

Metathetical Reactions of Silver Salts in Solution.

I. The Synthesis of Acyl Trifluoroacetates¹

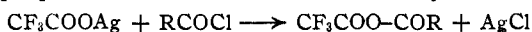
BY ARTHUR F. FERRIS AND WILLIAM D. EMMONS

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Recently it has been shown that an equimolar mixture of trifluoroacetic anhydride and a carboxylic acid is an extremely active acylating medium.² This high order of reactivity has been ascribed to the *in situ* formation of an acyl trifluoroacetate. Although cryoscopic evidence for the existence of this unsymmetrical anhydride has been obtained, an attempt to isolate acetyl trifluoro-

$$\text{CF}_3\text{CO-O-CO-CF}_3 + \text{RCOOH} \longrightarrow \text{CF}_3\text{COOCOR} + \text{CF}_3\text{COOH}$$

acetate by distillation of a trifluoroacetic anhydride-acetic acid mixture was unsuccessful.³ Anhydrides of this type have, however, been prepared in this laboratory by the metathetical reaction of silver trifluoroacetate in ether with the appropriate acid chloride. Mixed anhydrides ob-



tained in this manner were benzoyl trifluoroacetate (80% yield), furoyl trifluoroacetate (64% yield), phenylacetyl trifluoroacetate (58% yield), *o*-methoxybenzoyl trifluoroacetate (44% yield) and lauroyl trifluoroacetate (59% yield). The structures of these anhydrides are assigned on the basis of elemental analysis, saponification equivalents, infrared spectra, and their unequivocal method of synthesis.

In order to obtain satisfactory yields of these compounds, it was necessary to flash distil them.

It is possible that traces of silver trifluoroacetate may serve as a catalyst for this interchange reaction, since after an initial flash distillation the aroyl trifluoroacetates have been found sufficiently stable for conventional distillation. Usual distillation procedures applied to lauroyl and phenylacetyl trifluoroacetates caused significant losses of product, however. The effectiveness of flash distillation in purification of these anhydrides is illustrated by the fact that when phenylacetyl trifluoroacetate was distilled initially in the conventional manner only a 13% yield was obtained; the chief product in this case was, of course, phenylacetic anhydride. With some acid chlorides, the interchange reaction took place so readily that only the symmetrical anhydride could be isolated; thus, *o*- and *p*-chlorobenzoyl chlorides gave *o*- and *p*-chlorobenzoic anhydrides, respectively.

Investigation of these interesting compounds is currently underway. Acyl trifluoroacetates are extremely reactive and, indeed, drops of the anhydrides are hydrolyzed completely by standing in contact with moist air for even a few seconds. It has been suggested that these anhydrides react with most species by a mechanism involving prior ionization to form oxo-carbonium ions.⁵ The availability of pure samples of acyl trifluoroacetates should permit this hypothesis to be tested unequivocally.

Experimental⁶

The procedure for the preparation of the five acyl trifluoroacetates was essentially identical except as indicated in Table I, and has been described specifically for benzoyl trifluoroacetate. The properties of the anhydrides are summarized in Table I. All boiling points are uncorrected.

TABLE I

| R- | Yield, ^a % | Flash distillation | | B.p., ^c | | n _D ²⁰ | Frequency of carbonyl bands, cm. ⁻¹ | Carbon, % | | Hydrogen, % | | Saponification equivalents | |
|--|--------------------------|-----------------------|-----|--------------------|-----|------------------------------|--|-----------|-------|-------------|-------|-------------------------------|--------------------|
| | | °C. ^b | Mm. | °C. | Mm. | | | Calcd. | Found | Calcd. | Found | Calcd. | Found ^d |
| C ₆ H ₅ - | 80 | 120 | 1.0 | 57-58 | 1.7 | 1.4524 | 1845, 1773 | 49.55 | 50.13 | 2.31 | 2.53 | 109.1 | 107.3 |
| <i>o</i> -CH ₂ OC ₆ H ₅ - | 44 | 120 | 0.7 | 83-84 | 0.4 | 1.4717 | 1835, 1773 | 48.40 | 48.44 | 2.84 | 3.03 | 124.1 | 123.5 |
| C ₆ H ₅ O- | 64 | 115 | 1.0 | 42-43 | .6 | 1.4310 | 1838, 1775 | 40.24 | 41.26 | 1.45 | 1.30 | 104.0 | 103.5 |
| C ₆ H ₄ CH ₂ - | 58 | 115 | 0.5 | 57-58 | .3 | 1.4445 | 1860, 1792 | 51.73 | 51.99 | 3.04 | 3.17 | 116.1 | 114.2 |
| CH ₂ (CH ₂) ₁₀ - | 59 | 145 | 0.3 | 90-91 ^e | .05 | 1.4039 | 1859, 1787 | 56.74 | 57.12 | 7.82 | 7.85 | 148.2 | 144.9 |

^a Flash distilled product. ^b External pot temperature. ^c In conventional distillation apparatus. ^d Averages of two or more determinations. ^e M.p. 12-14°.

Otherwise anhydride interchange took place to a



considerable extent, and the principal product isolated was the symmetrical carboxylic acid anhydride.⁴ All of the acyl trifluoroacetates prepared here were chosen so that separation of the product from the two symmetrical anhydrides was facilitated by large differences in boiling points between each of the three components of the reaction mixture. Conditions for flash distillation were established so that the high molecular weight symmetrical anhydrides remained in the distillation flask.

(1) This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

(3) P. W. Morgan, *This Journal*, 78, 860 (1951).

(4) A. R. Emery and V. Gold, *J. Chem. Soc.*, 1448 (1950).

Benzoyl Trifluoroacetate.—A solution of 28.1 g. of benzoyl chloride in 50 ml. of anhydrous ether was added to 42.8 g. of silver trifluoroacetate⁷ dissolved in 200 ml. of ether. A vigorous exothermic reaction occurred, and silver chloride separated rapidly from solution. After 30 minutes the theoretical amount of silver chloride was collected on a filter, and the solvent was removed from the filtrate under reduced pressure. The light brown liquid residue was flash distilled at 1.0 mm. and an external pot temperature of 120°. The colorless distillate amounted to 33.9 g. (80%). This material was redistilled in conventional apparatus; b.p. 57-58° (1.7 mm.), yield 30.9 g. The refractive index had not changed significantly after the benzoyl trifluoroacetate had stood a week at room temperature. The infrared spectrum of the compound showed very sharp anhydride carbonyl bands at 1845 cm.⁻¹ and 1773 cm.⁻¹.

(5) E. J. Bourne, E. B. Randles, T. C. Tatlow and J. M. Tedder, *Nature*, 168, 942 (1951).

(6) We are indebted to Dr. Keith S. McCallum for infrared interpretations and to Mr. Al Kennedy and Miss Annie Smelley for micro-combustions and saponification equivalents.

(7) R. N. Hazeldine, *J. Chem. Soc.*, 584 (1951).

Trifluoroacetic anhydride itself shows bands at 1880 cm^{-1} and 1815 cm^{-1} . The absence of these higher frequency bands in the distilled product is further evidence for the structure and purity of benzoyl trifluoroacetate.

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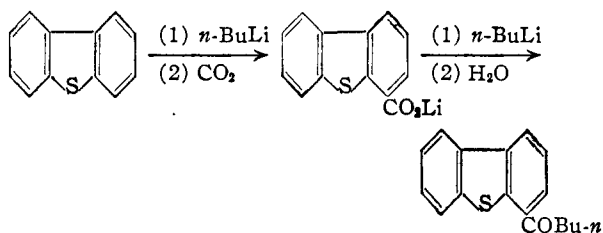
n-Butyl 4-Dibenzothiényl Ketone: A Carbonation By-product from the Metalation of Dibenzothiophene with *n*-Butyllithium

BY HENRY GILMAN AND DONALD L. ESMAY

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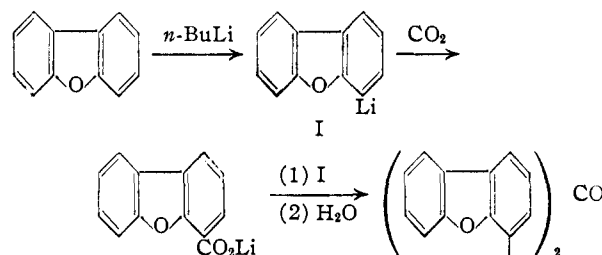
The reaction of organolithium compounds with carbon dioxide may yield, subsequent to hydrolysis and acidification, acids, ketones or tertiary alcohols.¹ The product obtained depends upon the type of RLi used and the reaction conditions employed. Pouring the solution of the organolithium derivative jetwise onto solid carbon dioxide (or a slush of ether and Dry Ice²) or spraying the organometallic compound into an atmosphere of gaseous carbon dioxide provides a high local concentration of carbon dioxide and thereby leads to high yields of the corresponding carboxylic acid salt. Even under these conditions, however, the secondary reaction which yields a ketone may be of some importance, and if the carbonation is carried out slowly, ketone formation often predominates. It is generally agreed that the reaction of an RLi compound with carbon dioxide probably gives first the acid salt, RCOOLi, which, in the presence of a local excess of the organolithium compound, may react further to give the dilithium salt of a dihydroxymethane, $\text{R}_2\text{C}(\text{OLi})_2$. This view finds support in previous work¹ which showed that the preformed lithium salt of an acid, RCOOLi, reacted with an organolithium compound, R'Li, to give excellent yields of the ketone, RCOR' (R and R' may be the same, or different).

We are reporting the identification of *n*-butyl-4-dibenzothiényl ketone as one of the products obtained during the preparation of 4-dibenzothiophenecarboxylic acid by carbonation of the reaction mixture obtained from the metalation of dibenzothiophene with *n*-butyllithium in ether.³ Since an

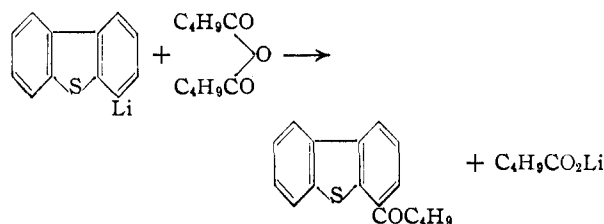


excess of *n*-butyllithium was used for the metalation, the unsymmetrical ketone was not a wholly unexpected by-product, although its isolation was somewhat surprising in view of the fact that the symmetrical di-4-dibenzofuryl ketone was isolated during the analogous preparation of 4-dibenzo-

furancarboxylic acid.⁴ In all probability, some di-4-dibenzothiényl ketone was also formed, even though none was isolated. No special search was made for the symmetrical ketone, however.



The structure of our compound was established by comparing its properties with those of an authentic specimen of *n*-butyl 4-dibenzothiényl ketone prepared by the reaction of 4-dibenzothiényllithium with *n*-valeric anhydride.⁵ A mixed melt-



ing point of the two compounds was not depressed, and, in addition, their 2,4-dinitrophenylhydrazones possessed identical properties.

Experimental⁶

Dibenzothiophene (44.9 g., 0.24 mole) was metalated with *n*-butyllithium⁷ (0.449 mole) by following the procedure previously reported from this Laboratory.³ Carbonation was effected by pouring the organolithium solution jetwise onto solid carbon dioxide. Hydrolysis and filtration gave 3.7 g. (5.7%) of an ether- and alkali-insoluble material melting at 109–113°. Recrystallization from ethanol yielded 3.1 g. (4.7%) of pure product, m.p. 116–117°. In the only other run in which an attempt was made to isolate the by-product quantitatively, a 2.6% yield of pure material melting at 116–117° was obtained. A mixed m.p. of the two compounds showed no depression. Varying quantities of the ketone were obtained from other, similar preparations.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{OS}$: S, 11.95. Found: S, 11.60, 11.74.

In order to establish that the compound was a ketone, the 2,4-dinitrophenylhydrazone was prepared.⁸ The small orange needles melted at 270–271° after recrystallization from chloroform.

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_4\text{N}_4\text{S}$: S, 7.15. Found: S, 6.92.

Two attempts to prepare the phenylhydrazone yielded an oil which could not be made to crystallize.

An authentic sample of *n*-butyl 4-dibenzothiényl ketone was prepared in low yield by treating an ether solution of *n*-valeric anhydride with an ether solution of 4-dibenzothiényllithium⁹ at -70° .⁵ The compound melted at 116–117°, and a mixed melting point with the carbonation by-product showed no depression. In addition, the 2,4-dinitrophenylhydrazone was prepared and found to agree in

(4) H. Gilman, M. W. Van Ess and D. M. Hayes, *ibid.*, **61**, 643 (1939).

(5) M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).

(6) All melting points are uncorrected.

(7) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *THIS JOURNAL*, **71**, 1499 (1949).

(8) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

(1) H. Gilman and P. R. Van Ess, *THIS JOURNAL*, **55**, 1258 (1933).
(2) H. Gilman and S. M. Spatz, *ibid.*, **63**, 1553 (1941); H. Gilman and J. A. Beel, *ibid.*, **71**, 2328 (1949).
(3) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); H. Gilman and J. F. Nobis, *THIS JOURNAL*, **67**, 1479 (1945).