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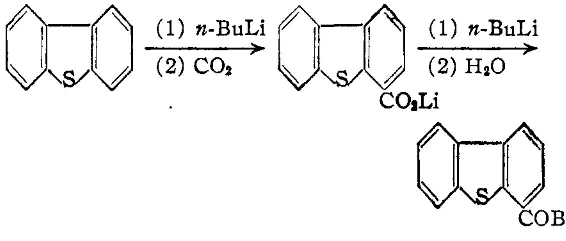
n-Butyl 4-Dibenzothienyl Ketone: A Carbonation By-product from the Metalation of Dibenzothiophene with *n*-Butyllithium

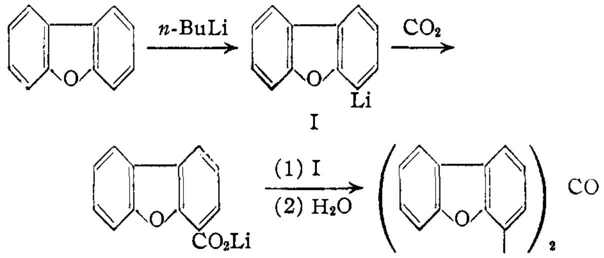
BY HENRY GILMAN AND DONALD L. ESMAY

RECEIVED SEPTEMBER 19, 1952

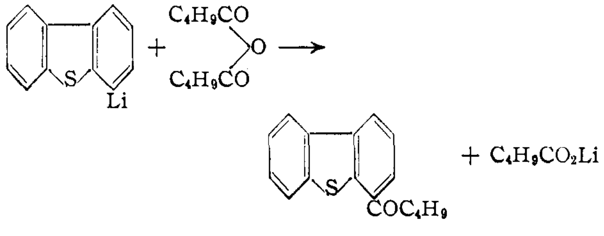
The reaction of organolithium compounds with carbon dioxide may yield, subsequent to hydrolysis and acidification, acids, ketones or tertiary alcohols.[1] The product obtained depends upon the type of RLi used and the reaction conditions employed. Pouring the solution of the organolithium derivative jetwise onto solid carbon dioxide (or a slush of ether and Dry Ice[2]) 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, $R_2C(OLi)_2$. This view finds support in previous work[1] 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-dibenzothienyl 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-dibenzofurancarboxylic acid.[4] In all probability, some di-4-dibenzothienyl 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-dibenzothienyl ketone prepared by the reaction of 4-dibenzothienyllithium with *n*-valeric anhydride.[5] A mixed melting point of the two compounds was not depressed, and, in addition, their 2,4-dinitrophenylhydrazones possessed identical properties.



Experimental[6]

Dibenzothiophene (44.9 g., 0.24 mole) was metalated with *n*-butyllithium[7] (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 $C_{17}H_{16}OS$: 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 $C_{23}H_{20}O_4N_4S$: 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-dibenzothienyl ketone was prepared in low yield by treating an ether solution of *n*-valeric anhydride with an ether solution of 4-dibenzothienyllithium[3] 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

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(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).

(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.

properties with those of the corresponding hydrazone of the by-product. A mixture of the two hydrazones showed no depression in the melting point.

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The Addition of Triphenylsilylpotassium to *trans*-Stilbene

BY HENRY GILMAN AND T. C. WU

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Incidental to a study of the properties of organosilicon-metallic compounds, we have observed that triphenylsilylpotassium adds to *trans*-stilbene to give β-triphenylsilyl-α,β-diphenylethylpotassium which on hydrolysis yields triphenyl-α,β-diphenylethylsilane [I].

$$(C_6H_5)_3SiK + C_6H_5CH{=}CHC_6H_5 \longrightarrow$$

$$(C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)K \xrightarrow{H_2O} (C_6H_5)_3SiCH(C_6H_5)CH_2(C_6H_5) \quad (I)$$

The yield of pure [I] was 55% when a solution of 3.6 g. (0.02 mole) of *trans*-stilbene in 50 ml. of benzene was added to a triphenylsilylpotassium suspension prepared[1] by cleaving 5.2 g. (0.01 mole) of hexaphenyldisilane with sodium-potassium alloy in ether, after removing the excess alloy by amalgamation. During the addition of *trans*-stilbene to the triphenylsilylpotassium the mixture changed in color from brownish-tan to deep brownish-red. After stirring the reaction mixture for 30 minutes at room temperature hydrolysis was effected by the slow addition of water. The organic layer was dried over sodium sulfate and the solvents were removed by distillation. The residue was recrystallized three times from petroleum ether (b.p. 60–70°) to give 4.8 g. (55%) of colorless granular crystals melting at 135–136°. *Anal.* Calcd. for $C_{32}H_{28}Si$: Si, 6.37. Found: Si, 6.40, 6.41. In another experiment the triphenylsilylpotassium suspension was added to the benzene solution of *trans*-stilbene to give a 39% yield of pure [I]. A like yield was obtained under these latter conditions when the reaction time was 24 hours.

This reaction which indicates a high order of reactivity of organometallic compounds is being extended to other organosilicon-metallic[2] compounds and other unsaturated systems like those containing the azomethylene, azo and carbonyl groups.

(1) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, THIS JOURNAL, **74**, 561 (1952).

(2) It will be interesting to observe whether related high orders of reactivity will be shown by other types having the generalized formula R_nMM' where M is a metal or metalloid and where M' is an alkali or alkaline earth metal.

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Decaethylcyclopentasiloxane

BY DALLAS T. HURD AND ROBERT C. OSTHOFF

RECEIVED SEPTEMBER 4, 1952

In the course of preparing a series of diethylsiloxanes, we have observed that the cyclic pentamer, *i.e.*, decaethylcyclopentasiloxane, is a solid. This was not anticipated; the minimum in the melting points of the known cyclic dimethylsiloxanes occurs with the pentamer and the observed melting points of the cyclic trimer and tetramer compounds are lower in the diethyl series than in the dimethyl series as shown in Table I.

TABLE I

MELTING POINTS OF CYCLIC DIORGANOSILOXANES

No. of Si atoms	M.p., °C. Dimethyl series[1]	Diethyl series
3	65	14
4	17.5	−50
5	−38	38
6	− 3	
7	−26	
8	31.5	

Attempts to obtain cyclic diethylsiloxanes beyond the pentamer compound were not successful (*v.i.*).

The cyclic pentamer of diethylsiloxane was studied in some detail. The compound is a soft transparent solid having the consistency of a very soft wax. It did not exhibit any liquid flow at room temperature and a sharp impression made in the soft solid with a needle showed no evidence of closure over a period of a week at normal room temperature. The material could, however, be extruded under slight pressure.

It is well known that molecules with near spherical symmetry can rotate (hindered) in the solid state and that this strongly affects the physical properties of such substances.[2] In particular, the heat and entropy of fusion are low, the melting point anomalously high and the phase between the melting and solid state transition points is clear (frequently isotropic) and of a waxy texture. It is believed that the physical properties of several of the siloxanes studied here are affected by the aforementioned molecular rotation in the solid state. For example, the freezing point of decaethylcyclopentasiloxane is very sensitive to impurities; this implies a high freezing point depression constant and hence a low heat of fusion. Decaethylcyclopentasiloxane is a clear solid near the melting point. Evidence of solid state transition points, although not specifically sought in this study, has been observed with various silicone compounds.[3] A definite first-order transition at −17.30° has been found in octamethylcyclotetrasiloxane (m.p. 17.538°), which has a low heat of fusion.[4]

Anal. Calcd. for decaethylcyclopentasiloxane: Si, 27.50; C, 47.00; H, 9.87; mol. wt., 511. Found: Si, 27.46; C, 46.8; H, 9.80; mol. wt. (from cryoscopic measurements in cyclohexane), 495.

The measured physical properties are summarized in Table II.

(1) E. G. Rochow, "Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 185.

(2) W. O. Baker and C. P. Smyth, *Ann. N. Y. Acad. Sci.*, XL, 447 (1940).

(3) Private communication from S. W. Kantor of this Laboratory, 1952.

(4) This investigation has been carried out by John D. Hoffman of this Laboratory and will be published in detail in the near future.