which was filtered from the mother liquors. This brown solid was then extracted with hot hexane; the solution, on cooling, deposited whitish crystals (A), weight 0.41 g. The mother liquors obtained from filtration of the flocculent precipitate were concentrated, yielding, on cooling, a black, crystalline mass. Several recrystallizations of this mass from hexane afforded two additional crops of off-white crystals B, 1.65 g, and C, 0.33 g.

Solids A, B and C all exhibited melting points with a wide range in the area between 79 and 95°, and nmr ($CDCl_3$) of all three contained the same general features: δ 8.2 (s, NH), 7.35 (m, ArH), 2.33 (q, J = 7 Hz, CH_3CH_2CO– of propionanilide), 2.10 (s, CH_3CO– of acetanilide), and 1.17 (t, J = 7 Hz, CH_3-CH_2CO– of propionanilide). All of these peaks with these characteristics were observed in the nmr of pure acetanilide and/or propionanilide. Ratios of the integration of the area under the peak at 2.10 to that under the peak at 1.17 were found to be 40:60, 49:51, and 50:50 for A, B, and C, respectively. Since these areas should be proportionate measures of the population of each of the two amides, it seems clear that about half of the propionanilide was converted to acetanilide.

Reaction of 1 with Amines. Representative Procedure (Aniline).—A mixture of 1.18 g (0.0127 mol) of aniline and 3.94 g (0.0102 mol) of **1** was heated at 150° for 3 hr. The mixture was allowed to cool and was then extracted with three 30-ml portions of chloroform. These extracts were filtered and concentrated to afford a white, crystalline residue, yield after drying, 1.46 g (86%), mp 113.5–115° (reported[13] for acetanilide, mp 113.9–114.4°). An ir spectrum ($CHCl_3$) of the product was identical with that of authentic acetanilide. The inorganic solid remaining after initial extraction of the reaction mixture with chloroform was filtered and pressed dry. Its ir spectrum[11] was essentially the same as that of bismuthyl acetate, $Bi(O)OCOCH_3$, described earlier.

For more reactive amines, it was necessary to carry out the reaction at lower temperatures in a nitrogen atmosphere; thus, reaction of *p*-anisidine at 105° for 24 hr under nitrogen afforded a 34% yield of recrystallized *N*-acetyl-*p*-anisidine, mp 127–128.5°, undepressed on admixture with an authentic sample, ir ($CHCl_3$) identical with that of authentic *p*-acetanisidide.

Reaction of 1 with Hydrazobenzene.—A mixture of 0.421 g (2.29 mmol) of hydrazobenzene and 1.09 g (2.84 mmol) of **1** was heated at 130° under nitrogen for 3 hr. The mixture was then allowed to cool and was extracted with three 30-ml portions of chloroform. The organic extracts were filtered, combined, and concentrated, affording an orange, crystalline residue. Recrystallization of the solid product from an ethanol–water mixture afforded orange crystals (0.220 g, 53%) of azobenzene: mp 68–70°, undepressed on admixture with an authentic sample; ir ($CHCl_3$) identical with that of authentic azobenzene.

Reaction of 1 with Alcohols. Representative Procedure (Dodecanol).—A mixture of 2.10 g (0.0113 mol) of dodecanol and 4.82 g (0.0124 mol) of **1** was heated at 150° for 24 hr. After the mixture was allowed to cool, it was extracted with three 30-ml portions of methylene chloride. The residual inorganic solid was rinsed with methylene chloride and pressed dry; its ir spectrum[11] identified it as bismuthyl acetate. The organic extracts were washed with saturated aqueous $NaHCO_3$, concentrated, and distilled to afford 1.53 g (60%) of a clear, colorless liquid: bp 94° (0.30 mm) [reported[16] bp 139–140° (9 mm)]; ir ($CHCl_3$) 1750 (ester C=O), 1370 cm^{-1} (CH_3C).

Reaction of 1 with Formates. Representative Procedure (Cholesteryl Formate).—A mixture of 4.87 g (0.0126 mol) of **1** and 5.18 g (0.0125 mol) of cholesteryl formate was heated at 190° for 48 hr. After the reaction mixture was allowed to cool, the resultant mixture of bismuth metal and brown solid was extracted with three 30-ml portions of methylene chloride. The organic extracts were dried ($MgSO_4$) and concentrated to yield 5.05 g of a brown solid. This was recrystallized from 95% ethanol to afford 4.68 g (87%) of yellow-white crystals: mp 112–113.5° (reported[17] mp 114°); ir ($CHCl_3$) (identical with that of the product isolated from reaction of cholesterol with **1**) exhibits increases in absorption at 1025, 1190–1250, and 1370 cm^{-1} compared with the spectrum of the starting formate; nmr (CCl_4) δ 1.94 (s, CH_3CO–). The addition of a small amount of benzoyl peroxide to a parallel reaction under conditions similar to these appeared to have no measurable effect on either the course or speed of the reaction.

Registry No.—**1**, 22306-37-2.

Acknowledgment.—The financial support of the National Science Foundation Undergraduate Research Participation Program for this work is gratefully acknowledged.

[16] M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **27**, 950 (1944).

[17] A. H. Milburn and E. V. Truter, *J. Chem. Soc.*, 1736 (1956).

Fluorinated Cyclopropenes and Cyclopropenium Ions[1]

DAVID C. F. LAW, STEPHEN W. TOBEY, AND ROBERT WEST*

Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706, and
The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts

Received December 1, 1971

Tetrachlorocyclopropene (**1**) was fluorinated with potassium fluoride in tetramethylenesulfone at 160–180° to give 1,2,3-trichloro-3-fluorocyclopropene (**2**), 1,2-dichloro-3,3-difluorocyclopropene (**3**), 1-chloro-2,3,3-trifluorocyclopropene (**4**), plus two ring-opened products, the pentafluoropropene **5** and the pentafluoropropane **6**. Tetrabromocyclopropene (**7**) was fluorinated under similar conditions to give 1,2-dibromo-3,3-difluorocyclopropene (**8**), 1-bromo-2,3,3-trifluorocyclopropene (**9**), **5**, and **6**. The fluorocyclopropenes **3**, **4**, **5**, and **6** reacted with antimony pentafluoride to give the fluorocyclopropenium hexafluoroantimonates, **15**, **16**, **17**, and **18**, respectively. The physical properties of the compounds herein described are compared with those of analogous, known species. A mechanism for the fluorination of **1** and **7** by potassium fluoride is proposed.

The Preparation of Fluorocyclopropenes.—Tetrachloro- and tetrabromocyclopropenes **1** and **7** undergo halogen exchange readily in the presence of Lewis acids through the intermediacy of the corresponding trihalocyclopropenium ions, which have been isolated and studied in some detail.[2] Thus tetrachlorocyclopropene (**1**) reacts with an excess of boron tribromide to give tetrabromocyclopropene (**7**).[3] Both **1** and **7** can be fluorinated at the allylic position by antimony trifluoride to give 1,2,3-trichloro-3-fluorocyclopropene

[1] Taken in part from the Ph.D. thesis of D. C. F. Law, University of Wisconsin, 1967, also presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract of Papers, S52.

[2] R. West, A. Sadô, and S. W. Tobey, *J. Amer. Chem. Soc.*, **88**, 2488 (1966).

[3] S. W. Tobey and R. West, *ibid.*, **88**, 2481 (1966).