COMMUNICATIONS TO THE EDITOR

THE REARRANGEMENT OF THE ISOMERIC 1,2-DIMETHYLAMINOCHLOROPROPANES. THE SYNTHESIS OF AMIDONE

Sir:

A recent note[1] describes the rearrangement and proof of structure of the new German analgesic drug Amidone, or No. 10820.[1]

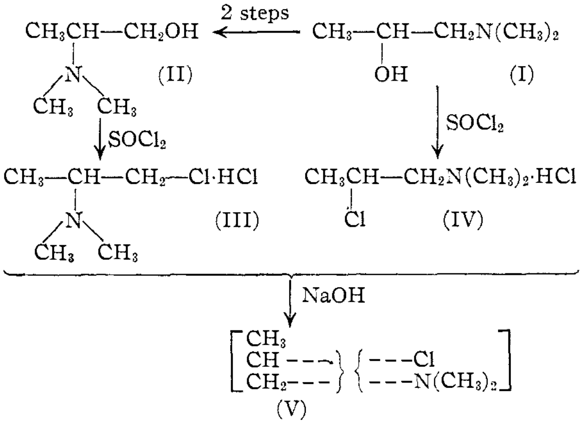
These investigators infer in their note that they have prepared 1-dimethylamino-2-chloropropane which on the sodamide condensation with diphenylacetonitrile rearranges through an ethyleneimmonium ion to give a mixture of 1-dimethylamino-2-methyl-3,3-diphenyl-butanenitrile and 2-dimethylamino-4,4-diphenylpentanenitrile.

Work in this laboratory confirms the physical constants for the two isomeric aminonitriles (low melting isomer m. p. 68.7–69°, high melting isomer 90.0–91.0° compared to 66–67° and 90–91°). Infrared absorption data collected on these two compounds also confirms the structures given by the above investigators.

The chlorination of 1-dimethylamino-2-propanol (I) (b. p. 124.0–124.5°) and 2-dimethylamino-1-propanol (II) (b. p. 145.0–145.5°) with thionyl chloride in anhydrous chloroform yields the corresponding dimethylaminochloropropane hydrochloride salts (III and IV). The latter salt (III) is much more soluble in chloroform than the former (IV). Both salts and a mixture of the two salts change crystalline form on heating and melt sharply 191.0–191.5° indicating that the two salts are isomeric and rearrange to the same compound under the influence of heat.

Isolation of the free bases from their salts gives dimethylaminochloropropanes (V) of identical boiling points (60–63° (110 mm.)) and identical infrared absorption curves confirming that the two products are identical. This product may be either of the two isomeric dimethylaminochloropropanes or an equilibrium mixture of the two. Thus, it appears that the isomeric 1,2-dimethylaminochloropropanes can rearrange, probably through the ethyleneimmonium ion, under the conditions used to isolate the free bases from their salts. The physical properties of this product indicate that it is in a non-polar form as contrasted to an ionic form since it is a liquid that may be distilled and on mixing with alcoholic silver nitrate gives a perfectly clear solution for a few seconds before depositing silver chloride.

The only product isolated from the reaction of the dimethylaminochloropropane (prepared from I) with moist silver oxide was the aminoalcohol II in very low yield (12%). The difficulty incurred in isolating products from this reaction mixture was such as not to preclude the possible presence of I also. These data show that I can be converted to II in low yields, but will not support the structure of the dimethylaminochloropropane, because of the apparent rearrangement possible during the chemical reaction.



Infrared absorption data for the dimethylaminochloropropane, the isomeric aminonitriles and Amidone will be presented later.

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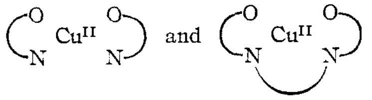
[1] Schultz, Robb and Sprague, This Journal, 69, 188 (1947).

STABILITY OF MULTIPLY-BONDED MOLECULAR ADDITION COMPOUNDS

Sir:

The marked increase in the stability of Werner complexes in which several coördinating groups are bound together into a "polydentate" structure has been emphasized recently by Calvin and Bailes,[1] who have compared copper chelates, for example, of the types:



(27)

It is pointed out that the precise source of this great increase in stability is as yet impossible to identify, although at least part of the answer may be the increase in entropy involved in the formation of the complex.

A more complete analysis of this entropy factor should provide a better understanding not only of Werner complexes, but also of other types of molecular complexes formed in colloid systems. Consideration of this entropy factor may be sim-

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[1] M. Calvin and R. H. Bailes, This Journal, 68, 949–954 (1946).