

Measurement of the temperature at the sample is accurate to  $\pm 0.1^\circ$ .

Dicyclohexylcarbodiimide was purchased from Matheson Coleman and Bell, further purified by fractional distillation, and collected at bp  $150^\circ$  (11 mm) [lit. bp  $148\text{--}152^\circ$  (11 mm)].<sup>6</sup>

**Registry No.**—Dicyclohexylcarbodiimide, 538-75-0.

**Acknowledgment.**—We thank the Research Corporation (Frederick Gardner Cottrell Grant) and the National Science Foundation (COSIP Grant) for support of this work.

(6) A. Amiard and R. Heymes, *Bull. Soc. Chim. Fr.*, 1360 (1956).

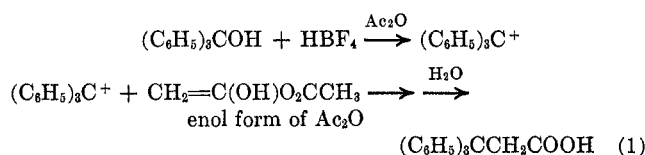
### The Alkylation of Acetic Anhydride by Triphenylmethyl Cation

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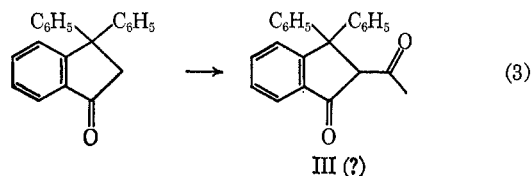
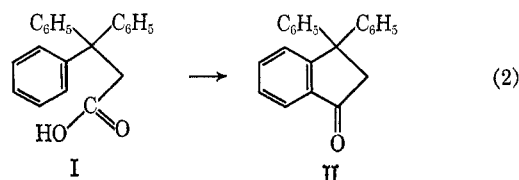
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A common method for preparing triphenylcarbonium ion salts is to add triphenylmethanol to acetic anhydride containing a strong acid such as  $\text{HBF}_4$ .<sup>1</sup> It was noticed that when such systems were allowed to stand, alkylation of acetic anhydride occurred, undoubtedly *via* traces of the enol form of acetic anhydride. The product was 3,3,3-triphenylpropionic acid (I), as shown in eq 1.



The reaction was briefly explored to determine its scope and limitations. The optimum yield was 50%, as shown in Table I. Higher yields are prevented by subsequent cyclization of I to 3,3-diphenylindanone (II, eq 2) and acylation of this to a compound that is probably 2-acetyl-3,3-diphenylindanone (III, eq 3).



The yields of I, II, and III as a function of time (Table I) indicate the sequence  $\text{I} \rightarrow \text{II} \rightarrow \text{III}$ .

The reaction is of interest as the first case of alkylation of acetic anhydride by a carbonium ion. It is also

(1) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

TABLE I  
PRODUCTS FROM THE REACTION OF  
 $(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$  WITH ACETIC ANHYDRIDE

Temp, °C	Time, hr	Yield, %			Recovered $(\text{C}_6\text{H}_5)_3\text{COH}$ , %
		I	II	III	
25	336	35			
50	1.0	31	0	0	69
	4.0	50	19	0	31
80	1.0	16	42	32	12
	4.0	2	18	76	3
100	0.5			55	
	1.0	1	30	69 <sup>a</sup>	0
	5.0			70	

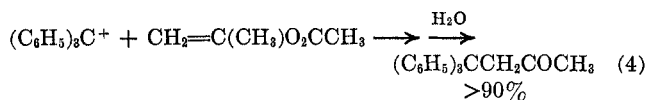
<sup>a</sup> Three identical runs gave yields of 62, 68, and 70%. Addition of 10% of 50% aqueous  $\text{HBF}_4$  gave a yield of 60%, so that added  $\text{HBF}_4$  does not seem to have much effect.

of interest as a side reaction to be avoided in the preparation of carbonium salts. Unfortunately, the scope seems quite limited and there are better ways of producing I.

In regard to scope, a variety of conditions with propionic and succinic anhydrides failed to produce an acidic carboxylic acid product. Thus, at the moment, the reaction is limited to acetic anhydride as the anhydride component. As for the carbonium ion component, presumably a variety of stable carbonium ions would have been successful in varying degrees, though this was not examined. In regard to the preparation of I, the alkylation of malonic acid with triphenylmethanol would be preferred.<sup>2,3</sup> We have also found that introduction of ketene<sup>4</sup> into a solution of  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$  in acetic anhydride followed by hydrolysis precipitates a >90% yield of I.

An attempt was made to alkylate acetone with  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$ . Even after 500 hr at  $25^\circ$  or  $75^\circ$  hr at  $55^\circ$ , no trace of 4,4,4-triphenyl-2-butanone was observed. The nmr would have detected a 2% yield. Mesityl oxide appeared from self-condensation of acetone. Triphenylmethanol was recovered and the recovery was in 96% yield from the  $25^\circ$  run.

4,4,4-Triphenyl-2-butanone was prepared in 90% yield by adding a solution of  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$  in  $\text{CH}_2\text{Cl}_2$  to isopropenyl acetate, letting the mixture stand for 10 hour, and hydrolyzing (eq 4). Curiously, addition of triphenylchloromethane to isopropenyl acetate failed to give any 4,4,4-triphenyl-2-butanone even after refluxing for 42 hr. Triphenylmethanol was recovered in 95% yield after hydrolysis.



The alkylation of acetic anhydride by  $(\text{C}_6\text{H}_5)_3\text{C}^+$  (eq 1) is closely related to the alkylation of malonic acid<sup>2,3</sup> and a variety of malonic acid derivatives<sup>3</sup> by  $(\text{C}_6\text{H}_5)_3\text{C}^+$ .

#### Experimental Section

All nmr spectra were recorded on solutions in  $\text{CH}_2\text{Cl}_2$  or  $\text{CCl}_4$  and are expressed in  $\delta$  ppm.

The acetic anhydride solutions of triphenylmethyl tetrafluoroborate were held under  $\text{N}_2$  as a precautionary measure.

(2) L. Hellerman, *J. Amer. Chem. Soc.*, **49**, 1737 (1927).

(3) S. Patai and S. Dayagi, *J. Chem. Soc.*, 716 (1962).

(4) Prepared by decomposition of acetone in a ketene lamp; J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

Triphenylmethyl tetrafluoroborate was prepared as described.<sup>1</sup> Separation of I from II and II from III after hydrolysis was based on the solubility of I and III in 5% aqueous NaOH. Where I and III occurred together, the relative amounts could be determined from the nmr spectrum of a solution of the mixture in CH<sub>2</sub>Cl<sub>2</sub>.

3,3,3-Triphenylpropionic acid (I) was identified by its melting point [179° (lit.<sup>2</sup> mp 178°)] and the nmr spectrum, which has been reported<sup>5</sup> and which was identical with an authentic sample.

3,3-Diphenylindanone (II) was identified by its melting point [131° (lit.<sup>6</sup> mp 132°)] and its nmr spectrum, which consisted of a singlet at  $\delta$  3.35 (CH<sub>2</sub>) and a sharp singlet at  $\delta$  7.27 (phenyls) superimposed on a broad multiplet at  $\delta$  6.8–7.6 (acylated benzene ring).

Although the structure of III was not rigorously established, the following data are reasonably indicative. The nmr spectrum consisted of singlets at  $\delta$  1.21 (CH), 1.73 (CH<sub>3</sub>), and 7.275 (phenyls). The  $\delta$  7.27 singlet is superimposed on a complex multiplet centered around  $\delta$  7.3, and there is another complex multiplet centered around  $\delta$  7.8. The two complex multiplets originate with the acyl-substituted ring. The areas were in the calculated ratios. Compound III dissolves in 5% NaOH and is precipitated by CO<sub>2</sub> in accord with the  $\beta$ -diketone structure. The infrared spectrum shows strong bands at 1600 and 1680 cm<sup>-1</sup> in accord with two different keto groups. The mass spectrum exhibited a parent peak at *m/e* 326 in accord with a molecular weight of 326 and a dominant band at *m/e* 43 indicative of CH<sub>3</sub>CO<sup>+</sup> and a CH<sub>3</sub>CO substituent. Compound III could be recovered unchanged from solution in 96% H<sub>2</sub>SO<sub>4</sub> for 2 min. The melting point of III was 164–166°.

A strong indication of the structure of III would have been deacetylation by alkali to II. Treatment of III with KOH in diethylene glycol at 230° for 15 min caused complete disappearance of III. The product mixture (after drowning and water washing) generated an nmr spectrum which consisted of relatively few sharp lines. However, the nmr bands of II accounted for only about 1% of the total area and the product mixture was not further investigated. Although it is believed that the trace of II came from III, the low yield diminishes the definitiveness of the experiment.

4,4,4-Triphenyl-2-butanone was identified by its melting point [142° (lit.<sup>7</sup> mp 141°)] and its nmr spectrum, which consisted of singlets at  $\delta$  1.78 (CH<sub>3</sub>), 3.80 (CH<sub>2</sub>), and 7.13 (phenyls) in the calculated ratios.

**Registry No.**—Acetic anhydride, 108-24-7; triphenylmethyl cation, 14699-91-3.

**Acknowledgment.**—Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

(5) Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1967, nmr No. 428.

(6) C. Moureu, C. Dufraisse, and F. Bayloq, *Bull. Soc., Chim. Fr.*, [4] **43**, 1370 (1928).

(7) R. L. Garner and L. Hellerman, *J. Amer. Chem. Soc.*, **68**, 823 (1946).

### Insertion Reaction of Carbon Disulfide with Sulfenamides

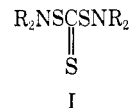
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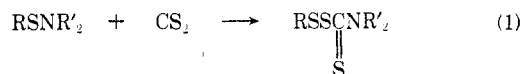
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Carbon disulfide is known to undergo "insertion reactions" with various nitrogen-carbon bonds,<sup>1</sup> nitrogen-trivalent phosphorus bonds,<sup>2</sup> nitrogen-trivalent

arsenic bonds,<sup>1,3</sup> nitrogen-silicon bonds,<sup>1,4</sup> and nitrogen-transition metal bonds.<sup>5</sup> Simple insertion of carbon disulfide into the nitrogen-sulfur bond has not been reported, although E. S. Blake,<sup>6</sup> in an attempt to form trithiocarbonate compounds (I) by reaction of carbon disulfide with a secondary amine sulfide, obtained instead the tetraalkyl thiuram disulfide.

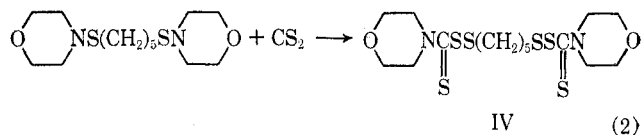


The present work demonstrates insertion of carbon disulfide into the nitrogen-sulfur bond of simple sulfenamides of secondary amines, resulting in the formation of aminocarbotrithioates (III and IV) in good yields (eq 1 and 2). This reaction constitutes a new procedure for the synthesis of aminocarbotrithioates. Known procedures involve reaction of aminocarbotrithioate salts with sulfonyl halides,<sup>7</sup> Bunte salts,<sup>8</sup> sulfonyl thiocyanates,<sup>9</sup> and thioisulfonates.<sup>10</sup>



IIa-IIg IIIa-IIIg

- a, R = CH<sub>3</sub>; NR'<sub>2</sub> = piperidino
- b, R = CH<sub>3</sub>; NR'<sub>2</sub> = morpholino
- c, R = allyl; NR'<sub>2</sub> = morpholino
- d, R = CH<sub>3</sub>; R' = C<sub>2</sub>H<sub>5</sub>
- e, R = C<sub>6</sub>H<sub>5</sub>; NR'<sub>2</sub> = morpholino
- f, R = CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>; NR'<sub>2</sub> = piperidino
- g, R = CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>; R' = CH<sub>3</sub>



Thus, the reaction of carbon disulfide and 1-(methylthio)piperidine (IIa) in ether solution at room temperature is complete in 5 min and afforded an 88% yield of methyl 1-piperidinecarbotrithioate (IIIa). These reactions are exceptionally clean, and purification procedures are made simple by the absence of by-products or of side reactions.

When R is electron-withdrawing, temperatures above the boiling point of carbon disulfide are required for reaction. Hence, the reaction of 4-(phenylthio)morpholine (IIe) with carbon disulfide to give phenyl 4-morpholinecarbotrithioate (IIIe) required heating at

(1) L. B. Clapp and J. W. Watjen, *J. Amer. Chem. Soc.*, **75**, 1490 (1953); N. Kreutzkamp and H. Y. Oei, *Arch. Pharm. (Weinheim)*, **299**, 906 (1966); A. O. Fitton, A. Rigby, and R. J. Hurlock, *J. Chem. Soc., C*, 996 (1968); A. O. Fitton and A. Rigby, *ibid.*, 230 (1969).

(2) G. Oetel, H. Malz, and H. Holzschmidt, *Chem. Ber.*, **97**, 891 (1964).

(3) Von H.-J. Vetter and H. Nöth, *Z. Naturforsch.*, **19b**, 167 (1964).

(4) R. H. Cragg and M. F. Lappert, *J. Chem. Soc., A*, 82 (1966); E. A. V. Ebsworth, G. Rocktäschel, and J. C. Thompson, *ibid.*, 362 (1967).

(5) D. C. Bradley and M. H. Gitlitz, *Chem. Commun.*, 289 (1965).

(6) E. S. Blake, *J. Amer. Chem. Soc.*, **65**, 1267 (1943).

(7) J. Teppema, U. S. Patent 2,024,613 (1935); R. Ghosh, U. S. Patent 3,232,974 (1966); U. S. Patent 3,284,291 (1966).

(8) A. A. Watson, *J. Chem. Soc.*, 2100 (1964).

(9) M. Hunt, U. S. Patent 2,390,713 (1945).

(10) J. E. Dunbar and J. H. Rogers, U. S. Patent pending; L. Field and J. D. Buckman, *J. Org. Chem.*, **33**, 3865 (1968).