

D. Through the Sodium Enolate (Equation 3).—The enolate was prepared from 4.25 g. of ethyl di-*p*-tolylmethylmalonate and 0.23 g. of sodium under 50 cc. of benzene; 2.72 g. of diphenylmethyl bromide was added and the solution refluxed for three hours. On crystallization from alcohol 2.05 g. (40%) of a product of m. p. 122–123° was obtained which was identical with that formed in 3A, B and C; mixed melting points showed no depression. A side reaction in this case was coupling of the halide, which was indicated by the isolation of 0.22 g. (12%) of tetraphenylethane.

In order to determine whether the dialkyl malonic esters could be cleaved by the bromomagnesium enolate of a monoalkyl malonic ester, the following experiment was performed. The bromomagnesium enolate of ethyl diphenylmethylmalonate was prepared by the addition of 8.2 g. (a slight excess) of ethyl benzaldehyde in 50 cc. of dry benzene to the filtered phenylmagnesium bromide prepared from 5.2 g. of bromobenzene and excess magnesium in 50 cc. of ether. Ethyl di-di-*p*-tolylmethylmalonate (VII) (2.69 g. or 0.005 mole) was added and the solution refluxed for twenty hours. The oily product was refluxed for five hours with 20% potash in 50% alcohol to remove the ethyl diphenylmethylmalonate (the dialkyl malonic esters are not saponified under these conditions), and the unsaponifiable material crystallized from alcohol. Ethyl diphenylmethyl di-*p*-tolylmethylmalonate (V), m. p. 122–123°, was isolated in 39% yield (1.0 g.).

The corresponding sodium enolate did not cause this cleavage. This was established by refluxing 0.005 mole of V and VII with 0.03 mole of the sodium enolate of ethyl

diphenylmethylmalonate in 75 cc. of benzene for twenty hours. In each case following the same procedure as outlined above over 90% of the unchanged dialkyl malonic esters was recovered.

Summary

Ethyl di-diphenylmethyl malonate has been proved to be a dialkyl malonic ester (III) rather than a ketene acetal (I), as was originally proposed. By analogy the corresponding derivative of ethyl cyanoacetate is probably a dialkyl cyanacetic ester rather than an O-alkyl derivative (II). In the hydrolysis of these remarkably stable esters the first reaction is the cleavage of a diphenylmethyl group. This cleavage originally led to the formulation of the compounds as O-alkyl derivatives, but must be interpreted now as resulting from the breaking of a carbon to carbon linkage weakened by the substituent groups.

In the synthesis of an unsymmetrical dialkyl malonic ester $RR'C(COOC_2H_5)_2$ through the bromomagnesium enolate disproportionation occurred and the two symmetrical homologs $RRC(COOC_2H_5)_2$ and $R'R'C(COOC_2H_5)_2$ were also produced.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

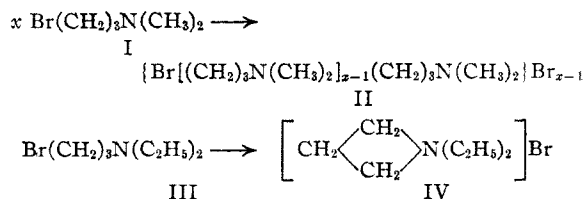
Quaternary Ammonium Salts from Bromopropylalkylamines. IV. Formation of Four-Membered Rings

By C. F. GIBBS AND C. S. MARVEL

Amines of the type $Br(CH_2)_nN(CH_3)_2$ have been found to undergo self-condensation to yield monomeric cyclic, dimeric cyclic or linear polymeric quaternary ammonium salts depending on the value of n .¹ We have now discovered that the size of the alkyl groups on the nitrogen atom affects the course of the reaction in the case of compounds in which n has the value 3. Thus, although bromopropyldimethylamine² (I) reacts with itself to give a linear polymeric quaternary ammonium salt (II), the corresponding diethyl derivative (III) under the same conditions reacts intramolecularly to give a cyclic quaternary ammonium salt (IV).

(1) Lehman, Thompson and Marvel, *THIS JOURNAL*, **55**, 1977 (1933).

(2) Gibbs, Littmann and Marvel, *ibid.*, **55**, 753 (1933).



The cyclic structure of the quaternary ammonium salt is established by its properties. It is crystalline, gives a neutral water solution, contains only ionizable bromine, and has a molecular weight which corresponds to that of the monomeric salt. The isomeric compound, diethylallylamine hydrobromide, which might form if bromopropyldiethylamine should lose hydrogen bromide and this acid should add to the nitrogen, has been prepared. Comparison of this

TABLE I

Compound	PHENOXY- AND BROMO-DIALKYLAMINES						Analyses, %	
	Yield, %	B. p., °C. at mm. press.	d_4^{20}	n_D^{20}	M. p., °C.	Calcd.	Found	
γ -Phenoxypropyl-diethylamine	87	118-120 (5)	<i>a</i>
Chloroplatinate	134-135	Pt 23.68	23.63	
γ -Phenoxypropyl-di- <i>n</i> -propylamine	90	137-139 (6)	0.938	1.4983	...	N 5.96	5.97	
γ -Phenoxypropyl-di- <i>n</i> -butylamine	95	148-150 (5)	.931	1.4939	...	N 5.32	5.65	
γ -Bromopropyldiethylamine	70	52-54 (5)	<i>a</i>	
Chloroplatinate	150-153	Pt 24.52	24.37	
γ -Bromopropyl-di- <i>n</i> -propylamine	66	77-78 (4)	
Chloroplatinate	194-196	Pt 22.86	23.34	
γ -Bromopropyldi- <i>n</i> -butylamine	57	96-98 (6)	1.073	1.4682	
Bromoaurate	130	Au 26.1	26.4	

^a Described by Marvel, Zartman and Bluthardt, *THIS JOURNAL*, **49**, 2299 (1927).

salt with the new quaternary ammonium salt shows that they are different compounds.

The di-*n*-propyl and di-*n*-butyl derivatives of bromopropylamine also react intramolecularly to give quaternary ammonium salts containing a four-membered ring. Thus it has been demonstrated that changing the alkyl groups on the nitrogen atom from methyls to larger ones such as ethyls, *n*-propyls or *n*-butyls, alters completely the course of the bifunctional reaction which takes place when the bromopropylamine derivative combines with itself. This type of reaction seems to offer a better opportunity of studying the effect of alkyl substituents on ring closure than do the various carbon ring closure reactions which have been studied previously.³

TABLE II

CYCLIC QUATERNARY AMMONIUM SALTS

(CH ₃) ₃ > N(R ₂)Br	M. p., °C.	Ionic Br	Total Br	Calcd. Br
R = ethyl	175-178	40.99	41.16	41.24
R = <i>n</i> -propyl	52-59	35.70	35.74	36.04
R = <i>n</i> -butyl	120-121	31.91	32.22	32.00

TABLE III

MOLECULAR WEIGHT DATA ON DIALKYLTRIMETHYLENEAMMONIUM SALTS

Compound	Sample, g.	Mol. wt.	Mol. wt./2	Mol. wt. found in water given, cc.					
				10	15	20	25	30	40
(C ₄ H ₉) ₄ NI	0.5050	368	184	202	182	173	180
(C ₂ H ₅) ₂ C ₄ H ₉ NI	.3770	284	142	173	..	152	137
(CH ₂) ₃ N(C ₂ H ₅) ₂ Br	.4496	194	97	92	105	104	102	101	106
(CH ₂) ₃ N(C ₃ H ₇) ₂ Br	.3890	222	111	126	..	116	116	110	..
(CH ₂) ₃ N(C ₄ H ₉) ₂ Br	.5494	250	125	142	134	127	128	124	..

Experimental

The phenoxypropyldialkylamines and bromopropyldialkylamines were prepared by methods analogous to those used for the corresponding dimethyl derivatives.⁴ The new amines were

(3) For a review of the valency-deflection hypothesis see "Annual Reports for the Progress of Chemistry for 1930," p. 152.

(4) See Ref. 1, and also Littmann and Marvel, *THIS JOURNAL*, **52**, 287 (1930).

usually characterized as the chloroplatinates. In one case the bromoaurate was used.

The new amines together with some derivatives and their properties are recorded in Table I.

Dialkyltrimethyleneammonium Bromides.—When the bromoamines were allowed to stand at 0 to 5°, at room temperature or at steam-bath temperature, they turned into crystalline solids. The temperature of formation did not alter the nature of the product. The diethyl derivative was extremely hygroscopic and was purified from absolute alcohol and dry ether. The di-*n*-propyl derivative was easily crystallized from dry acetone. It was only slightly hygroscopic. The di-*n*-butyl derivative formed more slowly than the others and the amine odor persisted for weeks. The product was crystallized from dry acetone and was very hygroscopic.

The quaternary ammonium salts were soluble in water. Their solutions were neutral to methyl orange. They did not add bromine from a solution of bromine in carbon tetrachloride. The analyses showed practically no non-ionic halogen. The properties of the new compounds are listed in Table II.

In addition to the agreements in total and ionic halogen and the neutrality of these salts, another evidence for the simple cyclic structure of

these products was obtained by determining their molecular weights in water solution. As the solutions were diluted the molecular weights approached values which were half the molecular weights as would be expected for uni-univalent salts. The molecular weights calculated from freezing point data at various dilutions are given in Table III. Tetra-*n*-butylammonium

iodide and triethyl-*n*-butylammonium iodide were used as reference compounds.

Diethylallylamine Hydrobromide.—This salt was prepared from diethylallylamine and dry hydrogen bromide.

It was recrystallized from acetone. It was not especially hygroscopic and did decolorize a solution of bromine in carbon tetrachloride. It melted at 189–190°. When a sample was mixed with diethyltrimethyleammonium bromide the mixture melted at 158–160°.

Anal. Calcd. for $C_8H_{14}NBr$: Br, 41.24. Found: Br, 41.17.

Summary

The bromopropylalkylamines in which the alkyl groups are ethyl, *n*-propyl and *n*-butyl, respectively, have been found to undergo spontaneous intramolecular condensation to give the corresponding cyclic dialkyltrimethyleammonium bromides. The reaction is of theoretical interest since the corresponding bromopropyl dimethylamines condense to produce only linear polymers.

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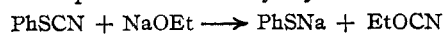
The Action of Sodium Ethoxide upon Phenyl Thiocyanate

By JOHN ROSS

Examining the reaction between ethyl thiocyanate and the sodium enolates of certain keto esters, Kohler¹ showed that the primary reaction was the formation of a metal mercaptide and a cyano substitution product of the keto ester. This result was the opposite of the transformations that occur when metallic sodium or alkali sulfides, hydroxides and mercaptides react with alkyl thiocyanates to eliminate the cyano group as the metallic cyanide or cyanate. In the previous investigations the reaction appears to follow one selected course only, but it would be expected that when the conditions are such as to favor the formation of a metal mercaptide or cyanide to an almost equal degree, then both the above modes of reaction might be found to proceed simultaneously.

Sodium ethoxide in alcohol reacts with phenyl thiocyanate to give sodium thiophenate, diphenyl disulfide and ethyl phenyl sulfide. In attempting to formulate a mechanism whereby these products could be obtained, the previous considerations suggest that both the above types of reaction had taken place to an unequal extent.

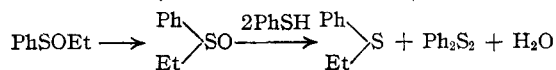
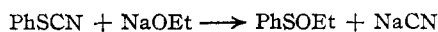
The main reaction (80%) is the production of sodium thiophenate and ethyl cyanate



The ethyl cyanate would isomerize to the isocyanate and combine with alcohol or sodium ethoxide to form ethyl ethyl carbamate $EtNHCOOEt$ or its sodium enolate.

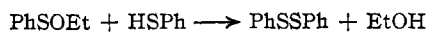
The secondary reaction (20%) follows the direct production of sodium cyanide and presumably ethyl benzenesulfenolate

(1) E. P. Kohler, *Am. Chem. J.*, **22**, 67 (1899).



If the ethyl benzenesulfenolate is transformed into the isomeric sulfoxide by migration of the ethyl group from oxygen to sulfur, then the sulfoxide might on reduction with thiophenol give ethyl phenyl sulfide and diphenyl disulfide. The amounts of ethyl phenyl sulfide and diphenyl disulfide isolated were approximately equivalent in accordance with the above equation.

It was found that thiophenol in the presence of a small amount of sodium ethoxide would reduce ethyl phenyl sulfoxide to give ethyl phenyl sulfide and diphenyl disulfide under conditions comparable with those of the reaction under discussion. Some ethyl benzenesulfenolate was prepared, but it was found that this ester reacted vigorously with thiophenol (in the presence of a trace of sodium ethoxide) to give entirely diphenyl disulfide, presumably according to the reaction



This behavior would appear to preclude altogether the formation of free ethyl benzenesulfenolate in the reaction. Although the conditions governing the transformation of ethyl benzenesulfenolate into ethyl phenyl sulfoxide are not completely known, the above hypothetical reaction mechanism is open to several objections. Wheeler and Barnes,² Bettschart and Bistrzycki³ and others have examined many cases of transformations in thio-carbamide derivatives where the hydrocarbon group is transferred from oxygen to sulfur under

(2) Wheeler and Barnes, *Am. Chem. J.*, **22**, 141 (1899).

(3) Bettschart and Bistrzycki, *Helv. Chim. Acta*, **2**, 118 (1919).