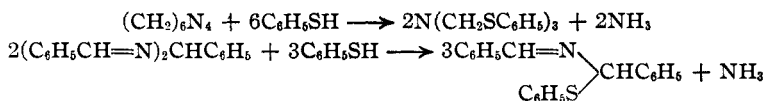


thiophenols, as well as benzyl mercaptan, undergo condensation in boiling 1,4-dioxane solution with such condensed ammonia-aldehydes as hexamethylenetetramine and hydrobenzamide, only part of the nitrogen of the base being eliminated as ammonia. The products are crystalline substances (except in a very few cases) which may be considered as substituted trimethylamines. The following typical examples of the reaction will serve to illustrate



The only analogous reactions which we have been able to find reported in the literature are those of hexamethylenetetramine with such weak acids as HCN [Eschweiler, *Ann.*, **278**, 230 (1894)] and N-nitromethylamine [Franchimont, *Rec. trav. chim.*, **29**, 355 (1910)], where a similar condensation takes place.

We are continuing our investigations and hope very shortly to be able to publish a detailed report of the work.

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RECEIVED JANUARY 28, 1933 PUBLISHED MARCH 7, 1933

ON THE MAXIMUM ROTATIONS IN THE HOMOLOGOUS SERIES OF α -BROMO ACIDS

Sir:

In the course of our work on the shift of the molecular rotations of members of homologous series, we were in need of resolving α -bromobutyric and α -bromocaproic acids to the maximum. The α -bromopropionic acid had already been resolved to the maximum of $[\text{M}]_D^{25} -43.6^\circ$ by Ramberg [*Ann.*, **370**, 234 (1909)] through the cinchonine salt.

We succeeded in resolving the α -bromobutyric acid through its brucine salt to $[\text{M}]_D^{25} +59.62^\circ$ and α -bromocaproic acid through its strychnine salt to $[\text{M}]_D^{25} -71.45^\circ$, thus showing that in this homologous series the values of the rotations of the individual members increase progressively. The progress in the case of the methyl esters was similar, being 83, 92 and 104° , respectively, for the three esters.

These results were obtained nearly a year ago and remained unpublished for the reason that they were intended to be part of a comparative study of the rotations of the corresponding α -hydroxy and α -amino acids.

We wish to record the results at this time for the reason that in the current number of the *Journal für praktische Chemie* there appeared an article by Ahlberg [*J. prakt. Chem.*, **135**, 335 (1932)] devoted exclusively to the

resolution of α -bromobutyric acid. The author failed to accomplish resolution by means of the brucine salt, but by means of the strychnine salt obtained a value for the maximum rotation lower than ours and of opposite sign, namely, $[\text{M}]_D^{25} - 54.0^\circ$.

It is interesting to note that through the strychnine salts both acids lead to active acids rotating in the same direction.

It may also be mentioned that α -bromobutyric acid had previously been resolved by Levene, Mori and Mikeska [*J. Biol. Chem.*, **75**, 337 (1927)] to a degree somewhat higher than that of Ahlberg.

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THE ROTATION OF MOLECULES OR GROUPS IN CRYSTALLINE SOLIDS

Sir:

In continuation of earlier studies of the possibility of rotation of molecules or groups in crystalline solids [Smyth and Hitchcock, *THIS JOURNAL*, **54**, 4631 (1932); *ibid.*, **55**, in press (1933); Kamerling and Smyth, *ibid.*, **55**, 462 (1933)], the dielectric constants of hydrogen sulfide, ammonia and methyl alcohol have been measured from -190° to a few degrees above the melting points over a frequency range of 300 to 60,000 cycles. In solid hydrogen sulfide two sharp transitions are shown by the dielectric constant at -146.7° and -170.0° , in excellent agreement with the values just reported by Kemp and Denison [*THIS JOURNAL*, **55**, 251 (1933)]. The dielectric constant of the solid, higher than that of the liquid, shows almost free molecular rotation above the lower transition. Below it, there appears to be practically no dipole rotation. The behavior of hydrogen sulfide is thus similar to that of the hydrogen halides and in marked contrast to that of ice.

The low dielectric constant of solid ammonia in contrast to the high value of the liquid and its small decrease with decreasing temperature show that the molecule behaves like large molecules, such as those of nitrobenzene, in possessing little or no rotation in the solid, thus differing from all the small molecules previously investigated by means of dielectric constants. The dielectric constant of solid methyl alcohol near the melting point is much lower than that of the liquid but high enough to give evidence of some dipole rotation, which decreases sharply at a transition point -114.0° , a value close to the average of those found from specific heat measurements, -115.7° by Kelley [*THIS JOURNAL*, **51**, 180 (1929)], and -112.0° by Parks [*ibid.*, **47**, 338 (1925)]. Under conditions such that a glass is probably formed, a change of dielectric constant with frequency is found. Higher alcohols are being investigated in order to learn whether