[CONTRIBUTION FROM THE ORGANIC DEPARTMENT, THE ABBOTT RESEARCH LABORATORIES]

Reactions of Aralkyl Amines with Carbon Dioxide

BY H. B. WRIGHT AND M. B. MOORE

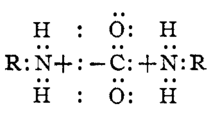
It has long been recognized that the strongly basic aralkyl amines react readily with carbon dioxide to form solid products. In some cases, these have been shown to be carbonates.[1] In others, they have been mentioned as carbonates, without any analytical data offered in proof.[2]

In connection with some work on β-arylethylamines in this Laboratory, the bases were allowed to stand in the air and the solid products analyzed. The first one so studied was *o*-methoxyphenethylamine, and the analytical data disagreed with the theoretical values for either the normal or the acid carbonate. Further calculations showed them to be in good agreement with the calculated values for the substituted ammonium carbamate, $RNHCOONH_3R$.

In view of this interesting observation, other amine–carbon dioxide addition products were studied. Some were prepared by passing dry carbon dioxide into a solution of the amine in dry ether (method A) and some by the simple method of allowing the bases to stand in the air until a solid product formed (method B). The crystalline compounds were washed with dry ether. In some cases, no further purification was carried out; in others, the samples were sublimed.

A few compounds of this type were found to have been previously reported. Fichter and Becker[3] prepared a series of substituted ammonium carbamates, including benzylammonium benzylcarbamate, and similar compounds from some aliphatic amines. More recently, esters of α-amino acids were shown to form compounds with carbon dioxide of the type, $RCH(COOR')NHCOONH_3CH(COOR')R$.[4,5]

Hayashi[6] studied the physicochemical properties of the compounds formed by reaction of carbon dioxide with a series of eighteen kinds of amines, including a number of aralkyl amines. He concluded that all form compounds "··· having the formula $2RNH_2$–CO_2," and proposed the electronic formula, with "semipolar double linkage between N and C··"



$$\begin{array}{cccccc} & \mathrm{H} & : & \ddot{\mathrm{O}}: & \mathrm{H} & \\ \mathrm{R}: & \underset{..}{\ddot{\mathrm{N}}}+ & : & -\underset{..}{\ddot{\mathrm{C}}}: & +\underset{..}{\ddot{\mathrm{N}}} & :\mathrm{R} \\ & \mathrm{H} & : & \mathrm{O}: & \mathrm{H} & \end{array}$$

Werner[7] prepared mixed substituted ammonium carbamates by replacing the amine in the electropositive group by another more basic amine; as dimethylammonium benzylcarbamate from benzylammonium benzylcarbamate. His method of preparation of the symmetrical carbamates was similar to that here described as method A.

Compounds of the formula $(R_3N)_2{\cdot}CO_2$ from aliphatic primary, secondary, or tertiary amines have recently been mentioned by Wolfe and Temple[8] with the notation that they readily sublime.

Except for those of Werner,[7] the substituted ammonium carbamates previously reported have been prepared with cooling, and were described as comparatively unstable at room temperature. However, with the exception of the phenethylamine "carbonate," m. p. 101–104°, described by Fileti and Piccini,[2] none of the parent amines were of the type $ArCH_2CH_2NH_2$. While the phenethylammonium phenethylcarbamate here reported melted somewhat lower than their product (see Table I), it seems probable that the two are identical.

The carbamates prepared are listed in Table I, with their melting points and analytical data. Carbon and hydrogen values are reported, as these are distinctly different from those for the carbonates, whereas this is not true for nitrogen. All are soluble in water and alcohol (12A), practically insoluble in ether or cold benzene and more soluble in warm benzene. The compounds from the phenethylamines exhibit very good stability at room temperature. In screw-capped bottles, they have been kept for eleven months, with no significant change in the analytical values, except in the case of *p*-isopropylphenethylamine (Table I). It may be noted that the original analysis here is barely acceptable, and the comparative instability of this member may be due to the catalytic effect of a trace of impurity.

All these carbamates exhibit a high vapor pressure at room temperature, and the vapor in the bottle above a sample is alkaline to litmus or other test paper.[9] That this is not due to decomposition is attested not only by the analyses, but by the fact that several samples were purified by sublimation at atmospheric pressure or at reduced pressure, as indicated in Table I. The extreme differences in boiling points of the amine and of carbon dioxide make it appear improbable that the supposed sublimation consists in a decomposition and a recombination of the constituents on the cool surface.

That these compounds appear to sublime intact, without appreciable decomposition into their substituents, might be considered an argument

---

[1] E. E. Moore and M. B. Moore, *Ind. Eng. Chem.*, **23**, 21 (1931).

[2] M. Fileti and A. Piccini, *Ber.*, **12**, 1308 (1879).

[3] F. Fichter and B. Becker, *ibid.*, **44**, 3481 (1911).

[4] M. Frankel, O. Neufeld and E. Katchalski, *Nature*, **144**, 832 (1939).

[5] M. Frankel and E. Katchalski, THIS JOURNAL, **65**, 1670 (1943).

[6] T. Hayashi, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **11**, 133 (1932).

[7] E. A. Werner, *J. Chem. Soc.*, **117**, 1046 (1920).

[8] J. K. Wolfe and K. L. Temple, THIS JOURNAL, **70**, 1414 (1948).

[9] First noted by Mr. E. F. Shelberg.

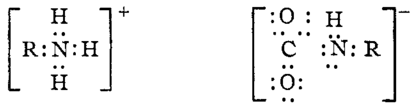
TABLE I

SUBSTITUTED AMMONIUM CARBAMATES, RNHCOONH$_3$R

R	M. p. (uncor.), °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$C_6H_5CH_2CH_2$[a]	96–98	$C_{17}H_{22}N_2O_2$	71.30	71.23, 71.14[g]	7.74	7.56, 7.63[g]
$C_6H_5CH_2CH_2$[b,c]		$C_{17}H_{22}N_2O_2$	71.30	71.19	7.74	7.50
p-$CH_3OC_6H_4CH_2CH_2$[a]	109–110	$C_{19}H_{26}N_2O_4$	65.87	66.09, 65.68[g]	7.56	7.44, 7.07[g]
o-$CH_3OC_6H_4CH_2CH_2$[b,d]	102–103	$C_{19}H_{26}N_2O_4$[e]	65.87	65.79, 65.99[g]	7.56	7.39, 7.66[g]
3,4-$(CH_3O)_2C_6H_3CH_2CH_2$[a]	94–95	$C_{21}H_{30}N_2O_6$	62.05	62.24	7.44	7.44
p-iso-$C_3H_7C_6H_4CH_2CH_2$[a]	79–81	$C_{23}H_{24}N_2O_2$	74.55	74.05, 72.46[g]	9.25	8.97, 8.00[g]
$C_6H_5CH_2$[a]	96[f]	$C_{15}H_{18}N_2O_2$	69.74	69.60	7.02	7.00

[a] Prepared by method A. [b] Prepared by method B. [c] Sublimed under reduced pressure. [d] Sublimed at atmospheric pressure, m. p. unchanged. [e] Calcd.: N, 8.09. Found: N, 7.94, 7.89. [f] Softens 91°, Fichter and Becker[3] found 100°. [g] Second analyses after approximately eleven months.

against the concept of their structure as substituted ammonium carbamates. In favor of this concept is the accepted formation of ammonium carbamate itself and the replacement of the positive radical by a more basic one.[7] An electronic formula of the type proposed by Hayashi[6] gives no indication of a difference between the two nitrogen atoms of the molecule, and the selective replacement of one would not be anticipated. For these reasons, our compounds are assumed to be substituted ammonium carbamates, whose electronic formula may be written



$$\left[\begin{array}{c} H \\ R:\ddot{N}:H \\ \ddot{H} \end{array}\right]^+ \qquad \left[\begin{array}{cc} :\ddot{O}: & H \\ \ddot{C} & :\ddot{N}:R \\ :\ddot{O}: & \end{array}\right]^-$$

It is of interest to note that the tendency toward easy formation of stable carbamates is limited, among the aralkylamines studied here, to those of the general formula $ArCH_2CH_2NH_2$. While the carbamate salt from benzylamine is reported, it was obtained in a pure condition only after several trials. Amines of the above general formula tend to form carbamates upon standing in the air (method B), which might be considered an ideal condition for carbonate formation, due to the presence of moisture together with the carbon dioxide. *m*-Methoxyphenethylamine appears to form a carbamate, but the quantity available was too small for further purification, after analyses proved unsatisfactory.

None of these carbamates showed any evidence of hygroscopic properties when allowed to stand in open containers. To test this, a sample of 3,4-dimethoxyphenethylammonium 3,4-dimethoxyphenethyl carbamate was allowed to stand on the balance, and no increase in weight ensued.

Other amines studied, such as ephedrine, N-methylbenzylamine and β-methylphenethylamine failed to form stable non-hygroscopic carbamates under the conditions described in method A. α-Phenethylamine and α-methyl-*p*-methoxyphenethylamine formed white solids which did not give satisfactory analyses and appear to be mixtures of the carbamate and carbonate. All depart from the above general formula, either by alkyl branching, or by alkylation of the primary amino group.

Acknowledgment.—The authors are indebted to Dr. K. E. Hamlin, Jr., and to Dr. R. B. Hasbrouck for certain of the amines studied, and to Mr. E. F. Shelberg, Chief Microanalyst, for the microanalyses herein reported.

Summary

Some β-arylethylamines of the general formula $ArCH_2CH_2NH_2$ have been shown preferentially to form compounds with carbon dioxide whose analyses preclude the possibility that they may be carbonates. These are considered to be substituted ammonium carbamates for the reasons outlined above. They differ from most of the substituted ammonium carbamates previously reported in their much greater stability. Aralkyl amines of slightly different structure failed to form such carbamates under the experimental conditions used.

NORTH CHICAGO, ILLINOIS RECEIVED JUNE 16, 1948