

mole of crystalline phosphorous acid dissolved in 100 ml of water, and 100 ml of concentrated HCl is treated with 2 moles of aqueous 37% formaldehyde solution (100% excess) as described in the preceding preparation. The resulting acids with alkyl groups lower than C<sub>5</sub> were isolated by evaporation of the reaction mixture to a syrupy state and subsequent dissolution in hot ethanol. Upon cooling to room temperature the acids crystallized. The acids having alkyl groups with five or more carbon atoms crystallized from the reaction mixture upon cooling to room temperature. They may be recrystallized from hot dilute hydrochloric acid solution. All acids of this class titrated as tribasic acids with inflection points at pH 4.5 (1 equiv) and pH 9 (2 equiv). Analytical data and melting points are listed in Table I.

**Polymethylenebis(nitrilodimethylene)tetrakisphosphonic Acids.**—A quantity of 0.25 mole of the diamine H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub>, 1 mole of crystalline phosphorous acid dissolved in 100 ml of water, and 100 ml of concentrated HCl was treated with 2 moles of 37% aqueous formaldehyde solution as described above. Upon cooling of the reaction mixture to room temperature, the acids generally separated as white crystalline materials. In some instances, when diamines with a large value of *n* were used, the corresponding acids crystallized from the solution during the reaction. The products were washed with cold water and dried at 120°. The yields recorded in Table II represent the amounts

of product that separated from the reaction mixture upon cooling to room temperature. Evaporation of the filtrate generally yielded additional fractions. However, no efforts have been made to isolate quantitatively the reaction products from the solution although P<sup>31</sup> indicated 95% conversion of the phosphorous acid to aminomethylphosphonic acids. All acids of this class titrated as hexabasic acids with inflection points at pH 4 (2 equiv) and pH 9 (4 equiv). Analytical data and melting points are listed in Table II.

**Triethylenetetraminehexa(methylenephosphonic Acid).**—A quantity of 48 g (0.33 mole) of triethylenetetramine was dissolved in 75 ml of concentrated HCl and a concentrated aqueous solution of 162 g (2 moles) of phosphorous acid. The resulting solution was heated to reflux temperature and 320 ml of 37% aqueous formaldehyde solution (4 moles) was added dropwise in the course of 1 hr. Ethanol precipitated 75 g (35.4%) of a slightly yellow product from the concentrated reaction solution.

*Anal.* Calcd for C<sub>12</sub>H<sub>34</sub>N<sub>4</sub>O<sub>18</sub>P<sub>6</sub>: C, 20.29; H, 5.11; N, 7.89; P, 26.17; mol wt, 710. Found: C, 19.94, H, 5.69; N, 8.53; P, 25.42; mol wt (by titration), 700.

**Acknowledgment.**—We wish to thank Dr. T. L. Westman for helpful discussions and J. P. Brennan for experimental assistance.

## Hydride Transfer. Reactions of Triphenylcarbonium Fluoroborate and Triphenylmethyl Bromide with Tertiary Amines

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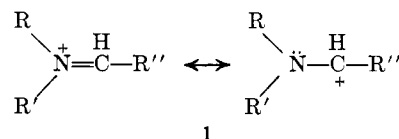
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Trialkylamines undergo hydride transfer reactions with triphenylcarbonium fluoroborate and triphenylmethyl bromide in chlorinated hydrocarbons, acetonitrile, excess amine solvents, and diluents at room temperature. If an amine contains only  $\alpha$  hydrogens the corresponding ternary iminium salt can be isolated. When  $\beta$ -hydrogen atoms are present the intermediate ternary iminium salt reacts with tertiary amine to produce an enamine and amine hydroanion salt. Enamines transfer hydride ions very rapidly to triphenylcarbonium fluoroborate and triphenylmethyl bromide. A mechanism is proposed to account for high yields of amine hydroanion salts and triphenylmethane from reactions of trialkylamines and trityl salts.

During the past decade triphenylcarbonium ion has been used to abstract hydride ions from a variety of olefinic and oxygen-containing compounds.<sup>1,2</sup> For example, Dauben and co-workers have prepared tropenium ion salts<sup>1a</sup> and tropenium-metal carbonyl complex ion salts<sup>1b,c</sup> from cycloheptatriene compounds, while Deno and collaborators<sup>2</sup> have examined acyclic and cyclic alcohols, ethers, and some esters with this reagent. Other workers have oxidized alcohols,<sup>3</sup> ethers,<sup>3,4</sup> and formic acid<sup>5</sup> with triphenylcarbonium ion. The facile hydride transfers from oxygen compounds can be attributed to stabilization of the incipient carbonium ions by resonance contributions of nonbonding electrons on oxygen.

In view of these various reports on hydride transfer reactions of oxygen compounds it is somewhat surprising that there is little work reported on the use of trityl salts<sup>6</sup> to abstract hydride ions from the isoelec-

tronic nitrogen compounds. For example, extraction of hydride ion from tertiary amines would be expected to be assisted by the formation of the stable ternary iminium salts (1)



Recently Meerwein and co-workers<sup>4</sup> oxidized tribenzylamine with triphenylcarbonium fluoroborate to obtain a 94% yield of the corresponding iminium salt; however, extension of this reaction to amines containing  $\beta$ -hydrogen atoms has not been reported. We have attempted to prepare dodecylidinedimethylaminium fluoroborate (1, R, R' = CH<sub>3</sub>; R'' = C<sub>11</sub>H<sub>23</sub>) by the reaction of dimethyldodecylamine with triphenylcarbonium fluoroborate in dichloromethane; however, despite a 62% yield of triphenylmethane, no ternary iminium salt was recovered. Instead, a 70% yield of dimethyldodecylamine hydrofluoroborate was realized (eq 1).

(6) Trityl salts will be used synonymously with triphenylcarbonium fluoroborate and triphenylmethyl bromide in this paper, since the reactive species in both of these compounds is probably the triphenylcarbonium ion.

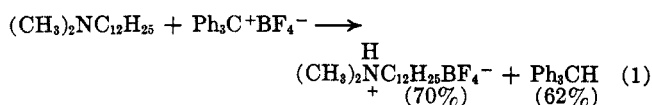
(1) (a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); (b) H. J. Dauben, Jr., and D. J. Bertelli, *ibid.*, **83**, 497 (1961); (c) H. J. Dauben, Jr., and L. R. Honnen, *ibid.*, **80**, 5570 (1958); (d) L. M. McDonough, Ph.D. Thesis, University of Washington, 1960, and references therein.

(2) N. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964), and references therein.

(3) P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.*, **78**, 1441 (1956).

(4) H. Meerwein, J. Hederich, H. Morschel, and K. Wunderlich, *Ann.*, **635**, 1 (1960).

(5) R. Stewart, *Can. J. Chem.*, **35**, 766 (1957).



This paper presents a limited investigation of the scope of trityl salt-tertiary amine reactions and offers a mechanism to explain the observations.

### Results

Equimolar amounts of dimethyldodecylamine and triphenylcarbonium fluoroborate react at room temperature to give high yields of triphenylmethane and dimethyldodecylamine hydrofluoroborate within a few hours. The yields of triphenylmethane, a measure of per cent hydride transfer, from reactions of trityl salts with dimethyldodecylamine in various diluents are summarized in Table I. In addition, entry 8 includes the amount of unreacted starting material and the yield of dimethyldodecylamine hydrobromide. Under typical reaction conditions neither the amine nor the trityl salt gave reaction with solvent.

The results from several amine-trityl salt reactions are presented in Tables I and II. Triphenylmethyl

TABLE I  
YIELDS OF TRIPHENYLMETHANE FROM REACTIONS OF  
DIMETHYLDODECYLAMINE WITH TRITYL SALTS<sup>a</sup>

Entry	Trityl salt	Solvent	Reaction time, hr	Yield of Ph <sub>3</sub> CH, %
1	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	3.0	67
2	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	67.5	76
3	Ph <sub>3</sub> CBF <sub>4</sub>	CHCl <sub>3</sub>	15.5	81
4	Ph <sub>3</sub> CBF <sub>4</sub>	CDCl <sub>3</sub>	5.0	20
5	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>3</sub> CN	3.0	88
6	Ph <sub>3</sub> CBF <sub>4</sub>	CCl <sub>4</sub>	1.0	90
7	Ph <sub>3</sub> CBF <sub>4</sub>	None <sup>b</sup>	1.5	40
8	Ph <sub>3</sub> CBr	CH <sub>2</sub> Cl <sub>2</sub>	2.5	25 <sup>c</sup>
9	Ph <sub>3</sub> CBr	CH <sub>2</sub> Cl <sub>2</sub>	2.5	10 <sup>d</sup>

<sup>a</sup> Equimolar quantities of amine and trityl salt reacted in each case except where stated. All reactions were conducted at room temperature and under argon. <sup>b</sup> Excess amine was used as diluent in this reaction. <sup>c</sup> Column chromatography of the reaction mixture over alumina also gave 67% triphenylcarbinol, presumed to represent starting trityl bromide after hydrolysis, and 71% dimethyldodecylamine hydrobromide. <sup>d</sup> Oxygen was bubbled into the reaction.

bromide and triphenylcarbonium fluoroborate were successfully employed as hydride acceptors, the latter reacting approximately twice as fast as the former (entries 1 and 8, Table I). Several solvents and diluents that are not reactive to either starting material are suitable for the reaction, including the use of excess amine (entry 7, Table I). The use of chloroform-*d* as a reaction solvent gave no deuterium incorporation in the products (entry 4, Table I). Although trityl salts are initially insoluble in carbon tetrachloride and amine diluents, the addition of amine causes rapid solubilization, probably due to quaternary ammonium salt formation. Rapid conversion to either hydride transfer products or to trityl tertiary amines readily proceeds from this point (entries 6 and 7, Table I, and 4, Table II). The reactions are best conducted under argon or purified nitrogen since the presence of dry oxygen appears to inhibit the hydride transfer reactions to some degree (*cf.* entries 8 and 9, Table I).<sup>7</sup>

To gain insight into the mechanism of trityl salt-tertiary amine reactions, a thorough study of the dimethylisobutylamine system was performed. Thus, Table III outlines the results obtained from the reactions of dimethylisobutyl- and dimethylisobutenylamine with trityl salts as well as the reaction of isobutylidenedimethylaminium fluoroborate with dimethylisobutylamine.

Tertiary amines containing at least one  $\alpha$  aliphatic hydrogen atom appear to be the only amines capable of undergoing hydride transfer reactions with trityl salts. Thus, tribenzylamine (entry 1, Table II), dimethyldodecyl- and dimethylisobutylamine (entry 1, Table III) give good yields of triphenylmethane. Tribenzylamine, which contains only  $\alpha$ -hydrogen atoms, produced the corresponding ternary iminium salt; however, dimethyldodecyl- and dimethylisobutylamine, containing both  $\alpha$ - and  $\beta$ -hydrogens, reacted further to build up amine hydroanion salts. With pyridine the stable trityl pyridinium salt (entry 2, Table II) was isolated, while no reaction was observed between triphenylamine and trityl bromide (entry 3, Table II).

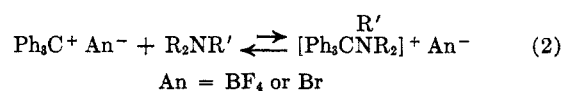
Secondary aliphatic amines give little or no hydride transfer reaction with triphenylcarbonium ion yielding instead the corresponding trityldialkylamine and dialkylamine hydroanions as previously observed.<sup>8</sup> This is a high-yield reaction (entries 4 and 5, Table II) with excess amine, evidence itself against any appreciable hydride transfer.

### Discussion

From inspection of eq 1 it is immediately apparent that both the tertiary amine and the trityl salt have been converted to products in relatively high yield by incorporation of hydrogen. Hydrogen abstraction from solvent was at first suspected; however, several observations rule against this possibility. Thus, reactions conducted in chloroform-*d* provided products containing no deuterium. Further evidence against reactant-solvent interactions is the observation that the same reaction takes place in carbon tetrachloride or in excess amine.

The products arising from the reactions of trityl salts with tertiary amines must then be accounted for by intermolecular hydrogen transfer of reactants. The high yields of unrearranged products eliminate intramolecular hydrogen transfer since, for example, an 80% yield of triphenylmethane cannot be explained in terms of hydrogen abstraction within the trityl moiety.

Simple combination of a tertiary aliphatic amine and triphenylcarbonium ion would give quaternary amine compounds (eq 2). However, both models and alkylation studies<sup>9</sup> of trityldialkylamines indicate


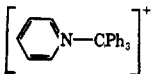


(7) A possible explanation for this phenomenon is that oxygen reacts with one of the proposed intermediates (reactions 3-5) in the hydride transfer reaction.

(8) (a) L. Zervas and D. M. Theodoropoulos, *J. Am. Chem. Soc.*, **78**, 1359 (1956); (b) L. W. Jones and M. W. Seymour *ibid.*, **80**, 1150 (1928).

(9) Attempts to alkylate trityldimethylamine with methyl iodide and dimethyl sulfate failed. Triethyloxonium fluoroborate was successfully treated, but none of the quaternary salt was isolated; instead, high yields of triphenylmethane and other products indicative of hydride transfer reactions through dimethylethylamine and triphenylcarbonium ion were formed.

TABLE II  
 REACTIONS OF AMINES AND TRITYL SALTS

Entry	Amine	Trityl salt	Solvent	Reaction time, hr	Products	Yield, %
1	(Ph-CH <sub>2</sub> ) <sub>3</sub> N <sup>a</sup>	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>3</sub> CN	0.5	Ph <sub>3</sub> CH (Ph-CH <sub>2</sub> ) <sub>2</sub> N=C <sup>+</sup> H-Ph BF <sub>4</sub> <sup>-</sup>	89 94
2		Ph <sub>3</sub> CBr	CH <sub>3</sub> CN	24	 Br <sup>-</sup>	40
3	Ph <sub>3</sub> N	Ph <sub>3</sub> CBr	CH <sub>2</sub> Cl <sub>2</sub>	17	Nr <sup>b</sup>	
4	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH <sup>c</sup>	Ph <sub>3</sub> CBr	None	1	Ph <sub>3</sub> CN(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	75
5	(CH <sub>3</sub> ) <sub>2</sub> NH <sup>c</sup>	Ph <sub>3</sub> CBr	CH <sub>3</sub> CN	3.5	Ph <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	97

<sup>a</sup> Taken from ref 4. <sup>b</sup> Nr = no reaction. <sup>c</sup> Excess amine was used in these reactions.

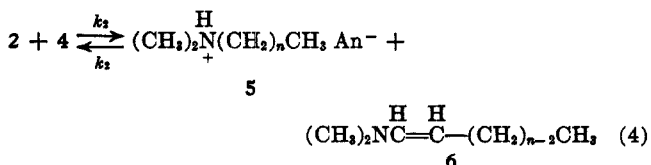
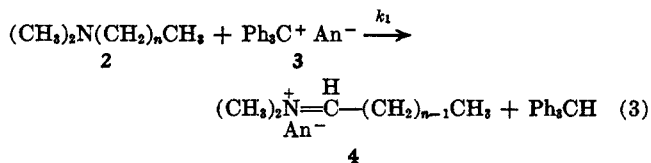
 TABLE III  
 REACTIONS OF DIMETHYLISOBUTYLAMINE, IMINIUM SALT, AND ENAMINE<sup>a</sup>

Entry	Amine compds	Trityl salt	Solvent	Reaction time	Products	Yield, <sup>b</sup> %
1	(CH <sub>3</sub> ) <sub>2</sub> N( <i>i</i> -C <sub>4</sub> H <sub>9</sub> )	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	4.5 hr	Ph <sub>3</sub> CH (CH <sub>3</sub> ) <sub>2</sub> N <sup>+</sup> ( <i>i</i> -C <sub>4</sub> H <sub>9</sub> )BF <sub>4</sub> <sup>-</sup> Oil	87 43 Ca. 40 <sup>c</sup>
2	(CH <sub>3</sub> ) <sub>2</sub> N <sup>+</sup> ( <i>i</i> -C <sub>4</sub> H <sub>9</sub> )BF <sub>4</sub> <sup>-</sup> (CH <sub>3</sub> ) <sub>2</sub> N( <i>i</i> -C <sub>4</sub> H <sub>9</sub> )	None	CH <sub>2</sub> Cl <sub>2</sub>	10 min	(CH <sub>3</sub> ) <sub>2</sub> NC=C(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> N <sup>+</sup> ( <i>i</i> -C <sub>4</sub> H <sub>9</sub> )BF <sub>4</sub> <sup>-</sup>	26 Not determined
3	(CH <sub>3</sub> ) <sub>2</sub> NC=C(CH <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	1 hr	Ph <sub>3</sub> CH	≅100
4	(CH <sub>3</sub> ) <sub>2</sub> NC=C(CH <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> CBF <sub>4</sub>	CDCl <sub>3</sub>	2 hr	Ph <sub>3</sub> CH	≅100
5	(CH <sub>3</sub> ) <sub>2</sub> NC=C(CH <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> CBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	4 hr	Ph <sub>3</sub> CH	70
6	(CH <sub>3</sub> ) <sub>2</sub> NC=C(CH <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> CBr	CH <sub>2</sub> Cl <sub>2</sub>	3 hr	Ph <sub>3</sub> CH	≅100
7	(CH <sub>3</sub> ) <sub>2</sub> NC=C(CH <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> CBr	CH <sub>3</sub> CN	17 hr	Ph <sub>3</sub> CH Dimer	93 28

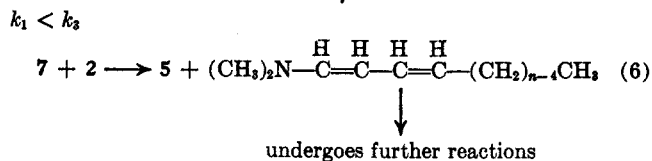
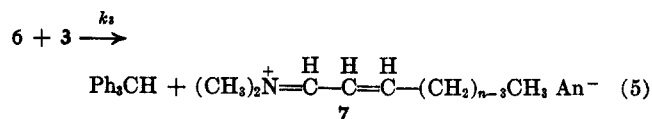
<sup>a</sup> All reactions were conducted with equimolar amounts of starting materials at room temperature except as noted. <sup>b</sup> Yields are based on the proposed reaction scheme (eq 3-6). Dimer yields not determined in entries 3-6. <sup>c</sup> Based on the assumption that the oil represents the dimer proposed in reaction 7. <sup>d</sup> Reaction run at -70°.

that this quaternary salt is severely sterically hindered favoring equilibrium toward the free amine. With relief of steric strain, such as in the use of pyridine in quaternary amine formation, the salt is readily isolated (entry 2, Table II).<sup>10</sup>

A proposed scheme to account for the products in these systems is presented in eq 3-6.



(10) Although pyridine contains  $\alpha$  hydrogens it does not undergo hydride transfer reactions with triphenylcarbonium ion. This is most probably due to a combination of the stability of the quaternary salt formed and the high energy of the intermediate required for hydride transfer from a vinylic position.



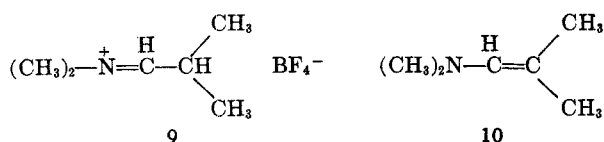
Since free amine and triphenylcarbonium ion are present in the reaction mixture, the reasonable initial intermolecular reaction is hydride transfer from an  $\alpha$ -methylene of the tertiary amine (eq 3). To account for the absence of ternary iminium salt and the presence of amine hydroanion salt, further reaction must take place. Ternary iminium salts can be formed by protonation of enamines;<sup>11,12</sup> it is likely, therefore, that enamines could result from reaction of ternary iminium salts with tertiary amines (eq 4). It is further pro-

(11) Cf. N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963), and references cited therein.

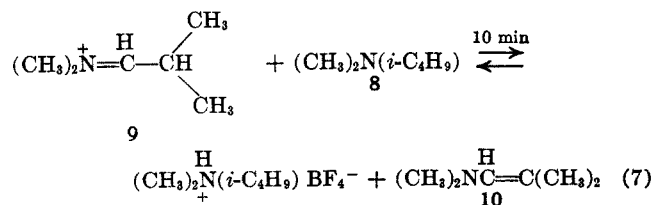
(12) E. J. Stamhuis, W. Maas, and H. Wynberg, *ibid.*, **30**, 2160 (1965), and references cited therein.

posed that the enamine also transfers hydride ion to triphenylcarbonium ion, and at a rate faster than hydride transfer from tertiary amines (reaction 5). Under these conditions no buildup of enamine and high yields of triphenylmethane would result. Similarly, further proton abstraction from the allylic-type cation (7) by tertiary amine would yield large amounts of amine hydroanion salt as well as a highly unsaturated amine product (reaction 6). Several observations in this reaction system are consistent with this scheme. Essentially a quantitative material recovery of trityl compounds is obtained from the reaction of trityl bromide with dimethyldodecylamine (entry 8, Table I). We were able, however, to recover only 71% of the theoretical yield of dimethyldodecylamine hydrobromide salt. The remaining 29% of material was a water-soluble, black residue that resisted all methods of purification. This residue is presumably the highly oxidized amine which has contributed all the hydrogen atoms by hydride and proton transfers. If the same reaction is run with a large excess of amine and the reaction products hydrolyzed after a short reaction time, a small amount of dodecanal can be recovered, indicating either the ternary iminium salt (4) or the enamine (6) as a reaction intermediate. Attempts to isolate other pure products from this reaction were unsuccessful.

To gain support for the foregoing proposal a more detailed examination of hydride transfer reactions has been conducted using the dimethylisobutyl grouping in these compounds. With this alkyl fragment it was possible to prepare and study the hypothetical intermediates in isolated experiments. This work involved the reaction of dimethylisobutylamine (8) with trityl salts, isobutylidenedimethylaminium fluoroborate (9) with 8, and dimethylisobutenylamine (10) with trityl salts.



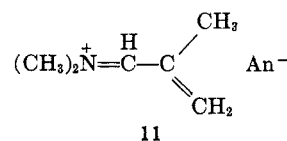
Dimethylisobutylamine (8) reacts with triphenylcarbonium ion to produce high yields of triphenylmethane, dimethylisobutylamine hydrofluoroborate, and an oil, similar to the observations made with dimethyldodecylamine. A  $\beta$  proton can be abstracted from isobutylidenedimethylaminium fluoroborate by 8 to give the corresponding enamine and dimethylisobutylamine hydrofluoroborate (eq 7).



The formation of 10 is rapid. After 10 min gas-liquid partition chromatography (glpc) indicated a ratio of 69:31 of amine to enamine. Work-up of products and distillation resulted in a 53% recovery of 8 and a 26% yield of 10. These data then clearly support reaction 4 of the proposed mechanism. If

the reaction is run for longer periods a slow disappearance of 10 is observed, presumably due to self-condensation and other dimerization reactions. Whether these side reactions are important with trityl salts present is highly doubtful since further work has shown that enamines react readily with trityl salts (entries 3-7, Table III).

The reaction of dimethylisobutenylamine (10) with triphenylcarbonium ion is exceedingly facile. Quantitative yields of triphenylmethane can be recovered from the reaction of 10 with either triphenylcarbonium fluoroborate or triphenylmethyl bromide at room temperature within 1 hr. At  $-70^\circ$  for 4 hr a 70% yield of triphenylmethane was recovered using triphenylcarbonium fluoroborate as a hydride acceptor. This observation then lends credence to the earlier supposition that hydride abstraction from enamines is rapid and therefore accumulation of these products in hydride transfer systems is prevented (reaction 5). Identification of the unsaturated amine product (oil) resulting from hydride transfer proved difficult. Attempts to trap the expected salt



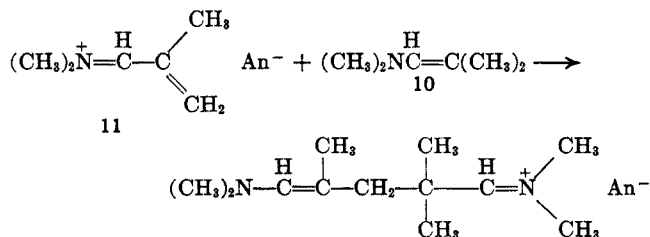
were unsuccessful. The isolated oil showed infrared absorptions at 5.8 and 5.95  $\mu$ , indicative of both iminium salt and enamine functions.<sup>13</sup> These absorptions were identical with those of the oil isolated from the reaction of dimethylisobutylamine (8) and triphenylcarbonium ion. To identify the oil it was reduced with sodium borohydride in alcohol solvent to convert both the enamine and iminium salt functions to their saturated analogs.<sup>14</sup> Elemental analysis as well as infrared, nuclear magnetic resonance (nmr), and mass spectra indicate that the reduction product is a dimer of 11 which has incorporated one molecule of alcohol (see Experimental Section).<sup>15</sup> Unfortunately, this product is unstable to glpc, column chromatography, and silica gel tlc, and further purification was unattainable.<sup>16</sup>

From this study of the dimethylisobutylamine series it is reasonable to assume that all aliphatic tertiary amines containing  $\beta$ - and  $\gamma$ -hydrogen atoms will react by the path outlined. These results do show that a tertiary amine transfers hydride ion to triphenylcarbonium ion to form the ternary iminium salt which rapidly

(13) Cf. J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 95 (1963).

(14) Reference 13, p 80.

(15) We envision C-alkylation by 10 on the terminal carbon of 11 as the main mode of coupling.



(16) This would suggest that at least part of the alcohol is attached to the iminium salt function to form the unstable  $>\text{N}-\text{CHOR}$  group; cf. H. H. Hellman and G. Opitz, " $\alpha$ -Aminoalkylierung," Verlag Chemie, Weinheim, 1960; N. J. Leonard and A. S. Hay, *J. Am. Chem. Soc.*, **78**, 1984 (1956), and references therein.

reacts with tertiary amine present to form the corresponding enamine and amine hydroanion salt. No buildup of these intermediates is found owing to the extremely rapid reaction of enamines with triphenylcarbonium ion.

An interesting point concerning these reactions is the high selectivity of the triphenylcarbonium ion for secondary hydride ion. For example, dimethyldodecylamine apparently transfers hydride ions almost exclusively from the dodecyl chain<sup>17</sup> despite the statistical favor of two methyl groups over one methylene group (adjacent to nitrogen) and the supposed high degree of steric strain in hydride transfer reactions.<sup>18</sup> Apparently the stability of the incipient ternary iminium salt compared to a primary iminium salt overcomes these other factors. The synthetic application of this oxidation of amines appears to be very limited. Thus, only in certain selective amines containing no  $\beta$ -hydrogen atoms can a high yield of iminium salts by hydride transfer be isolated. In a few cases where we attempted to apply this reaction to amines containing  $\beta$ -hydrogen atoms but no  $\gamma$ -hydrogen, *i.e.*,  $(\text{CH}_3)_2\text{N}-\text{CH}_2\text{CH}_2\text{CN}$  and  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{Ph}$ , extensive oxidation was noted as evidenced by the high recovery of triphenylmethane, but the corresponding enamines were not isolated. Perhaps modifying the reaction conditions would increase the synthetic utility of this oxidation process.

### Experimental Section

**Materials and Instrumentation.**—Triphenylmethyl bromide was prepared from triphenylcarbinol and acetyl bromide using the method of Bachmann.<sup>19</sup> Triphenylcarbonium fluoroborate was prepared by the method of Dauben, Honnen, and Harmon.<sup>20</sup>

Dimethyldodecylamine (Armour Chemical Co.) was distilled from potassium hydroxide before use. Methylation of isobutylamine with formaldehyde and formic acid provided dimethylisobutylamine, bp 80–81°. Isobutylidenedimethylaminium fluoroborate was prepared from dimethylamine hydrofluoroborate and isobutyraldehyde using the direct method of Leonard and Paukstelis.<sup>21</sup> A 90% yield of iminium salt was obtained. This salt was identified by its infrared spectrum (5.85  $\mu$ ) and nmr

absorptions at  $\tau$  1.85 ( $-\text{HC}=\overset{\text{H}}{\text{N}}<$ ),  $\tau$  6.6 [ $(\text{CH}_3)_2\overset{\text{H}}{\text{N}}=$ ],  $\tau$  7.1 ( $=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}<$ ), and  $\tau$  8.8 [ $>\text{C}-\overset{\text{H}}{\text{C}}(\text{CH}_3)_2$ ].

Dimethylisobutenylamine was prepared from dimethylamine and isobutyraldehyde according to the method of Brannock and Burpitt,<sup>22</sup> bp 87°. Triphenylamine was purchased from Aldrich Chemical Co. and used as received.

All solvents used were of reagent quality and were distilled from Linde 3A Molecular Sieves and deoxygenated with argon before use. In addition, chloroform was further purified by washing with sulfuric acid and water before distillation according to the procedure of Williams.<sup>23</sup> This method was necessary to prevent reaction of tertiary amines with chloroform.

Chloroform-*d* was purchased from Merck, Canada, and used as received.

**Reaction of Dimethyldodecylamine with Triphenylcarbonium Fluoroborate in Dichloromethane (Entry 1, Table I).**—To 2.1 g

(17) An alternate explanation would be the initial formation of the primary iminium salt followed by 1,3 hydride transfer to give the ternary compound.

(18) Cf. R. Stewart, "Oxidation Mechanism," W. A. Benjamin, Inc., New York, N. Y., 1964, p 22, and references therein.

(19) W. E. Bachmann, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 841.

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

(21) N. J. Leonard and J. V. Paukstelis, *ibid.*, **28**, 3021 (1963).

(22) K. C. Brannock and R. D. Burpitt, *ibid.*, **26**, 3576 (1961).

(23) H. Williams, *ibid.*, **29**, 2046 (1964).

(0.01 mole) of triphenylcarbonium fluoroborate dissolved in 50 ml of dichloromethane was added 2.4 g (0.01 mole) of dimethyldodecylamine in 20 ml of dichloromethane over a 30-min period. The solution temperature rose from 25 to 29° and the color turned from yellow to dark green to light yellow during this time. After stirring at room temperature for 2.5 hr, pentane was added to the reaction mixture to precipitate a white solid which was filtered. The infrared spectrum of the white solid (yield 2.1 g,

72%) showed a strong  $>\overset{\text{H}}{\text{N}}-\text{H}$  absorption (3.1  $\mu$ ) and no absorption in the iminium salt range (5.8–6.0  $\mu$ ). The nmr spectrum showed peaks at  $\tau$  6.8 ( $>\overset{\text{H}}{\text{N}}-\text{CH}_2$ ),  $\tau$  7.0 [ $>\overset{\text{H}}{\text{N}}(\text{CH}_3)_2$ ],  $\tau$  8.9 ( $>\text{C}-\text{CH}_2-$ ), and  $\tau$  9.1 ( $>\text{C}-\text{CH}_3$ ). These  $\tau$  values are consistent with the dimethyldodecylamine hydrofluoroborate structure.

The filtrate was evaporated to yield crude triphenylmethane, mp 79–82°. Two recrystallizations from ethanol gave a pure product: mp 90–91°, 1.64 g (67%).

**Reaction of Dimethyldodecylamine with Triphenylcarbonium Fluoroborate in Chloroform-*d* (Entry 4, Table I).**—To 215 mg ( $6.5 \times 10^{-4}$  mole) of triphenylcarbonium fluoroborate dissolved in 4 ml of chloroform-*d*, 145 mg ( $6.8 \times 10^{-4}$  mole) of dimethyldodecylamine was added and stirred at room temperature for 5 hr. The solution was then evaporated under reduced pressure and the residue was washed with several portions of dry hexane. The hexane-insoluble solid weighed 44 mg (22%) and its infrared spectrum was identical with that of dimethyldodecylamine hydrofluoroborate. The hexane layer was evaporated under reduced pressure and chromatographed on alumina (Woelm, activity I), eluting with hexane. A total of 30 mg (19%) of triphenylmethane was recovered (mp 90–91°). Nmr shows the absence of deuterium in the product.

**Reaction of Dimethyldodecylamine with Triphenylmethyl Bromide in Dichloromethane (Entry 8, Table I).**—To a solution of 7.5 g (0.0234 mole) of triphenylmethyl bromide in 75 ml of dichloromethane was added 5.0 g (0.0234 mole) of dimethyldodecylamine over 45 min. The reaction was exothermic (4°) and changed from yellow to dark green. After stirring for 2 hr the solution was evaporated at reduced pressure and washed with dry ether. The ether insoluble residue was recovered and recrystallized from methylene chloride-pentane to yield 4.85 g (71%) of dimethyldodecylamine hydrobromide, mp 174–174.5°.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{32}\text{BrN}$ : C, 57.1; H, 10.9; Br, 27.2; N, 4.75. Found: C, 57.5; H, 11.2; Br, 28.0; N, 4.74.

The mother liquor was concentrated to yield a black, intractable, water-soluble residue.

The ether layer was evaporated under reduced pressure and the resulting solid chromatographed on alumina (Woelm, activity I) eluting with 80:20 hexane-benzene. A total of 1.4 g (24.5%) of pure triphenylmethane was recovered, mp 90–91°. Further elution with ether yielded 3.1 g (67%) of triphenylcarbinol, mp 161–162°.

**Reaction of Dimethyldodecylamine with Triphenylmethyl Bromide. Hydrolysis of Products to Yield Dodecanal.**—To 5.0 g (0.0155 mole) of triphenylmethyl bromide, 25 g (0.117 mole) of dimethyldodecylamine was added with stirring over a 5-min period. The reaction was maintained at 5° by cooling with an ice bath. After an additional 80 min of stirring, 10% HCl was added while maintaining the temperature at 5° until the mixture was acidic. The mixture was extracted with ether, the ether layer was dried with magnesium sulfate and evaporated under reduced pressure. The liquid residue was examined by glpc (Carbowax 20M, 125°) and the presence of lauraldehyde was indicated by comparison with an authentic sample. A 2,4-dinitrophenylhydrazone derivative was formed: mp 104–106° (lit.<sup>24</sup> 105–105.6°). No depression in melting point was observed when mixed with an authentic sample. A total of 320 mg (5.5%) of 2,4-dinitrophenylhydrazone derivative was recovered.

Other volatile components in the ether layer were in small amounts and could not be identified by glpc.

**Reaction of Pyridine and Triphenylmethyl Bromide in Acetonitrile (Entry 2, Table II).**—To a solution of 5.2 g (0.016 mole) of triphenylmethyl bromide in 50 ml of acetonitrile, 7.1 g (0.09 mole) of pyridine was added. The solution was stirred for 24 hr and then evaporated under reduced pressure. After washing with pentane a slightly tan solid was recovered, mp 139° dec. Nmr analysis of the product shows pyridinium hydrogens ( $\tau$

(24) R. Ellis, A. M. Gaddis, and G. T. Currie, *Anal. Chem.*, **30**, 471 (1958).

0.9–1.9) and phenyl hydrogens ( $\tau$  2.7) in a ratio of 1:3. A total of 2.6 g (40%) was recovered.

*Anal.* Calcd for  $C_{22}H_{20}BrN$ : C, 71.7; H, 5.02; Br, 19.9; N, 3.47. Found: C, 71.3; H, 5.25; Br, 20.6; N, 3.53.

**Attempted Reaction of Triphenylamine and Triphenylmethyl Bromide in Dichloromethane (Entry 3, Table II).**—A solution of 3.0 g (0.0093 mole) of triphenylmethyl bromide and 2.3 g (0.0093 mole) of triphenylamine in 50 ml of dichloromethane was stirred at room temperature for 17 hr. There was no visible sign of reaction. The solution was then evaporated under reduced pressure and the resulting solid mixture examined by infrared and nmr. The mixture appeared to be unreacted triphenylamine and triphenylmethyl bromide.

**Reaction of Diethylamine and Triphenylmethyl Bromide (Entry 4, Table II).**—To 16.1 g (0.05 mole) of dry triphenylmethyl bromide was added 37 g (0.5 mole) of anhydrous diethylamine and the mixture was stirred for 1 hr. During this time the triphenylmethyl bromide dissolved and the temperature rose to 57°. Pentane was then added to precipitate diethylamine hydrobromide (7.7 g, 0.05 mole, 100%) which was filtered. The pentane layer was evaporated under reduced pressure and the product was recrystallized twice from absolute ethanol to yield 11.8 g (0.038 mole, 75%) of trityldiethylamine: mp 104.0–104.5°, lit.<sup>8a</sup> mp 107°.

*Anal.* Calcd for  $C_{22}H_{28}N$ : C, 87.6; H, 7.99; N, 4.44. Found: C, 87.6; H, 7.95; N, 4.45.

**Reaction of Triphenylmethyl Bromide and Dimethylamine in Acetonitrile (Entry 5, Table II).**—Into a solution of 22.6 g (0.07 mole) of triphenylmethyl bromide in 200 ml of acetonitrile was bubbled excess dimethylamine until the reaction ceased to be exothermic (*ca.* 2 hr). Stirring was continued for 1.5 hr then pentane was added to precipitate dimethylamine hydrobromide. This was removed by filtration and the pentane-acetonitrile layer evaporated under reduced pressure. The solid product was recrystallized from ethanol, mp 92.0–92.5°, to yield 19.5 g of trityldimethylamine (97% yield). Another recrystallization from ethanol raised the melting point to 94.2–94.6°, lit.<sup>8b</sup> mp 95–97°.

*Anal.* Calcd for  $C_{21}H_{21}N$ : C, 87.8; H, 7.36; N, 4.87. Found: C, 87.8; H, 7.10; N, 4.89.

**Reaction of Dimethylisobutylamine and Triphenylcarbonium Fluoroborate in Dichloromethane (Entry 1, Table III).**—To a solution of 5.0 g (0.015 mole) of triphenylcarbonium fluoroborate dissolved in 30 ml of dichloromethane, 1.9 g (0.019 mole) of dimethylisobutylamine was added over 15 min. The solution temperature rose 10° and turned dark brown and then gradually became lighter. After 4.5 hr of stirring, an infrared spectrum of the solution showed strong peaks at 5.82 and 5.95  $\mu$ . Pentane was added to produce an oil which was separated from the pentane-dichloromethane layer and was washed with additional pentane. Water dissolved the oil which was treated with sodium hydroxide, ether extracted, dried, and distilled to yield 325 mg of dimethylisobutylamine. On the basis that this represents dimethylisobutylamine hydrofluoroborate, the yield of product is 43%. No other volatile product was recovered from the ether layer. The pentane-dichloromethane layer was evaporated under reduced pressure and chromatographed on Fluorosil. Elution with hexane gave 3.2 g of triphenylmethane: mp 85–88°, yield 87%. One recrystallization from ethanol raised the melting point to 90–91°.

**Reaction of Isobutylidenedimethylaminium Fluoroborate and Dimethylisobutylamine in Dichloromethane (Entry 2, Table III).**—To 3.8 g (0.02 mole) of isobutylidenedimethylaminium fluoroborate dissolved in 40 ml of dichloromethane, 2.0 g (0.02 mole) of dimethylisobutylamine was added over a 1-min period. After stirring for 10 min a sample of the reaction solution showed the

presence of dimethylisobutylamine and dimethylisobutylamine by glpc on Carbowax 20M at 130°. The ratio of amine to enamine was 69:31. Infrared spectra indicated the presence of

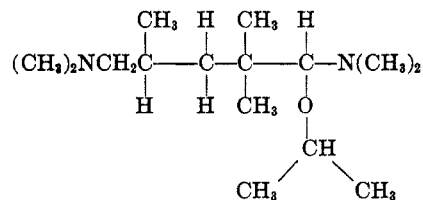
$>\overset{+}{N}H$  (3.1  $\mu$ ) and showed additional peaks at 5.85  $\mu$  ( $>C=\overset{+}{N}<$ )

and 5.95  $\mu$  ( $>N-\overset{+}{C}=C<$ ). Pentane was added to the reaction solution to produce a white precipitate which was filtered. The filtrate was distilled to recover a mixture of dimethylisobutylamine and dimethylisobutenylamine. Glpc shows a ratio of 81:19 (amine-enamine) and a recovery of 0.0106 mole of amine (53%) and 0.0052 mole (26%) of enamine.

In another reaction conducted under the same conditions the solution was analyzed for enamine by glpc at 20-min time intervals. The enamine peak gradually diminished until it was not distinguishable after 2 hr.

**Reaction of Triphenylmethyl Bromide and Dimethylisobutenylamine in Acetonitrile (Entry 7, Table III).**—To 20.0 g (0.62 mole) of triphenylmethyl bromide dissolved in 100 ml of acetonitrile, 6.2 g (0.62 mole) of dimethylisobutenylamine was added over a 30-min period. The solution turned dark and the temperature rose 12° (25–37°) during the addition. After stirring for 24 hr at room temperature, glpc analysis of an aliquot showed no volatile material. Ether was added and an oil was separated from the solution. Infrared spectra showed bands at 5.85  $\mu$

( $>C=\overset{+}{N}<$ ) and 5.95  $\mu$  ( $>N-\overset{+}{C}=C<$ ). The oil was dissolved in 100 ml of 2-propanol and to this was added 37 g (1.5 moles) of  $NaBH_4$ . The solution was refluxed for 17 hr, cooled, concentrated under reduced pressure, and washed with aqueous sodium hydroxide. Extraction with ether yielded 4.9 g of liquid which gave no infrared absorption in the 5–6- $\mu$  region and showed 3° amine bands (3.6, 9.6  $\mu$ ). Glpc (160°, Carbowax 20M) showed three components but attempted collection of these components resulted in decomposition on the column. Thin layer chromatography (tlc) analysis (silica gel) separated five components; however, attempted isolation of this mixture again gave decomposition products. Similar results were obtained with silica gel column chromatography. The product was distilled using a 3-in. alembic distillation apparatus. The major fraction was collected at 95–110° (0.2 mm); nmr spectra of this sample indicated the presence of  $N-CH_3$  ( $\tau$  7.6),  $N-CH_2$  ( $\tau$  7.4),  $C-CH_2$  and  $C-CH_2-$  ( $\tau$  8.6–9.1) groups as well as a small  $O-CH$  peak ( $\tau$  6.3). Integration of the aforementioned peaks showed a ratio of 1.6:14:17 for the  $O-CH$ ,  $N-CH_2$  and  $N-CH_3$ , and  $C-CH_2$  and  $C-CH_3$  peaks, respectively. On the assumption that the dimer structure is



the ratio of the peak areas should be 2:14:18. Mass spectral analysis of the product had no parent peak at 258 but did produce a 196 peak (258 –  $OCHCH_3$ ) and a base peak at 58 [ $(CH_3)_2-$

$NCH_2-$ ]. The elemental analysis is accommodated reasonably well by the reduced dimer structure with one molecule of 2-propanol incorporated in the molecule. The yield was 2.58 g (28%).

*Anal.* Calcd for  $C_{15}H_{24}N_2O$ : C, 69.71; H, 13.26; N, 10.84; O, 6.19. Found: C, 70.58; H, 12.18; N, 10.79; O, 6.37.