

was dissolved completely, and the aqueous layer separated. The organic phase was extracted with a solution of 150 ml. of concentrated hydrochloric acid in 800 ml. of water (in two portions). The aqueous layers were combined, extracted once with about 300 ml. of ether to remove any non-basic material and then heated on a steam-bath at 70–80° for 30 minutes to complete the hydrolysis of the  $\alpha$ -chloro to the  $\alpha$ -hydroxy amide. After cooling, the solution was treated portionwise with a solution of 240 g. of sodium hydroxide in 400 ml. of water. The liberated base was extracted with 1.6 l. of ether (in two portions). The organic layers were combined, washed with 500 ml. of water and dried over magnesium sulfate. After standing overnight, the solution was treated with Darco, filtered, and the solvent evaporated to yield 514 g. (91%) of a pale red sirupy liquid. This material was suitable, without further purification,

for conversion to the compounds 6, 7, 8, 9, 10 and 11 of Table I.

**N-(2-Diethylaminoethyl)-N-methylbenzylamide Methochloride.**—A solution of 656 g. (1.9 moles) of the above N-(2-diethylaminoethyl)-N-methylbenzylamide in 2 l. of acetonitrile was cooled and treated with 300 g. (5.9 moles) of methyl chloride gas. The product slowly crystallized from the reaction mixture. After standing for four days at room temperature, the colorless product was filtered and dried; weight 610 g. Concentration of the filtrate to about one-half the volume, followed by cooling, yielded an additional 57 g. (total yield 89%) of pure material.

A similar yield of product was obtained when a methanol solution of the base and methyl chloride was heated at 100° in a closed vessel for six hours.

NEW BRUNSWICK, N. J.

[CONTRIBUTION NO. 937 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

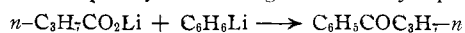
## The Reactions of Certain Fluorinated and Chlorinated Acetic Acids with Phenyllithium in Refluxing Ether<sup>1</sup>

By THOMAS F. McGRATH<sup>2</sup> AND ROBERT LEVINE

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The addition of trifluoroacetic acid to two or more equivalents of phenyllithium in refluxing ether gave none of the expected trifluoroacetophenone. Instead, some or all of the following cleavage products were obtained: benzoic acid, benzophenone, triphenylmethane and tetraphenylethylene. It is suggested that the trifluoroacetic acid is cleaved by phenyllithium to carbon dioxide and fluoroform and these compounds react with phenyllithium to give the observed products. Evidence in support of this scheme is given. The same products are obtained when trichloroacetic acid is treated with phenyllithium, while a mixture of benzophenone and 1,1-diphenylethanediol (49%) is obtained from the reaction of chloroacetic acid and phenyllithium.

In 1933, Gilman and VanEss<sup>3</sup> reported that ketones can be prepared by treating the lithium salts of carboxylic acids with alkyl- and aryl lithium compounds. Thus, the reaction of lithium *n*-butyrate with phenyllithium gives *n*-butyrophenone



in 62% yield. This reaction has been extended by several other workers<sup>4–6</sup> and it has been found that ketones may be prepared in good yields by the reaction of carboxylic acids with at least two equivalents of an organolithium compound.

It seemed that the Gilman-VanEss<sup>3</sup> method might be used to synthesize a series of alkyl and aryl perfluoroalkyl ketones. However, when lithium trifluoroacetate was added to an equivalent of phenyllithium in refluxing ether, none of the desired trifluoroacetophenone was obtained. Instead, a mixture of benzoic acid and benzophenone was isolated.

Therefore, the course of the reaction between trifluoroacetic acid and phenyllithium was investigated. The addition of trifluoroacetic acid to one equivalent of an ether solution of phenyllithium gave, on hydrolysis, a mixture of benzene and the trifluoroacetic acid-water azeotrope. However, when the molar ratio of base to acid was 2:1 or greater a mixture of some or all of the following products was obtained: benzoic acid, benzophe-

none, triphenylmethane, tetraphenylethylene, benzene and biphenyl. These results are summarized in Table I.

TABLE I  
REACTIONS OF TRIFLUORO- AND TRICHLOROACETIC ACID WITH PHENYLITHIUM IN REFLUXING ETHER

Moles of base/acid	RCO <sub>2</sub> H		Products, mole <sup>a</sup>			
	RCO <sub>2</sub> H	RCOR	R <sub>3</sub> CH	R <sub>2</sub> C=CR <sub>2</sub>	RH	RR
1	0	0	0	0	0.86 <sup>b</sup>	0
2	.16	.16	.06	.02	°	.02
3	.08	.19	.06	.02	°	.04
4	0	.52	.08	.04	°	.16
	0 <sup>d</sup>	.18 <sup>d</sup>	.09 <sup>d</sup>	.03 <sup>d</sup>	°	.05 <sup>d</sup>
5	0	.52	.09	.06	°	.18
	0 <sup>d</sup>	.24 <sup>d</sup>	.13 <sup>d</sup>	.04 <sup>d</sup>	°	.08 <sup>d</sup>
7	0	.36	.21	.06	°	.20

<sup>a</sup> R = C<sub>6</sub>H<sub>5</sub>; data based on one mole of halogenated acid. <sup>b</sup> CF<sub>3</sub>CO<sub>2</sub>H-H<sub>2</sub>O azeotrope also isolated. <sup>c</sup> RH not isolated quantitatively. <sup>d</sup> CCl<sub>3</sub>CO<sub>2</sub>H used; in all other runs CF<sub>3</sub>CO<sub>2</sub>H was used.

The reaction cannot be explained by a simple scheme involving the cleavage of trifluoroacetophenone by phenyllithium since this scheme does not account for the formation of benzoic acid and since an authentic sample of trifluoroacetophenone<sup>7</sup> gives diphenyltrifluoromethylcarbinol in 93% yield on treatment with phenyllithium. Furthermore, the cleavage of phenyl trityl ketone,<sup>8</sup> conceivably formed from trifluoroacetic acid *via* lithium triphenylacetate, cannot be involved since this ketone is neither formed when triphenylacetic

(1) Part of this work was performed under Contract No. AT(30-1)-970 between the U. S. Atomic Energy Commission and the University of Pittsburgh.

(2) Monsanto Chemical Company Fellow, 1953–1954.

(3) H. Gilman and P. R. VanEss, *THIS JOURNAL*, **55**, 1258 (1933).

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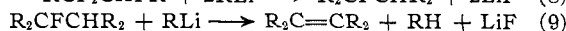
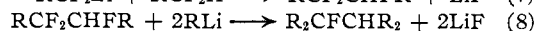
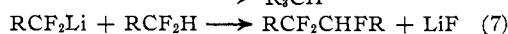
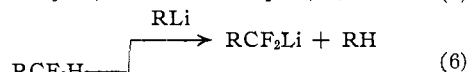
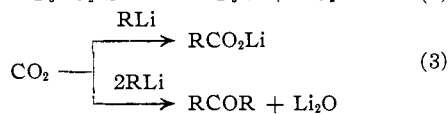
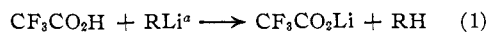
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acid<sup>9,10</sup> is treated with an excess of phenyllithium nor is it cleaved by phenyllithium under the conditions used in our experiments.

The following scheme satisfactorily explains the origin of the reaction products and evidence in its behalf is available



<sup>a</sup> R = C<sub>6</sub>H<sub>5</sub>

Evidence for step 1 was presented earlier in this discussion. Equation 2 indicates that phenyllithium effects the decarboxylation of lithium trifluoroacetate to lithium trifluoromethide and carbon dioxide. The lithium trifluoromethide then abstracts a proton from the ether solvent to give fluoroform (step 4) while the carbon dioxide reacts with phenyllithium (step 3) to give benzoic acid and benzophenone as has been demonstrated earlier by Gilman and VanEss.<sup>3</sup> It should be pointed out that Henne, *et al.*,<sup>11</sup> and La Zerte, *et al.*,<sup>12</sup> have shown that the sodium salts of perfluorinated acids are decarboxylated to fluorocarbon hydrides when heated in protonic solvents. These reactions might well proceed *via* organosodium intermediates.

Furthermore, Haszeldine<sup>13</sup> and Henne and Francis<sup>14</sup> have reported that Grignard reagents containing perfluoroalkyl groups, *e.g.*, *n*-C<sub>3</sub>F<sub>7</sub>MgI, react with ether at room temperature to give a mixture of a fluorocarbon hydride and a perfluorinated olefin.



More recently McBee and co-workers<sup>15</sup> have found that, although the low temperature halogen-metal interchange reaction between perfluoro-*n*-propyl iodide and methylithium in ether gives a high yield of perfluoro-*n*-propyllithium, refluxing the solution results in the conversion of this organometallic to hexafluoropropene in 97% yield. These workers<sup>15</sup>

(9) C. R. Hauser and W. B. Renfrow, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(10) R. Levine, E. Baumgarten and C. R. Hauser, *THIS JOURNAL*, **66**, 1230 (1944).

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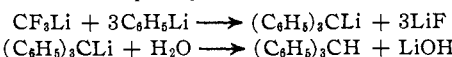
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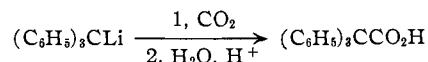
(14) A. L. Henne and W. C. Francis, *THIS JOURNAL*, **75**, 992 (1953).

(15) O. R. Pierce, E. T. McBee and G. F. Judd, *ibid.*, **76**, 474 (1954).

also have found that apparently lithium trifluoromethide cannot be prepared by the halogen-metal interchange method.<sup>16</sup> Therefore, if lithium trifluoromethide is actually formed in the trifluoroacetic acid-phenyllithium reaction, it is not unlikely that it will react with ether, especially at its reflux temperature, to give fluoroform. Further evidence for step 4 was obtained by carbonating the reaction mixture from one equivalent of trifluoroacetic acid and five equivalents of phenyllithium prior to hydrolysis. Theoretically, the triphenylmethane could be formed not only from fluoroform (steps 5 and 6) but also from lithium trifluoromethide *via* lithium triphenylmethide.



If lithium triphenylmethide were present then carbonation should convert it to triphenylacetic acid.



However, no triphenylacetic acid was obtained in this reaction. Only the cleavage products and a large amount of benzoic acid, formed by the carbonation of the excess phenyllithium, were isolated.

Steps 5-9 indicate that both triphenylmethane and tetraphenylethylene arise from the interaction of fluoroform and phenyllithium. This scheme was shown to be plausible by bubbling fluoroform through phenyllithium and obtaining approximately the same yields of triphenylmethane (16%) and tetraphenylethylene (17%). Further evidence for steps 5 and 6 would be available if the observed products could be obtained by treating benzal fluoride with phenyllithium. However, since this halide is apparently not commercially available and our attempts to prepare it failed, the reaction between benzal chloride and phenyllithium was studied instead<sup>17</sup> and from the reaction of this halide with two equivalents of phenyllithium a mixture of triphenylmethane (5%) and tetraphenylethylene (20%) was obtained.

As may be seen in Table I, trichloroacetic acid behaved similarly to trifluoroacetic acid when treated with phenyllithium. The reaction of dichloroacetic acid with phenyllithium gave only a tarry mixture from which it was impossible to isolate any pure products. However, from the reaction of chloroacetic acid with phenyllithium there was obtained a small amount of the cleavage product, benzophenone, and a 49% yield of 1,1-diphenylethanediole. This glycol, which probably was formed by the reaction of three moles of phenyllithium with one of the acid followed by the replace-

(16) Since one of the products of this reaction is tetrafluoroethylene, it might appear that in our study the tetraphenylethylene was formed from the reaction of tetrafluoroethylene with phenyllithium. However, when tetrafluoroethylene was treated with phenyllithium, no tetraphenylethylene was obtained (unpublished observations from this Laboratory).

(17) In this connection we have found that the reaction of chloroform with phenyllithium also gives a mixture of triphenylmethane and tetraphenylethylene. Furthermore, G. Wittig and H. Witt (*Ber.*, **74**, 1474 (1941)) have treated benzyl fluoride and benzyl chloride with phenyllithium. From the former reaction a mixture of 1,1,2-triphenylethane and diphenylmethane was obtained, while the latter reaction gives 1,1,2-triphenylethane.

ment of the chlorine atom by a hydroxyl group during hydrolysis, was not an entirely unexpected product since Peters, *et al.*,<sup>18</sup> obtained it in an unreported yield from the reaction of chloroacetic acid with seven equivalents of phenylmagnesium bromide.

### Experimental

**Phenyllithium.**—The phenyllithium used in all the following reactions was an approximately one molar solution in anhydrous ether and was prepared from bromobenzene and lithium ribbon.

**Reaction of Equivalents of Phenyllithium with Lithium Trifluoroacetate.**—Solid lithium trifluoroacetate (12.0 g., 0.1 mole) was added to phenyllithium (0.1 mole) with rapid stirring and the mixture then refluxed for two hours. The reaction was quenched by being poured onto a mixture of ice and concentrated hydrochloric acid and extracted several times with ether. The combined extracts were dried over Drierite and the solvent and low boiling materials were removed at atmospheric pressure. Vacuum distillation of the residue gave 3.0 g. of material, b.p. 99–105° at 1 mm., which, on processing, gave 1.0 g. of benzoic acid, m.p. 120–121° alone and when mixed with an authentic sample, and 1.8 g. of benzophenone, m.p. 48.2–48.8°; 2,4-dinitrophenylhydrazone, m.p. 238–239°.<sup>19</sup>

**Reactions of Phenyllithium with Trifluoroacetic Acid.**  
(A) **Equivalents of Base and Acid.**—Trifluoroacetic acid (22.8 g., 0.2 mole), dissolved in 75 ml. of anhydrous ether, was added dropwise with rapid stirring to phenyllithium (0.2 mole). During the addition of the acid the ether refluxed rapidly. After the spontaneous refluxing ceased, the mixture, which was originally red in color and had turned to yellow, was refluxed for two hours longer and then processed to give 13.5 g. (86%) of benzene, b.p. 78–80°, and identified as *m*-dinitrobenzene, m.p. 88–89°, and 17.4 g. of the trifluoroacetic acid–water azeotrope, b.p. 104–106°.<sup>20</sup>

(B-1) **Five Equivalents of Base and One of Acid.**—Experiment A was repeated except that 57.0 g. (0.5 mole) of trifluoroacetic acid was added dropwise (3–4 hours) to 2.5 moles of phenyllithium. After distilling the low boiling materials at atmospheric pressure, the semi-solid, tarry residue was distilled in vacuum using the previously described<sup>21</sup> apparatus for the distillation of solids. In this way the following compounds were obtained (boiling points are at 2 mm. and mixed melting points between each compound and an authentic sample showed no depression): diphenyl (14.5 g., 0.09 mole, b.p. 97–100°, m.p. 68–69° (from 60–70° petroleum ether)); benzophenone (47.7 g., 0.26 mole, b.p. 125–127°, m.p. 48–48.8° (from 95% ethanol)); triphenylmethane (10.5 g., 0.045 mole, b.p. 175–177°, m.p. 93–93.4° (from 95% ethanol)) and tetraphenylethylene (9.96 g., 0.03 mole, b.p. 184–186°, m.p. 223.6–224.2° (from 95% ethanol)). The tetraphenylethylene was characterized further by elemental analysis (Calcd. for C<sub>24</sub>H<sub>20</sub>: C, 93.98; H, 6.02. Found: C, 93.96; H, 6.04) and by its ultraviolet spectrum.<sup>22</sup> A large amount of non-distillable tarry material, probably polymerized tetraphenylethylene, remained in the distillation flask.

(18) F. N. Peters, E. Griffith, D. R. Briggs and H. E. French, *THIS JOURNAL*, **47**, 449 (1925).

(19) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

(20) Technical Bulletin on Trifluoroacetic Acid, Minnesota Mining and Manufacturing Co.

(21) L. B. Barkley, J. K. Sneed, T. F. McGrath and R. Levine, *J. Chem. Ed.*, **30**, 115 (1953).

(22) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum 160.

(B-2) **Five Equivalents of Phenyllithium and One of Trichloroacetic Acid.**—When experiment B-1 was repeated except that 40.8 g. (0.25 mole) of trichloroacetic acid, dissolved in 150 ml. of ether, was added to 1.25 moles of phenyllithium, there was obtained a mixture of biphenyl (3.1 g., 0.02 mole), benzophenone (10.8 g., 0.06 mole), triphenylmethane (8.0 g., 0.03 mole), tetraphenylethylene (3.1 g., 0.01 mole) and 15 g. of a non-distillable tar.

(B-3) **Five Equivalents of Phenyllithium and One of Trifluoroacetic Acid Followed by Carbonation.**—Experiment B-1 was repeated except that after the two-hour reflux period the reaction mixture was poured onto a slurry of Dry Ice in absolute ether. After the excess Dry Ice had evaporated, water was added to dissolve the lithium salts which were present and the ether and alkaline aqueous phases then separated. From the ether phase there was isolated a mixture of biphenyl (8.2 g., 0.05 mole), benzophenone (47.3 g., 0.26 mole), triphenylmethane (9.5 g., 0.04 mole) and tetraphenylethylene (8.2 g., 0.03 mole). Acidification of the basic phase with concentrated hydrochloric acid gave benzoic acid (100.1 g., 0.84 mole). Apparently no triphenylacetic acid was formed in this reaction.

**Reaction of Phenyllithium with Fluoroform.**—Fluoroform<sup>23</sup> (35.0 g., 0.5 mole) was bubbled into 2.5 moles of a rapidly stirred solution of phenyllithium over a three-hour period. During this reaction, the water-cooled condenser of the reactor was replaced by a Dry Ice condenser. Then the reaction mixture was refluxed for an additional two hours and processed in the regular manner to give biphenyl (9.5 g., 0.06 mole), triphenylmethane (19.1 g., 16%), tetraphenylethylene (13.7 g., 17%) and 10 g. of non-distillable tar.

**Reaction of Phenyllithium with Benzal Chloride.**—Benzal chloride<sup>24</sup> (16.1 g., 0.1 mole), dissolved in 100 ml. of anhydrous ether, was added dropwise to 0.2 mole of phenyllithium. After the halide was added, the mixture was stirred and refluxed for two hours and then processed to give triphenylmethane (1.2 g., 5%), tetraphenylethylene (3.3 g., 20%) and 15 g. of non-distillable tar.

**Reaction of Phenyllithium with Chloroacetic Acid.**—Chloroacetic acid (31.5 g., 0.33 mole), dissolved in 125 ml. of anhydrous ether, was added dropwise to 1.0 mole of phenyllithium. Then the mixture was refluxed for two hours and processed to give benzophenone (2.6 g., 0.01 mole) and 34.7 g. (49%) of 1,1-diphenylethanediol, m.p. 121–121.4° (from 60–70° petroleum ether).<sup>25</sup> *Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>: C, 78.50; H, 6.54. Found: C, 78.58; H, 6.47. This glycol gave a diacetate, m.p. 145–146° (from 95% ethanol).<sup>26</sup> *Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>: C, 72.48; H, 6.12. Found: C, 72.19; H, 6.08.

**The Preparation of Diphenyltrifluoromethylcarbinol.**—Trifluoroacetophenone<sup>7</sup> (34.8 g., 0.2 mole), dissolved in 100 ml. of anhydrous ether, was added to 0.2 mole of phenyllithium over a one-hour period. The mixture then was stirred at room temperature for two hours, poured onto a mixture of ice and concentrated hydrochloric acid and extracted with several portions of ether. The combined ethereal extracts were dried over Drierite, the solvent removed and the residue distilled in vacuum to give 46.8 g. (93%) of diphenyltrifluoromethylcarbinol, b.p. 109–110° at 1.5 mm., m.p. 74–74.7° (from 60–70° petroleum ether).<sup>7</sup>

**Acknowledgment.**—The authors wish to thank Professor Henry S. Frank for participating in discussions during the course of this study.

### PITTSBURGH 13, PENNSYLVANIA

(23) Samples of fluoroform were kindly supplied by Minnesota Mining and Manufacturing Co., and E. I. du Pont de Nemours and Co., Inc.

(24) A sample of this halide was kindly supplied by the Heyden Chemical Co.

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