

TABLE I  
 PREPARATION OF ESTERS

Acid	Alcohol or phenol	Yield, %	M.p., °C.	Ester Ref. m.p.
Acetic	Cholesterol	88	113-114	114 <sup>a</sup>
Benzoic	Resorcinol	89	116-117	115 <sup>b</sup>
<i>p</i> -Nitrobenzoic	Methanol	92	95-96 <sup>a</sup>	95.1 <sup>c</sup>
	Ethanol	90	56-57 <sup>a</sup>	56.3 <sup>c</sup>
	2-Propanol	96	109-110 <sup>a</sup>	108.3 <sup>c</sup>
	<i>t</i> -Butyl alcohol	85	115-116 <sup>t,a</sup>	115.5 <sup>d</sup>
	Furfuryl alcohol	90	75-76	75-77 <sup>e</sup>
	Benzyl alcohol	96	84-85	85-86 <sup>f</sup>
	Benzhydrol	90	130-131	131-132 <sup>g</sup>
3,5-Dinitrobenzoic	Benzoic	90	122-123	123 <sup>h</sup>
	Phenol	78	127-128	129 <sup>i</sup>
	2-Naphthol	88	166-167	169 <sup>j</sup>
	Methanol	90	107-108	107.9 <sup>k</sup>
	2-Propanol	90	120-121	122.1 <sup>k</sup>
	<i>t</i> -Butyl alcohol	92	140-141	141.5 <sup>l</sup>
	2,3-Dimethyl-2-butanol	78	109-110	111 <sup>m</sup>
	Cyclohexanol	82	111-112	112-113 <sup>l</sup>
	<i>l</i> -Menthol	89	153-154	153 <sup>n</sup>
<i>d</i> -Borneol	85	154-155	156-157 <sup>o</sup>	
1-Phenylethanol	88	95-96	95 <sup>p</sup>	
Cinnamyl alcohol	90	120-121	121 <sup>q</sup>	
1-Dodecanol	82	59-60	60 <sup>r</sup>	

<sup>a</sup> A. Windaus, *Z. physiol. Chem.*, **101**, 276 (1918). <sup>b</sup> J. Ross, J. H. Perry, R. L. Brandt, A. I. Gebhart, J. E. Mitchell and S. Yolles, *Ind. Eng. Chem.*, **34**, 924 (1942). <sup>c</sup> M. D. Armstrong and J. E. Copenhaver, *THIS JOURNAL*, **65**, 2252 (1945). <sup>d</sup> R. Adams, E. K. Rideal, W. B. Burnett, R. L. Jenkins and E. E. Dreger, *ibid.*, **48**, 1758 (1926). <sup>e</sup> R. D. Kleene and S. Fried, *ibid.*, **62**, 3516 (1940). <sup>f</sup> R. Kothe, *Ann.*, **266**, 313 (1902). <sup>g</sup> J. Meisenheimer and W. Schmidt, *ibid.*, **475**, 157 (1929). <sup>h</sup> J. Meisenheimer, *Ber.*, **38**, 874 (1905). <sup>i</sup> L. C. Raiford, R. Taft and H. P. Lankelma, *THIS JOURNAL*, **46**, 2051 (1924). <sup>j</sup> E. d.B. Barnett and I. G. Nixon, *Chem. News*, **129**, 190 (1924). <sup>k</sup> G. B. Malone and E. E. Reid, *THIS JOURNAL*, **51**, 3424 (1929). <sup>l</sup> T. Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926). <sup>m</sup> P. Sutter, *ibid.*, **21**, 1266 (1938). <sup>n</sup> J. Read, W. J. Grubb and D. Malcolm, *J. Chem. Soc.*, 170 (1933). <sup>o</sup> W. Hüchel, *Ann.*, **549**, 186 (1941). <sup>p</sup> F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).

<sup>q</sup> F. Willi and F. Knörr, *Chem. Ber.*, **85**, 841 (1952). <sup>r</sup> R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 288. <sup>s</sup> Mixed melting point undepressed. <sup>t</sup> Infrared spectrum identical with authentic sample.

tion from ether and mixed pentanes, 90% recovery, m.p. 41.5-42.5° (lit.<sup>12</sup> 43°).

**Benzanilide.**—A solution prepared by adding 6.4 ml. of benzenesulfonyl chloride to 12 g. of benzoic acid in 20 ml. of pyridine (see above) was cooled to room temperature under the tap and then 4.7 g. (0.05 mole) of aniline was added. The solution became hot; it was cooled under the tap with stirring until the reaction mixture solidified (about 10 min.). The product was treated with a solution of 10 g. of sodium hydroxide and 5 g. of sodium bisulfite in 200 ml. of water. The dead-white product was collected by filtration and dried in vacuum; yield, 9.2 g. (94%), m.p. 160.5-161° (lit.<sup>13</sup> 160-161°).

Other amides made in this way include acetanilide (49% crude), m.p. 110-111° (lit.<sup>14</sup> m.p. 114°) and 2-furo-*p*-toluidide (90%), m.p. 107° (lit.<sup>15</sup> m.p. 107.5°).

When the molar ratio of the aromatic sulfonyl halide to the carboxylic acid is greater than one-half the product is orange colored and difficult to purify. The conversion of carboxylic acid to its substituted amide drops due to the formation of sulfonamide from the excess of sulfonyl halide. The sulfonamide can be recovered from the alkaline mother liquors by acidification and is obtained in the amounts to be expected from the excess of sulfonyl halide over that required for formation of the symmetrical anhydride.

**Preparation of Esters.**—The following procedure is the most generally successful so far devised for this reaction. With highly reactive alcohols it may prove desirable to modify this procedure by using less sulfonyl halide and to add it more slowly. The acid is dissolved in 20-50 parts of pyridine (in some cases a salt separates) and two molecular equivalents of benzenesulfonyl or toluenesulfonyl chloride is added. The solution is chilled in ice and one molecular equivalent of the alcohol or phenol is added. The solution is kept cold for about one hour and then poured into three or four volumes of an ice and water mixture. Solid esters are collected by filtration. Esters which have been prepared in this way are listed in Table I.

(12) H. T. Clarke and E. J. Rahrs, in H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 91.

(13) C. N. Webb, *ibid.*, p. 82.

(14) J. H. Matthews, *THIS JOURNAL*, **39**, 1125 (1917).

(15) E. Baum, *Ber.*, **37**, 2949 (1904).

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## Complex Salts of Monosubstituted Amides with the Hydrohalic Acids and the Halogens

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A number of salts of *N*-(*t*-butyl)-acetamide (A) corresponding to A·HX, A<sub>2</sub>·HX, and A<sub>2</sub>·HX<sub>2</sub> have been prepared (X = halogen); the latter compounds are halogenating agents. A structure is proposed for the 2:1 complexes similar to that of the carboxylic acid dimers. Complexes of this type are apparently general for monosubstituted and unsubstituted amides.

During an attempted nitrosation of *N*-(*t*-butyl)-acetamide (A) with nitrosyl bromide,<sup>1,2</sup> orange-colored crystals separated which contained active bromine and analyzed for C<sub>12</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>Br<sub>3</sub>. A mixture of A (C<sub>8</sub>H<sub>13</sub>NO) and bromine in carbon tetrachloride on recrystallization yielded only the amide; however, after exposure to the atmosphere (HBr

formed) the same orange-colored crystals were obtained, suggesting that the analysis above corresponded to (A)<sub>2</sub>·HBr·Br<sub>2</sub>. Subsequently the same compound was prepared by the step-wise procedure shown below, thereby confirming this partial structure. The same compound was also obtained from a mixture of standard solutions of A, bromine and hydrogen bromide in the correct proportion.

The properties of these intermediates as well as those of the related iodine complex IV are given in Table I. The hydrochlorides corresponding to I

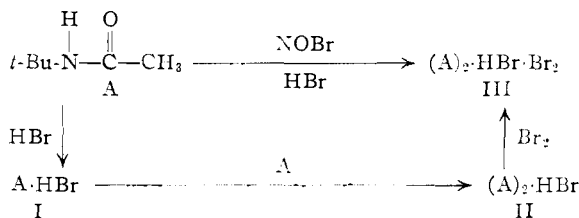
(1) E. H. White, *THIS JOURNAL*, **77**, 6008 (1955).

(2) Nitrosyl bromide is partially dissociated into bromine and nitric oxide at 0° (C. M. Blair, Jr., P. D. Brass and D. M. Yost, *ibid.*, **56**, 1916 (1934)).

TABLE I  
 SALTS OF N-(*t*-BUTYL)-ACETAMIDE (A), ANALYSES,<sup>a</sup> %

Salt	M.p., °C. <sup>b</sup>	Calculated					Found				
		C	H	N	Halogen	Mol. wt./2	C	H	N	Halogen	Mol. wt. <sup>c</sup>
Pure salts											
A·HBr (I)	152, dec.	36.75	7.20	7.14	40.75		36.91	7.07	7.41	40.80	
A <sub>2</sub> ·HBr (II)	126-127	46.30	8.74	9.00	25.67	156	46.42	8.91	8.71	25.66	139
A <sub>2</sub> ·HBr·Br <sub>2</sub> (III)	126-127	30.59	5.77	5.95	50.89	232	30.66	5.81	5.92	50.82	252
A <sub>2</sub> ·HI·I <sub>2</sub> (IV)	114-115	23.54	4.45	4.58	62.20	306	23.68	4.65	4.68	62.32	304
Impure salts											
A <sub>2</sub> ·HBr·Cl <sub>2</sub> (V)	126-127			7.33	39.5 <sup>d</sup>				6.77	39.3	
A <sub>2</sub> ·HBr·I <sub>2</sub> (VI)	125-127	25.50	4.82	4.96	59.06 <sup>d</sup>		26.47	5.00	4.88	58.0	
							26.04	4.80	5.51	58.2	
A <sub>2</sub> ·HCl	104-110				13.29 <sup>d</sup>					12.59	
A <sub>2</sub> ·HCl·Br <sub>2</sub> (VII)	109-111										

<sup>a</sup> Schwarzkopf Microanalytical Laboratory, Woodside 77, L. I., N. Y. <sup>b</sup> Uncorrected. <sup>c</sup> Determined in acetonitrile solutions by the isothermal distillation technique (E. P. Clark, *Anal. Chem.*, **13**, 820 (1941)). The value found for II in a benzene solution was 909 (*i.e.*, association). <sup>d</sup> Total halogen.



and II proved to be rather unstable; their properties as well as those of A<sub>2</sub>·HBr·Cl<sub>2</sub> (V), A<sub>2</sub>·HBr·I<sub>2</sub> (VI) and A<sub>2</sub>·HCl·Br<sub>2</sub> (VII), which were not obtained in the pure state<sup>3</sup> (presumably because of fractionation of the halogens), are listed also, to illustrate the possible variations of composition. The simple salts (I and II) are quite hygroscopic, whereas the perhalides are only slightly so. The perhalides are decomposed by hydroxylic solvents; III decomposes immediately in water whereas IV is stable for several days under the same conditions. The simple salts can be determined acidimetrically and the perhalides iodimetrically.

The amide perhalides may be useful for controlled halogenations, just as pyridinium hydrobromide perbromide<sup>4</sup> and the dioxane-bromine complex<sup>5</sup> have proved useful. In the only case tested, cyclohexene and III reacted instantaneously at -60° in chloroform to yield, exclusively, *trans*-1,2-dibromocyclohexane.<sup>6</sup>

A number of salts related to the ones described in this paper are known. The salts of formamide<sup>7</sup> and acetamide<sup>8</sup> corresponding to II have been reported<sup>9</sup>; also Frost<sup>10</sup> has prepared salts of glycine

- (3) No intensive efforts were made to prepare the pure compounds.  
 (4) C. Djerassi and C. R. Scholz, *THIS JOURNAL*, **70**, 417 (1948); R. Lombard and G. Heywang, *Bull. soc. chim.*, 331 (1952).  
 (5) L. A. Yanovskaya and A. P. Terent'ev, *J. Gen. Chem. U.S.S.R.*, **22**, 1594, 1598 (1952); O. Hassel, *Acta Chem. Scand.*, **8**, 873 (1954).  
 (6) Determined by comparison of the infrared spectrum with those of the authentic *cis* and *trans* isomers (kindly furnished by Professor H. L. Goering, see *THIS JOURNAL*, **74**, 3588 (1952)).  
 (7) P. Walden, *Chem. Zentr.*, **83**, I, 122 (1912).  
 (8) A. Werner, *Ber.*, **36**, 154 (1903).  
 (9) Two interesting compounds which are related stoichiometrically (but not insofar as bonding is concerned) are [(pyridine)<sub>2</sub>Br]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (H.

Carlsobn, *ibid.*, **68B**, 2209 (1935)) and  $\left[ \left( \text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \begin{array}{l} \text{Et} \\ \text{Et} \end{array} \right)_2 \right]^+ \text{ICl}_2^-$  (Ya. A. Fialkov and I. D. Muzyka, *J. Gen. Chem. U.S.S.R.*, **21**, 905 (1951)).

(10) W. S. Frost, *THIS JOURNAL*, **74**, 1346 (1952).

and hydriodic acid containing two moles of the former per mole of hydriodic acid. In addition, numerous perhalides of various types are known<sup>10,11</sup>; a few more closely related to III are salts of the type Y·HBr·Br<sub>2</sub> where Y = pyridine,<sup>4</sup> 2-phenylamino-benzothiazole<sup>12</sup> and 2-phenylamino-4-methyl-5-bromothiazole.<sup>13</sup>

 TABLE II  
 ULTRAVIOLET SPECTRA<sup>a</sup>

Compound	Solvent	Concn., M	λ <sub>max</sub> , mμ	log ε	Lit. ref.
IV	Methanol	5.49 × 10 <sup>-5</sup>	221 <sup>b</sup>	4.49 <sup>c</sup>	<sup>e</sup>
			292	4.66 <sup>d</sup>	
			359	4.41 <sup>d</sup>	
	Ether	4.91 × 10 <sup>-5</sup>	294	4.52 <sup>d</sup>	
			364	4.25 <sup>d</sup>	
			364		<sup>f</sup>
KI <sub>3</sub>	Methanol	4.50 × 10 <sup>-5</sup>	222 <sup>b</sup>	4.52 <sup>c</sup>	<sup>g</sup>
			292	4.59 <sup>d</sup>	
			358	4.34 <sup>d</sup>	
I <sub>2</sub>	Ether	3.29 × 10 <sup>-4</sup>	249	3.78	<sup>h</sup>
			468	3.06	
	CCl <sub>4</sub>	3.87 × 10 <sup>-4</sup>	518	2.95	<sup>i</sup>

<sup>a</sup> Spectra taken with a Cary recording spectrophotometer, model 11 S. <sup>b</sup> This band was found at 223 mμ for an aqueous soln. of KI<sub>3</sub>. Spectra in this region apparently have not been determined previously for the triiodide ion, probably because of the interference of the iodide ion which absorbs at 226 mμ (H<sub>2</sub>O, log ε 4.11; Awtrey (ref. g) reports *ca.* 226 mμ, log ε 4.1). <sup>c</sup> These values increase with dilution. <sup>d</sup> These values decrease with dilution. <sup>e</sup> F. L. Gilbert, R. R. Goldstein and T. M. Lowry (*J. Chem. Soc.*, 1092 (1931)) report λ<sub>max</sub> 290 (log ε 4.55), λ<sub>max</sub> 358 (log ε 4.38) for *p*-bromophenyltrimethylammonium triiodide in ethanol. <sup>f</sup> R. E. Buckles, J. P. Yuk and A. I. Popov (*THIS JOURNAL*, **74**, 4379 (1952)) report 295 mμ (log ε 4.65) and 365 mμ (log ε 4.40) for tetramethylammonium triiodide in ethylene chloride. <sup>g</sup> For water solutions, A. D. Awtrey and R. E. Connick (*ibid.*, **73**, 1842 (1951)) report λ<sub>max</sub> 288 (log ε 4.60), λ<sub>max</sub> 353 (log ε 4.42). For absolute ethanol solutions, Lowry (footnote c) reports λ<sub>max</sub> 290 (log ε 4.60), λ<sub>max</sub> 360 (log ε 4.46). <sup>h</sup> H. A. Benesi and J. H. Hildebrand (*THIS JOURNAL*, **71**, 2703 (1949)) report λ<sub>max</sub> 462 (log ε 2.94). <sup>i</sup> O. J. Walker (*Trans. Faraday Soc.*, **31**, 1432 (1935)) reports λ<sub>max</sub> 518 (log ε 2.95).

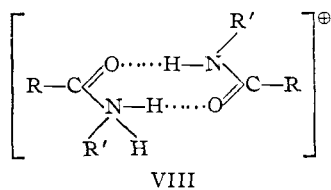
(11) (a) W. A. Bonner, *ibid.*, **74**, 5078 (1952); (b) J. A. Vona and P. L. Merker, *J. Org. Chem.*, **14**, 1048 (1949).

(12) R. F. Hunter, *J. Chem. Soc.*, 125 (1930).

(13) R. F. Hunter and E. R. Parker, *ibid.*, 1175 (1934).

**Structure.**—The molecular weights of II, III and IV (Table I) in acetonitrile were approximately equal to one-half of the formula weights, indicating a dissociation into two particles. Since the ultraviolet spectrum of IV in methanol was practically the same as that of  $KI_3$  (Table II),<sup>14</sup> one of the particles from IV is the triiodide ion,  $I_3^-$ . Similar spectra (indicative of  $I_3^-$ ) were obtained in less polar solvents (Table II), although the bands were slightly shifted in position. The spectrum of iodine in these solvents was markedly different from that of IV.

The second particle from IV (and by analogy from II, III, V, VI and VII) must be (by difference) a cation with the general formula  $A_2H^+$  (VIII). This unit is rather stable inasmuch as (i) compounds II, III and IV could be sublimed unchanged *in vacuo*, *i.e.*, no hydrohalic acid was lost, (ii) the reaction of the 1:1 bromide I with bromine yielded an oil; however, during two days at 0.1 mm., hydrogen bromide was lost and the crystalline 2:1 tribromide<sup>15</sup> III was formed, and (iii) the cation exists as such in solution, *i.e.*, the infrared spectra are characteristic of the cation (*vide infra*). By analogy with the structures proposed for dimers of the carboxylic acids<sup>16</sup> and for  $\delta$ -valerolactam,<sup>17</sup> the following structure is proposed for the cation ( $A_2H^+$ ).<sup>18</sup>



The infrared spectra of the 2:1 complexes (from 7 to 15  $\mu$ ) are far more intense than the sum of the spectra of the components (amide + 1:1 amide hydrohalide) and are characterized by broad, contiguous absorption bands. Other than the differences at 3.1, 4.1 and 6.2  $\mu$ , the spectra of the simple complexes (*i.e.*, II and the corresponding hydrochloride) and the perhalides (III, etc.) are identical. The infrared spectra of the various perhalides (III, IV, V, VI and VII) are identical; the spectra, therefore, are characteristic of the cation alone. The spectra of III in acetonitrile, chloroform, nujol or potassium bromide pellets were essentially the

(14) Direct comparison with the spectrum of iodine in methanol was not practical because of a rapid reaction yielding the triiodide ion. In the presence of ozone, however, the  $\lambda_{\text{max}}$  of iodine itself has been found in methanol at 477  $m\mu$ ,  $\log \epsilon$  5.98 (A. Batley, *Trans. Faraday Soc.*, **24**, 438 (1928)).

(15) Similarly, the 1:1 hydrobromide of acetamide loses hydrogen bromide to form the 2:1 salt (A. Pinner and F. Klein, *Ber.*, **10**, 1896 (1877)).

(16) W. Klyne, "Progress in Stereochemistry," Butterworths Scientific Publications, London, 1954, p. 224.

(17) S. Mizushima, *Adv. Protein Chem.*, **9**, 304 (1954); on the other hand, the association of monosubstituted amides apparently involves *trans*-hydrogen bonding leading to long chains of amide molecules.

(18) Structures with a single hydrogen bond are unlikely, since N,N-diethylacetamide did not form a 2:1 complex with hydrogen bromide, whereas complexes of this type were prepared containing N-(*n*-butyl)acetamide alone as well as those containing one mole of this amide with one mole of N,N-diethylacetamide. In view of the molecular weights in acetonitrile (Table I) and the similarity of the infrared spectra in this solvent and in the solid state, the cation is not polymeric in nature.

same,<sup>19</sup> indicating that the complex cation exists in both the solid state and in solution. The spectrum of IV is very similar to that of  $[N-(n\text{-butyl})\text{-acetamide}]_2\text{HI}_3$ , and the spectrum of II is very similar to that of the mixed complex  $[A + N,N\text{-diethylacetamide}]\text{HBr}$ ; the infrared spectrum of VIII, therefore, in general nature is essentially independent of R'.

**Analogs.**—N-(*n*-Butyl)acetamide was converted into the 2:1 complex salt of  $HI_3$  as shown by the infrared spectra and by titration; it was not obtained crystalline, however. Diethylacetamide (I) formed a 1:1 hydrobromide but did not form the

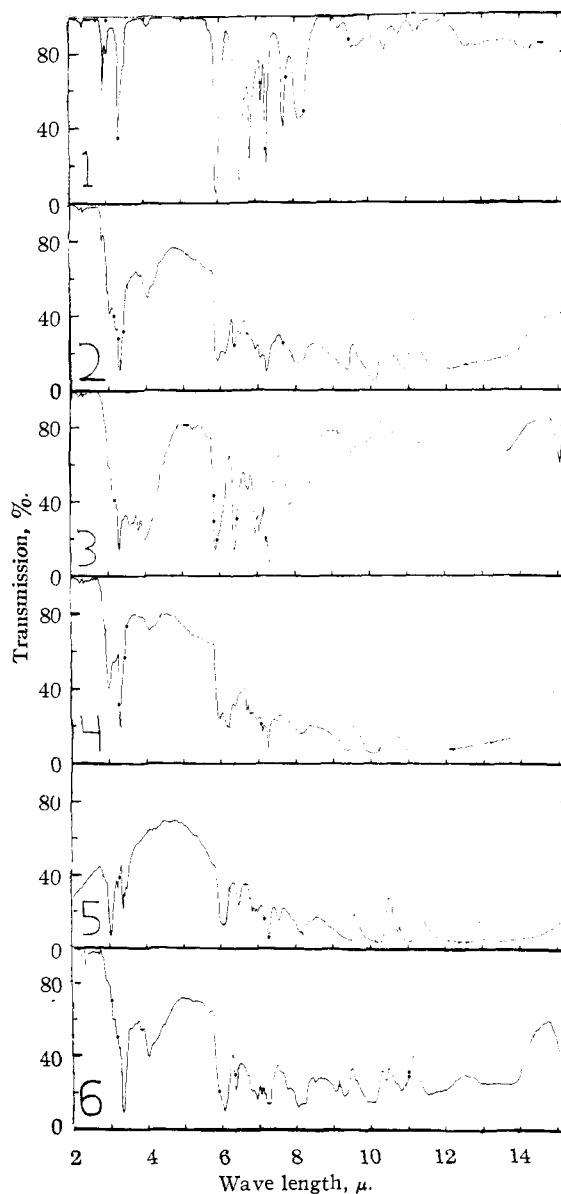


Fig. 1.—Infrared spectra: 1, compd. A (0.30 *M* in  $\text{CHCl}_3$ ); 2, compd. II (0.31 *M* in  $\text{CHCl}_3$ ); 3, compd. I (0.37 *M* in  $\text{CHCl}_3$ ); 4, compd. III (0.31 *M* in  $\text{CHCl}_3$ ); 5, compd. IV (KBr pellet); 6, mixture of A and diethylacetamide hydrobromide (1:1) in  $\text{CHCl}_3$  (0.3 *M*).

(19) However, the shapes of some of the bands are slightly altered in the solvent absorption regions. In addition, a band at 6.2  $\mu$  is missing in the nujol and KBr spectra (Fig. 1).

2:1 bromide corresponding to II. On the other hand, an equimolar mixture of this 1:1 hydrobromide (E·HBr) and N-(*t*-butyl)-acetamide (A) did form a 2:1 complex salt (general formula, [A + E]HBr).<sup>18</sup>

### Experimental<sup>20</sup>

**N-(*t*-Butyl)-acetamide Hydrobromide (I).**—Anhydrous hydrogen bromide was passed into a solution of 4.36 g. (0.0379 mole) of N-(*t*-butyl)-acetamide<sup>21</sup> (A) in chloroform (25 ml.) for *ca.* 30 min. Upon the addition of carbon tetrachloride, 7.06 g. (0.0360 mole, 95%) of the hygroscopic salt crystallized, m.p. 152° dec. Titration to a phenolphthalein end-point with 0.1 *N* sodium hydroxide gave, in a single trial, an equivalent weight of 205 (calcd. 196).<sup>22</sup>

**A<sub>2</sub>HBr (II).**—N-(*t*-Butyl)-acetamide (0.451 g., 3.93 mmoles) and the hydrobromide (I) (0.77 g., 3.93 mmoles) were dissolved in chloroform (*ca.* 5 ml.). Carbon tetrachloride was added until crystallization was complete, to yield 1.06 g. of the hygroscopic salt (3.41 mmoles, 87%), m.p. 126–127°. The m.p. on admixture with the amide A was 79–94°, and with the 1:1 hydrobromide I was 143° dec. Impure samples were purified by sublimation at 0.01 mm. and *ca.* 50°.

**A<sub>2</sub>HBr<sub>3</sub> (III).**—This compound was prepared by the following methods: (1) The stoichiometric amounts of bromine and the bromide complex (II) were dissolved in chloroform and the orange crystals were precipitated with carbon tetrachloride. (2) Standard solutions of bromine, hydrogen bromide, and the amide (A) in carbon tetrachloride were mixed in the correct proportion. The perbromide crystallized out immediately. Occasionally oils were obtained which crystallized after seeding or upon the addition of ether. (3) An excess of bromine was added to the hydrobromide I and the mixture was held at 0.01 mm. for 50 hr. at 25°. The crystalline residue was pure III. (4) An excess of bromine was added to a concentrated solution of the amide in ether and the solution was exposed to the atmosphere for several days.

Yields of *ca.* 90% were obtained by methods 1 and 2. The orange crystals melted at 125–126°; sublimation at 0.01 mm. (*ca.* 50°) raised this value to 126–127° (compounds II, III, V and VI have the same m.p.). On admixture with A, the melting point was 75–108°; with the hydrobromide I, 113–147°; and with the bromide complex II, 100–115°. The equivalent weight determined iodimetrically was 239 (calcd. 235.6).<sup>22</sup>

The distillation of a large amount of chloroform (containing ethanol as a preservative) from III, resulted in the co-distillation of bromine, leaving the 2:1 hydrobromide II in solution. The infrared spectra of III and IV in chloroform were identical. In potassium bromide, the spectrum of III was the same as that of IV except that in the region near 7  $\mu$ , the curve was identical to the solution spectrum, in contrast to that of IV.

**A<sub>2</sub>HI<sub>3</sub> (IV).**—A solution of 5.0 g. (0.0435 mole) of the amide A in water (*ca.* 100 ml.) was added to 47.8 ml. of a solution 0.454 *M* in both iodine and hydriodic acid (0.0217 mole of each) (prepared by dissolving iodine in the concentrated acid and diluting). The precipitate after drying weighed 12.4 g. The complex was extracted from this precipitate with ether, leaving crystals with a metallic luster which were insoluble in ether but soluble in chloroform. Without further purification, these analyzed for A·HI· $\frac{1}{2}$  H<sub>2</sub>O.

*Anal.* Calcd. for C<sub>6</sub>H<sub>13</sub>NO<sub>1.5</sub>I: C, 28.58; H, 6.00; N, 5.56; I, 50.84. Found: C, 28.93; H, 5.82; N, 5.37; I, 50.87. Pentane was added to the ether extracts to yield deep-red needles of A<sub>2</sub>HI<sub>3</sub>, m.p. 114–115°.<sup>22</sup>

**Attempted Preparation of A<sub>2</sub>HBr·Cl<sub>2</sub> (V).**—Chlorine was passed into chloroform (20 ml.) for *ca.* 15 min. and the solution was then added to a solution of the complex bromide II (1.89 g., 6.08 mmoles) in chloroform (10 ml.). Carbon tetrachloride was added and the solution cooled to yield 1.91 g. (5.0 mmoles, 82%) of the yellow crystalline complex V, m.p. 126–127°.<sup>22</sup>

(20) Table I, footnotes *a* and *b*. Most of the experimental work reported was carried out in a dry-box.

(21) I. J. Ritter and P. F. Micleri, *THIS JOURNAL*, **70**, 4015 (1948).

(22) See also Table I.

The equivalent weight determined iodimetrically was 198, calcd. 191. Only partially liquid products were obtained by sublimation at 0.01 mm.

**Attempted Preparation of A<sub>2</sub>HBr·I<sub>2</sub> (VI).**—A solution of the complex bromide II (0.95 g., 3.05 mmoles) in chloroform (10 ml.) was added to 31.8 ml. of 0.096 *M* I<sub>2</sub> in chloroform (3.05 mmoles). The addition of carbon tetrachloride yielded VI (1.47 g., 2.60 mmoles, 85%), m.p. 125–127°.<sup>22</sup>

The equivalent weight determined iodimetrically was 280, calcd. 282.5. Sublimation of this complex iodide at 0.01 mm. resulted in decomposition. Attempts to prepare A<sub>2</sub>·HBr·I<sub>4</sub> by doubling the amount of iodine used in the preparation given led only to non-crystalline products.

**Hydrochlorides of N-(*t*-Butyl)-acetamide.**—The 1:1 hydrochloride<sup>23</sup> was prepared by passing hydrogen chloride through a solution of the amide A in chloroform for several hours. The large crystals obtained melted at 115–119° (77–100° in a sealed tube). Titration with sodium hydroxide to a phenolphthalein end-point gave an equivalent weight of 121, calcd. 151.6. The salt lost hydrogen chloride rapidly after two days in a dry-box; the equivalent weight was 146. After evacuating the crystals for 4 hr. at 0.1 mm., the value was 269 (calcd. for A<sub>2</sub>·HCl, 267). At this point, the m.p. in open and in sealed tubes was 107–108°. After an additional day at 0.1 mm., the equivalent weight was 4850.

A fairly pure sample of A<sub>2</sub>·HCl was prepared by passing hydrogen chloride through a solution of A in carbon tetrachloride; the hygroscopic salt crystallized out as formed, m.p. 104–110°, equiv. wt. 298 (calcd. 267).<sup>22</sup>

Attempts to prepare A<sub>2</sub>·HCl<sub>2</sub> from A<sub>2</sub>·HCl and Cl<sub>2</sub> were unsuccessful, only the reactants could be isolated.

**Attempted Preparation of A<sub>2</sub>·HCl·Br<sub>2</sub> (VII).**—A 1.0 *M* solution of A in carbon tetrachloride (14 ml., 14 mmoles) was added to a mixture of bromine in carbon tetrachloride (3 ml. of a 2.33 *M* soln., 7 mmoles) and hydrogen chloride in the same solvent (69 ml. of a 0.102 *M* soln., 7 mmoles). The precipitate was filtered and recrystallized from chloroform–carbon tetrachloride mixtures to yield 1.26 g. of the salt (2.95 mmoles, 42%), m.p. 109–111°, equiv. wt. 454 (calcd. 426.5).

**Complexes of Normal and *sec*-Butylacetamide.**—N-(*sec*-butyl)-acetamide hydrobromide was prepared following the procedure given for the tertiary isomer, m.p. 117–120°. Attempts to prepare various crystalline 2:1 salts failed, only oils were obtained.

The complex [N-(*n*-butyl)-acetamide]<sub>2</sub>HI<sub>3</sub> was prepared as a black oil by the procedure given for the tertiary isomer, equiv. wt. 281 (calcd. 306). The infrared spectrum was the same as that of the crystalline *t*-butyl isomer, except for a difference in the shapes of the bands at 9.45 and at 7.52  $\mu$ , and a reversal of the relative intensities of the 6.09 and 6.22  $\mu$  bands.

**Diethylacetamide Salts.**—Diethylacetamide was prepared from diethylamine and acetic anhydride, and the product was distilled several times from solid potassium hydroxide at 20 mm. Hydrogen bromide was passed into a chloroform solution of the amide for *ca.* one hr. A mixture of ether and carbon tetrachloride (the latter alone yielded an oil) was added to yield a hydrobromide, m.p. 123–125°, equiv. wt. 144 (calcd. 196). The crystals were sublimed at 0.01 mm. to yield the hygroscopic 1:1 salt, m.p. 120–124°, equiv. wt. 198 (calcd. 196).

*Anal.* Calcd. for C<sub>6</sub>H<sub>14</sub>NOBr: C, 36.75; H, 7.20; N, 7.14; Br, 40.75. Found: C, 36.56; H, 7.00; N, 6.82; Br, 40.83.

The infrared spectrum of an equimolar mixture of the amide and the 1:1 hydrobromide was equal to the sum of the spectra of the two compounds, *i.e.*, the characteristic broad intense absorption bands of the 2:1 complex were absent. On the other hand, the infrared spectrum of an equimolar mixture of diethylacetamide hydrobromide and N-(*t*-butyl)-acetamide was far more intense than the sum of the spectra of the components—the intensity values indicated that a true 2:1 mixed complex had been formed, and not just 0.5 mole of II. This spectrum was the same as that of A<sub>2</sub>·HBr (II) except for an extra band at 10.44  $\mu$ , and a few minor differences in the intensities from 6 to 6.8  $\mu$  (Fig. 1). This mixture was recrystallized from chloroform by gradually adding ether, then hexane. Five fractions

(23) R. Scholl, A. O. Weil and K. Holdermann (*Ann.*, **338**, 16 (1905)) reported the preparation of this salt but listed no physical constants.

were taken. The second proved to be practically pure diethylacetamide hydrobromide (1:1) and the fifth proved to be the 1:1 hydrobromide of *N*-(*t*-butyl)-acetamide (from the infrared spectra). The mother liquid from the fifth crop on evaporation yielded a mixture of the pure amides. The complex is apparently unstable in the crystalline state, relative to the 1:1 amide salts.

The infrared spectra of equimolar mixtures of acetic acid and diethylacetamide, acetic acid and diethylacetamide hydrobromide, and trichloroacetic acid with the diethylacetamide were equal to the sum of the spectra of the components, *i.e.*, no intense absorption bands characteristic of the 2:1 complexes were noted.

**Bromination of Cyclohexene.**—A solution of cyclohexene (1.64 g., 0.02 mole) in chloroform (35 ml.) was cooled to  $-60^\circ$  and a solution of  $A_2 \cdot HBr_3$  (III) (9.42 g., 0.02 mole) in chloroform (75 ml.) was slowly added with suitable precautions to keep the stirred mixture anhydrous. The solution added was decolorized practically instantaneously. The solution was washed with dilute sodium bisulfite, then ex-

tracted continuously with water for several hours at  $20^\circ$  to remove the amide (A). The chloroform was dried and removed and the product distilled at  $46-47^\circ$  (0.5 mm.) to yield 3.1 g. (0.0128 mole, 64%) of dibromocyclohexane, m.p.  $-3^\circ$ ,  $n_D^{25}$  1.5495 (lit.<sup>24</sup> m.p.  $-8$  to  $-4^\circ$ ,  $n_D^{25}$  1.5490 to 1.5507). A comparison of the infrared spectrum with those of authentic samples of *cis*- and *trans*-1,2-dibromocyclohexane<sup>6</sup> showed that the product was exclusively the *trans* isomer. The products from the reaction of cyclohexene with bromine in chloroform at  $-60^\circ$ , or with the bromine-dioxane complex<sup>6</sup> at  $-60^\circ$ , were also exclusively *trans*-1,2-dibromocyclohexane.<sup>6</sup>

**Acknowledgment.**—The author wishes to thank Mr. Charles B. Davidson and Mr. William J. Considine for carrying out some of the experiments reported in this paper.

(24) S. Winstein, *THIS JOURNAL*, **64**, 2792 (1942).

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF TORONTO AND IOWA STATE COLLEGE]

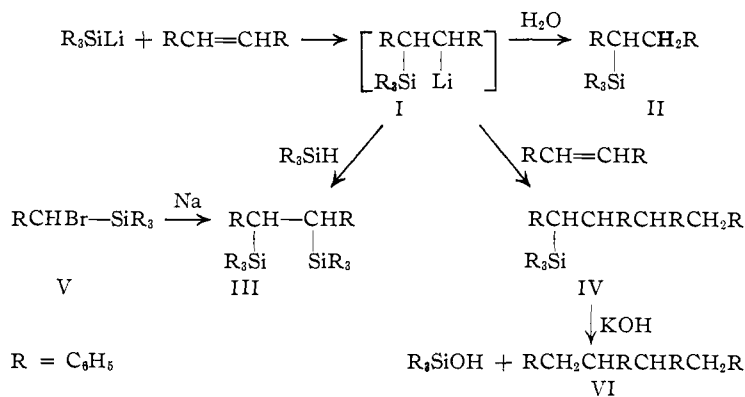
## The Reactions of Triphenylsilyllithium with Stilbene

BY A. G. BROOK, K. M. TAI AND HENRY GILMAN

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The addition of triphenylsilyllithium to *trans*-stilbene yields a variety of products, from which 1,2-bis-(triphenylsilyl)-1,2-diphenylethane and 1-triphenylsilyl-1,2,3,4-tetraphenylbutane have been isolated and identified. In connection with the structure proof of these compounds the identity of 1,2,3,4-tetraphenylbutane, m.p.  $89-91^\circ$ , has been confirmed by several varied syntheses.

The addition of triphenylsilylpotassium in ether to *trans*-stilbene yields after hydrolysis the expected 1-triphenylsilyl-1,2-diphenylethane (II).<sup>1</sup> It was therefore surprising to find that the addition of the analogous triphenylsilyllithium, dissolved in ethylene glycol dimethyl ether,<sup>2</sup> to *trans*-stilbene did not yield this product, but instead gave a number of more complex products including 1,2-bis-(triphenylsilyl)-1,2-diphenylethane (III) and 1-triphenylsilyl-1,2,3,4-tetraphenylbutane (IV) and much polymeric material which contained silicon.

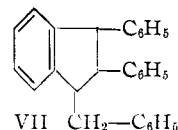


The constitution of III was established by alkaline cleavage, the only products isolated being bibenzyl and triphenylsilanol. The question of the location of the triphenylsilyl groups was settled when the same compound was produced by Wurtz coupling of  $\alpha$ -bromobenzyltriphenylsilane (V), confirming the structure as 1,2-bis-(triphenylsilyl)-1,2-diphenylethane.

(1) H. Gilman and T. C. Wu, *THIS JOURNAL*, **75**, 234 (1953).  
 (2) A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

Alkaline cleavage of the other product isolated IV yielded triphenylsilanol and a hydrocarbon melting at  $89-91^\circ$ , which analysis suggested was 1,2,3,4-tetraphenylbutane (VI). This same compound (VI), in agreement with Bergmann,<sup>3</sup> was isolated from the reduction of tetraphenylthiophene with sodium and amyl alcohol, together with 1,2-diphenyl-3-benzylhydrindene (VII) (m.p.  $180-182^\circ$ ). The same two compounds (VI, VII) were also produced by the reduction of 1,2,3,4-tetraphenylbutadiene-1,3 with sodium and amyl alcohol following published directions,<sup>4</sup> although these authors isolated only VII from this reaction to which they, after others,<sup>5</sup> incorrectly assigned the structure of tetraphenylbutane. Finally hydrogenation of tetraphenylbutadiene at high pressures yielded only VI. Thus it seems certain that the hydrocarbon melting at  $89-91^\circ$  is tetraphenylbutane, and hence the silicon compound from which it was isolated probably has the structure of 1-triphenylsilyl-1,2,3,4-tetraphenylbutane.

The complex nature of the reaction products makes it impossible to speculate with certainty about the mechanism of the reaction. However the formation of the dimer IV and of the polymeric material which con-



(3) E. Bergmann, *J. Chem. Soc.*, 505 (1936).

(4) L. I. Smith and H. H. Hoehn, *THIS JOURNAL*, **63**, 1184 (1941).

(5) E. S. Wallis and F. H. Adams, *ibid.*, **55**, 3850 (1933).