[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Pyrolysis of the Products of the Reaction of *o*-Aminobenzenethiols with Ketones[1]

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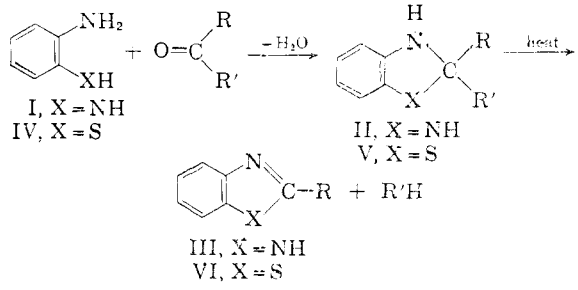
The condensation of *o*-aminobenzenethiol and certain of its derivatives with representative ketones to yield 2,2-disubstituted benzothiazolines has been investigated. Pyrolysis of the benzothiazolines yields a 2-substituted benzothiazole with concurrent elimination of a hydrocarbon. The kinetics of the pyrolysis reaction have been studied and the previously advanced mechanism for this type of cleavage has been confirmed and broadened.

The thermal decomposition of 2,2-disubstituted benzimidazolines to yield 2-substituted benzimidazoles and hydrocarbons has been the subject of intensive study in these laboratories.[2] The basic reactions involved are represented by I–III. During the course of this study certain inconsistencies which are difficult to explain have appeared. The elimination of hydrocarbon in passing from II to III is subject to powerful base



catalysis[3] but apparently insensitive to catalysis by peroxides. This suggested an ionic mechanism for the reactions whereby the hydrocarbon radical (R′) is eliminated as a carbanion.[3] However, when R and R′ in II are different alkyl groups, the observed preferential order of elimination of R′ was exactly the opposite to that which would be expected on the basis of carbanion elimination. Thus it was found that the substituent most highly branched at the α-carbon atom was eliminated exclusively. Further, in a study of the effect of substituents in the *m*- and *p*-positions of a benzyl group corresponding to R in II no electronic effect was noted as would be expected if an ionic mechanism were operative.[2] Finally, substitution of a methyl group for a hydrogen on one of the nitrogens in II resulted in a marked acceleration in the rate of elimination of R′H whereas analogous substitution of a phenyl group had substantially no effect on the reaction.[3] On the other hand, a radical mechanism appeared to be ruled out on the basis of failure of peroxide catalysis and the complete absence of such products as dialkyls which could reasonably be expected to result from union of two R′ radicals.

In order to gain additional information about this interesting cleavage of a carbon-to-carbon bond under relatively mild conditions, the study has now been extended to the decomposition of a series of 2,2-disubstituted benzothiazolines (IV–VI). Two reports of such decompositions have appeared. Kreysa[4] describes the formation of 2-methylbenzothiazole when *o*-aminobenzenethiol was heated with 1-phenyl-2-propanone. No attempt was made to isolate any intermediate benzothiazoline nor was the formation of any hydrocarbon reported. Kiprianov and Portnyagina[5] prepared a series of 2,2-disubstituted benzothiazolines from the reaction of ketones with various *o*-aminobenzenethiols. The thermal decomposition of only one was investigated and the results reported are in distinct disagreement with our findings.

There are several advantages in investigating the nitrogen–sulfur system. The effect of a sulfur atom compared to a nitrogen on the rate and course of the reaction is of interest because of the differences in character of the two atoms. If the reaction is electronically controlled then an effect of substituents placed *meta* or *para* to the nitrogen atom should be apparent, possibly in conformity to Hammett's equation. Non-conformity to such electronic effects would then indicate either a non-ionic mechanism or, in all likelihood, an ionic mechanism subject to steric control. Finally, the 2,2-disubstituted benzothiazolines are relatively unknown compounds and some controversy has existed concerning their formation and properties.

Although the condensation of acids, derivatives of acids and aldehydes with *o*-aminobenzenethiol has been the subject of considerable study,[6] comparatively little attention has been given to the reaction of ketones with *o*-aminobenzenethiol. Prior to the work of Kreysa[4] and Kiprianov,[5] Bogert and Stull[7] reported that the condensation did not occur. However, the method of working up the reaction mixtures involved the use of strong acid which would undoubtedly have cleaved any benzothiazoline formed to its original components. Lankelma and Sharnoff[8] were successful in condensing certain ketones with 2-amino-4-chlorobenzenethiol in pyridine solution to give products identified as benzothiazolines. Finally, after this work was complete, Teuber and Waider[9] described the preparation of a number of 2,2-disubstituted

(1) The work here reported is based on a dissertation submitted by Ellsworth C. McClenachan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, January, 1959.

(2) For the previous paper in this series see R. C. Elderfield and K. L. Burgess, THIS JOURNAL, **82**, 1975 (1960).

(3) R. C. Elderfield and J. R. McCarthy, *ibid.*, **73**, 975 (1951).

(4) F. J. Kreysa, V. Maturi, J. J. Finn, J. G. McClarnon and F. Lombardo, *ibid.*, **73**, 1155 (1951).

(5) A. Kiprianov and V. Portnyagina, *J. Gen. Chem. (USSR), English Ed.*, **25**, 2223 (1955).

(6) *Cf.* "Heterocyclic Compounds," R. C. Elderfield, Editor, John Wiley and Sons, Inc., New York, N. Y., Vol. 6, 1956, p. 506 ff.

(7) M. T. Bogert and A. Stull, THIS JOURNAL, **47**, 3078 (1925).

(8) H. P. Lankelma and P. X. Sharnoff, *ibid.*, **54**, 379 (1932).

(9) H. J. Teuber and H. Waider, *Chem. Ber.*, **91**, 2341 (1958).

TABLE I

2,2-DISUBSTITUTED BENZOTHIAZOLINES

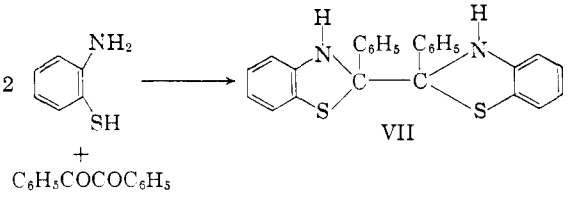
Benzothiazoline	Yield, %	Method of prepn.	B.p. °C.	B.p. Mm.	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2,2-Dimethyl	86.6	A			46–48[a]	65.4	65.5	6.7	6.8	8.5	8.5
2-Methyl-2-ethyl	84.5	A	101–103	1[b]		67.0	67.2	7.3	7.3		
2-Methyl-2-(*n*-propyl)	69	A	142–144	5		68.4	68.5	7.8	7.8		
2-Methyl-2-isopropyl[c]		A									
2-Methyl-2-isobutyl	78	A	108–110	0.3		69.5	69.5	8.3	8.1		
2-Methyl-2-(*t*-butyl)	92	A	119–120	1.5	53–54[d]	69.5	69.5	8.3	8.2		
2-Methyl-2-(*n*-hexyl)[c]		A									
2-Methyl-2-phenyl	73.5	B	139–142	0.02		74.0	73.8	5.8	6.0		
2-Methyl-2-(*p*-tolyl)	61.5	C	180–183	1.5		75.0	74.9	6.3	6.4		
2-Methyl-2-(*p*-anisyl)	66	C	201–204	1	104–105[e] 240–242	70.0	70.1	5.9	5.6	5.4	5.3
2-Methyl-2-(*m*-nitrophenyl)[c]		A									
2-Methyl-2-cyclopropyl[f]	58	A	110–112	0.75							
2-Ethyl-2-(*n*-butyl)	91	C[g]	134–136	1		70.5	70.5	8.6	8.7		
2-Phenyl-2-(2'-phenylbenzothiazolinyl)	95	A			116–117	73.6	73.5	4.8	4.4		
2,2-Tetramethylene	48	B	126–129	1	57–58[h]	69.1	69.0	6.8	6.9	7.3	7.3
2,2-Pentamethylene	58	A	112–114	0.75	114–115[i]	70.2	70.2	7.4	7.4	6.8	6.9
2,2-(2'-Methyl)-pentamethylene[f]	50	A	122–125	.5							
2-Methyl-2-(*t*-butyl)-6-methoxy[f]	42	A	140–143	.75							
2,2-Dimethyl-5-chloro	39	..	76–80	.05	37–38[j]						
2,2-Dimethyl-6-chloro[c]		A									
2-Methyl-2-(*t*-butyl)-6-chloro[f]	44	A	149–152	.75							

[a] Crystallized from 30–60° petroleum ether; reported m.p. 46–48°[5]; 46.5°.[9] [b] Reported[9] b.p. 151–152° (20 mm.). [c] This benzothiazoline was used directly without purification for the decomposition. [d] Crystallized from 30–60° petroleum ether. [e] Crystallized from ethanol; two crystalline modifications. [f] This decomposed so rapidly that satisfactory analytical data could not be obtained; identification was on basis of infrared and pyrolysis products. [g] Reaction mixture allowed to stand on steam-bath overnight. [h] Reported m.p. 51.5°,[9] 55°.[5] [i] Reported[9] m.p. 115°. [j] Reported[8] m.p. 37°.

benzothiazolines by condensation of *o*-aminobenzenethiol with ketones in boiling methanol.

In order to provide a direct comparison between the course of the decomposition of the benzothiazolines and the benzimidazolines, the benzothiazolines selected for study were those derived from the ketones chosen by Elderfield and McCarthy[3] in the earlier work. In addition other ketones which provided isolatable benzothiazolines were condensed with *o*-aminobenzenethiol. The substituted *o*-aminobenzenethiols chosen for study were those which would give the maximum range of electronic effects and which involved few synthetic difficulties. These included 4-chloro-, 5-chloro- and 5-methoxy-2-aminobenzenethiol.

The general procedure used for the preparation of the 2,2-disubstituted benzothiazolines consisted in refluxing the *o*-aminobenzenethiol with the appropriate ketone in excess ketone as solvent. After cooling, the water formed was removed either with anhydrous calcium sulfate or by azeotropic distillation with the ketone. When the hydrochloride of the *o*-aminobenzenethiol was used the solvent was pyridine or N,N-dimethylaniline since it was noted that the amine hydrochlorides did not yield benzothiazolines when condensation with ketones alone was attempted. This failure was apparently due to the presence of acid which hydrolyzed any benzothiazoline which may have been formed. The benzothiazolines derived from aliphatic ketones were oils purified by distillation with the exception of two which crystallized on long standing. Crystallization of the benzothiazolines derived from ketones other than those of the aliphatic series followed no definite pattern. In a few instances, the benzothiazolines were sufficiently unstable to preclude obtaining satisfactory analytical data. Proof of structure and characterization was of necessity limited to examination and comparison of the infrared spectra taken in conjunction with the products of thermal decomposition. Benzothiazoline formation apparently took place normally with the exception of two reactions. In the reaction of benzil with *o*-aminobenzenethiol the reaction apparently involved both ketone groups judging from infrared and analytical data. The reaction product is assigned structure VII. With



VII

methyl neohexyl ketone no detectable benzothiazoline was formed when the reactants were refluxed for 48 hr. Distillation under reduced pressure resulted in the quantitative recovery of the starting materials. Pertinent data on the benzothiazolines are given in Table I.

The procedure used for the thermal decomposition of the benzothiazolines was essentially that of

TABLE II

THERMAL DECOMPOSITION OF 2,2-DISUBSTITUTED BENZOTHIAZOLINES

Benzothiazoline	Init. gas. evol. temp., °C. ± 8°	Hydrocarbon evolved	Benzothiazole formed	Yield of pure benzothiazole %
2,2-Dimethyl	275	Methane	2-Methyl	37
2-Methyl-2-isobutenyl	212	Methane	2-Methyl[a]	41
2-Methyl-2-ethyl	255	Ethane	2-Methyl	60.6
2-Methyl-2-(*n*-propyl)	245	Propane	2-Methyl	69.3
2-Methyl-2-(isopropyl)	230	Propane	2-Methyl	Low
2-Methyl-2-(isobutyl)	248	Isobutane	2-Methyl	65.5
2-Methyl-2-(*t*-butyl)	215	Isobutane	2-Methyl	81
2-Methyl-2-(*n*-hexyl)	..	*n*-Hexane	2-Methyl	..
2-Methyl-2-phenyl	285	Methane	2-Phenyl	70
2-Methyl-2-(*p*-tolyl)	270	Methane	2-(*p*-Tolyl)	53.5
2-Methyl-2-(*p*-anisyl)	233	Methane	2-(*p*-Anisyl)	46
2-Methyl-2-(*m*-nitrophenyl)	260	Methane	....[b]	..
2-Methyl-2-cyclopropyl	265	Cyclopropane	2-Methyl	61.5
2-Methyl-2-benzyl	..	Toluene	2-Methyl	..
2-Ethyl-2-(*n*-butyl)	240	Ethane–butane	2-(*n*-Butyl)	44
			2-Ethyl	40
2,2-Dibenzyl	..	Toluene	2-Benzyl	79.5
2,2-Tetramethylene	..	.....	2-(*n*-Butyl)	30
2,2-Pentamethylene	..	.....	2-(*n*-Amyl)	40
2,2-(2'-Methyl)-pentamethylene	..	.....	2-(*n*-Hexyl)	62
2-Methyl-2-(*t*-butyl)-6-methoxy	205	Isobutane	2-Methyl-6-methoxy	62
2,2-Dimethyl-5-chloro	270	Methane	2-Methyl-5-chloro	..
2,2-Dimethyl-6-chloro	270	Methane	2-Methyl-6-chloro	..
2-Methyl-2-(*t*-butyl)-6-chloro	210	Isobutane	.....[b]	..

[a] This is an abnormal case; see ref. 3. [b] Severe carbonization prevented isolation of the benzothiazole.

Elderfield and McCarthy[3] used in the study of the decomposition of the benzimidazolines. The compound to be decomposed was heated with or without a solvent in a vessel connected to an eudiometer and the "initial gas evolution temperature" was noted in those instances in which gaseous hydrocarbon was evolved. This may be defined as that temperature at which the slope of the line in a plot of gas evolved *versus* temperature increases markedly. Undoubtedly a small amount of decomposition occurs before this temperature is reached. For example, whereas the initial gas evolution temperature noted with 2-methyl-2-(*t*-butyl)-benzothiazoline was 215°, kinetic data were obtained at temperatures as low as 185°. In the early experiments the decompositions were carried out under carbon dioxide, but it was found that identical results were obtained in the absence of an inert gas and use of such a blanket was discontinued. In a few experiments for reasons of economy, the decompositions were carried out in a solvent—either Dow–Corning 550 Hi-vac silicone oil or diphenyl ether. Control experiments showed that the temperatures noted were the same in the presence and absence of a solvent. Finally, in order to ensure that the present data are strictly comparable to the earlier data of Elderfield and McCarthy,[3] representative benzimidazolines were prepared and decomposed in the apparatus used in the present study. The results were identical with those previously obtained[3] thus eliminating any technical or personal variables in the two investigations. The gases evolved in these decompositions were analyzed by vapor phase chromatography. Results of the various decompositions are summarized in Table II.

In general, the initial gas evolution temperatures observed in the decomposition of the benzothiazolines were on an average about 20° higher than those found with the corresponding benzimidazolines.[3] The hydrocarbon products were identical in both series with the exception of the compounds carrying methyl and cyclopropyl substituents in the 2-position. The decomposition of 2-methyl-2-cyclopropylbenzimidazoline gave methane exclusively, whereas in the benzothiazoline series, cyclopropane was the hydrocarbon eliminated. As in the benzimidazoline series, hydrocarbon elimination was strongly catalyzed by added base. In the presence of sodium *n*-octyloxide the initial gas evolution temperature observed with 2-methyl-2-(*t*-butyl)-benzothiazoline was lowered from 215° for the uncatalyzed decomposition to 145°.

When the decomposition was carried out in the presence of *t*-butyl peroxide no lowering of the initial gas evolution temperature was observed. Strong illumination by photoflood lamps of a solution of 2-methyl-2-(*t*-butyl)-benzothiazoline in diphenyl ether caused very rapid development of colored products. No pure substance could be isolated from the reaction mixture even by chromatography over alumina which normally effects clean separations of benzothiazolines from benzothiazoles. Further, addition of hydroquinone to a solution of the same benzothiazoline in diphenyl ether produced no effect on the initial gas evolution temperature.

Finally, the kinetics of the decomposition of representative benzothiazolines have been studied. Typical rate curves are given in Fig. 1. In this, the concentration, c, to which the ordinates refer

represents the ratio $(V - V_t)/V$ where V is the total volume of gas evolved and V_t is the volume of gas evolved at any time, t. From the slope of the curves specific reaction rates were determined and from these approximate values for the energies of activation were calculated.[10] These data are given in Table III.

TABLE III

KINETICS OF DECOMPOSITION OF 2,2-DISUBSTITUTED BENZOTHIAZOLINES

Intermediate	Reaction temp. °C. ± 1°	Rate constant, $min.^{-1}$	$\Delta E^{\pm}$, energy of activation, kcal./mole ±1.3
2-Methyl-2-(*t*-butyl)-benzothiazoline	212	0.717	
2-Methyl-2-(*t*-butyl)-benzothiazoline	185	.292	14.7
2-Methyl-2-(*n*-propyl)-benzothiazoline	248	.082	
2-Methyl-2-(*n*-propyl)-benzothiazoline	275	.259	24.0
2-Methyl-2-(*n*-propyl)-benzimidazoline[3]	282	.027	
2-Methyl-2-(*n*-propyl)-benzimidazoline[3]	258	.010	24.0

2-Methyl-2-phenylbenzothiazoline was readily prepared in contrast to the difficulty attending the preparation of the corresponding benzimidazoline.[3] The substance, obtained as a pale yellow oil, resisted all attempts at crystallization. In contrast to the report of Kiprianov and Portnyagina[5] that when heated at 250–260° the benzothiazoline yields 2-methylbenzothiazole and benzene, we find that methane is eliminated and 2-phenylbenzothiazole is formed in about 70% yield. This observation has been confirmed in numerous experiments and introduction of various substituents into the phenyl group did not change the course of the reaction. The only effect of such substituents was a slight lowering of the initial gas evolution temperature regardless of the nature of the substituents.

As already indicated, available evidence indicates that the substituent which is eliminated is the more bulky one. Although it is true that the phenyl group is usually considered as a bulky group, and perhaps should be expected to be eliminated preferentially, obviously it is not. This observation is not unexpected if the benzothiazole is considered as a more highly resonance stabilized system than the benzothiazoline. Retention of the phenyl group would be expected to add further to this stabilization through conjugation with the azomethine linkage. It is also possible that the geometry of the transition state is such that the phenyl group may be oriented in such a way as to present less bulk than the methyl group.[11]

Two benzothiazolines were extremely stable to heat. No decomposition was noted when the condensation products of benzil (VII) and benzophenone with *o*-aminobenzenethiol were heated at temperatures of over 300° for 36 to 48 hr. The stability of these substances is hard to explain since 2,2-diphenylbenzimidazoline gives 2-phenylbenzimidazole in good yield at 190°.

(10) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 17.

(11) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 159.

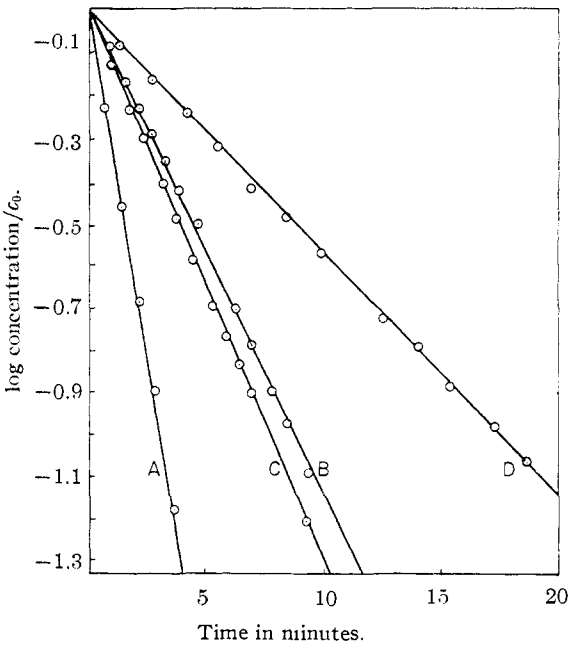
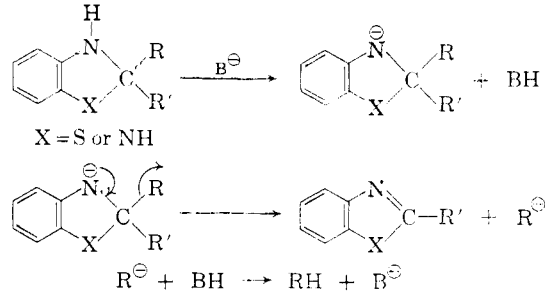


Fig. 1.—Rate of decomposition of 2,2-disubstituted benzothiazolines: A, 2-methyl-2-(*t*-butyl)-benzothiazoline at 212°; B, same as A at 185°; C, 2-methyl-2-(*n*-propyl)-benzothiazoline at 275°; D, same as C at 248°.

In considering the mechanism of this apparently general reaction several factors must be taken into account. At the outset it is obvious that a major portion of the driving force must come from the gain in resonance energy in passing from the saturated benzothiazolines (or benzimidazolines) to the pseudo aromatic benzothiazoles (or benzimidazoles). The observed preferential order of elimination of alkyl groups from the 2-position of the intermediates at first glance is at variance with the concept of elimination of such groups as carbanions. On the other hand, no evidence is at hand which justifies the assumption that such substituents are eliminated as carbonium ions. The evidence for an ionic mechanism is strong, *e.g.*, powerful base catalysis. On the other hand, the absence of inductive effects by substituents in the unsymmetrically substituted 2,2-dibenzylbenzimidazolines and in the Bz-substituted benzothiazolines argues strongly against electronic control of the reaction. The arguments against a radical mechanism are equally strong. Among these may be cited the demonstrated failure of catalysis by peroxides, the absence of effect by "radical traps" on the reaction and the complete absence of substances arising as a result of disproportionation or radical coupling in the products of the reaction.

One is then forced to a reconsideration of the original mechanism proposed by Elderfield and McCarthy[3] with the added condition that steric factors are dominant in determining the course of the reaction. For the base - catalyzed reaction this is represented by the sequence

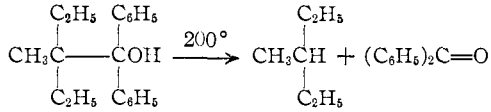


In the absence of added base the weakly basic intermediates act as catalysts.

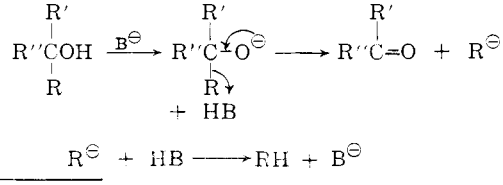
A study of molecular models of the compounds under consideration shows that there is a good deal of crowding in the 2-position of the intermediate benzothiazolines and benzimidazolines in addition to a slightly more strained ring in the benzimidazolines. This may well explain the slight but significant increase in the initial gas evolution temperature observed with the benzothiazolines. The idea that steric effects are controlling in the decomposition also receives support from the observed order of elimination of alkyl substituents in both series. The reduction in decomposition temperature, lowered energies of activation, increase in rate of hydrocarbon elimination and preferential cleavage of the bulkiest group with increasing α-substitution in the 2-substituent all provide support for this view.

Further, the observed fact that a methyl substituent on one nitrogen of the benzimidazolines promotes the decomposition whereas a similarly situated phenyl group is without substantive effect receives support from a study of models. On the assumption that the phenyl substituent can assume a planar configuration with respect to the nitrogen whereas the methyl group remains relatively bulky, the observed relative effect of a methyl *versus* a phenyl group becomes easily explained.

A situation substantially similar to that obtaining in the decompositions under discussion is found in the thermal decomposition of certain tertiary carbinols to yield ketones and hydrocarbons, *e.g.*[12]



This decomposition is also subject to base catalysis and the observed order of elimination of substituents is closely similar to that observed in the cases under discussion with the most highly α-substituted groups tending to be preferentially eliminated. A mechanism for this elimination exactly similar to that proposed by one of us[3] for the benzimidazoline decomposition has recently been proposed.[13,14]



We therefore feel that there is no justification for rejecting the mechanism originally proposed[3] for these reactions, except to incorporate the feature of steric control. Further, the concept can be expanded to state that whenever a group capable of forming an anion is found adjacent to a tertiary carbon atom (or its equivalent) carbon–carbon bond cleavage will occur on relatively mild heating with the formation of a more highly oxidized compound and a carbanion corresponding to one of the radicals attached to the tertiary carbon atom. The exact nature of the carbanion depends on the geometry of the system, rather than on carbanion stability.

Experimental[15-17]

Preparation of the Benzothiazolines.—Typical procedures will be described and deviations therefrom noted as required.

Procedure A. 2,2-Dimethylbenzothiazoline.—A mixture of 35 g. of redistilled *o*-aminobenzenethiol and 59.5 g. of acetone was refluxed for 8 hr. After cooling, the excess acetone and water were removed under reduced pressure. The resulting thick yellow oil was refrigerated overnight. Vigorous scratching resulted in rapid crystallization. Residual oil was removed by filtering through a sintered glass funnel. Recrystallization from chloroform–petroleum ether gave 40 g. of white plates, m.p. 46–48°. The infrared spectrum showed peaks at 3500 and 660 cm.$^{-1}$ and no peaks at 2500 or 1750 cm.$^{-1}$ which is consistent with the benzothiazoline structure.

Procedure B. 2-Methyl-2-phenylbenzothiazoline.—A mixture of 30 g. of *o*-aminobenzenethiol and 120 g. of acetophenone was refluxed for 24 hr. The residue after cooling was distilled under reduced pressure yielding unreacted ketone and 40 g. (75.5%) of the thiazoline, b.p. 139–142° (0.02 mm.).

Procedure C. 2-Methyl-2-(4′-methylphenyl)-benzothiazoline.—A mixture of 30 g. of *o*-aminobenzenethiol and 75 g. of *p*-methylacetophenone was refluxed for 24 hr. After cooling, water was removed by drying over a small amount of anhydrous calcium sulfate and the resulting oil was distilled under reduced pressure.

Procedure D. 2,2-Tetramethylenebenzothiazoline.—A mixture of 30 g. of *o*-aminobenzenethiol and 42 g. of cyclopentanone was heated for 24 hr. on the steam-bath. After drying over anhydrous calcium sulfate and removal of excess ketone, distillation gave the benzothiazoline as a pale yellow oil, b.p. 126–129° (1 mm.), which crystallized slowly on standing. Several recrystallizations from petroleum ether gave white plates, m.p. 57–58°. The substance is quite unstable in the presence of air and decomposes to a black tarry material in 3 weeks. It is somewhat more stable when stored under nitrogen.

2-Methyl-2-(*t*-butyl)-6-methoxybenzothiazoline.—To an ether solution of 2-amino-5-methoxybenzenethiol prepared according to Ast and Bogert[18] from 17 g. of *p*-anisidine was added 25 g. of methyl *t*-butyl ketone. After removal of the ether, the mixture was refluxed for 2 hr. and dried over anhydrous calcium sulfate. Distillation gave 10 g. of the benzothiazoline as a very unstable dark yellow oil, b.p. 140–143° (0.75 mm.). The over-all yield was 42%. Because of its instability a satisfactory analysis could not be obtained for the substance. The infrared spectrum was consistent with that expected for a benzothiazoline.

2,2-Dimethyl-5-chlorobenzothiazoline.—A solution of 10 g. of 2-amino-4-chlorobenzenethiol hydrochloride[19] in 30 ml.

(12) Mme. Ramart-Lucas, *Ann. chim.*, [8] **30**, 349 (1913).

(13) H. D. Zook, J. L. Greene, J. March and D. F. Smith, Abstracts of Papers, 133rd National Meeting, American Chemical Society, San Francisco, Cal., April, 1958, p. 12N.

(14) H. D. Zook, J. March and D. F. Smith, THIS JOURNAL, **81**, 1617 (1959).

(15) All melting points and boiling points are uncorrected for stem exposure.

(16) Microanalyses by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(17) Infrared spectra were taken on a Perkin–Elmer recording infrared spectrophotometer, model 21.

(18) M. G. Ast and M. T. Bogert, *Rec. trav. chim.*, **54**, 917 (1935).

(19) H. P. Lankelma and P. X. Sharnoff, THIS JOURNAL, **53**, 311 (1931).

of dimethylaniline was added to 3.2 g. of acetone. After refluxing overnight, the amine was removed by distillation. The dark oily residue was washed with water, dried over anhydrous calcium sulfate and distilled under reduced pressure to give 4 g. (39.2%) of colorless oil, b.p. 76–80° (0.05 mm.). On cooling, the oil crystallized as white plates, m.p. 37–38°.

Condensation of o-Aminobenzenethiol with 1,3-Diphenyl-2-propanone.—The intermediate benzothiazoline was not isolated. A mixture of 12 g. of o-aminobenzenethiol and 21 g. of 1,3-diphenyl-2-propanone was heated at 250° for 2 hr. in a flask equipped with a distilling head. A toluene–water azeotrope (12 ml., b.p. 83°) distilled. From this 6.95 g. (79.5%) of toluene was obtained. The residue in the flask was taken up in ether and either anhydrous hydrogen chloride or alcoholic picric acid was added on which the appropriate salt separated. The hydrochloride melted at 145–149° and the picrate at 144–145°. 2-Benzylbenzothiazole boils at 198–200° (5 mm.). The picrate gave the following analytical data.

Anal. Calcd. for $C_{20}H_{14}N_4O_7S$: C, 52.9; H, 3.1; N, 12.3. Found: C, 53.3; H, 2.9; N, 12.3.

Pyrolysis of the Benzothiazolines.—The apparatus in which the decompositions were carried out consisted of a 50-ml. round-bottom flask equipped with a thermometer well and a reflux condenser. An exit tube leading from the condenser was connected to an ice trap and subsequently to a 400-ml. eudiometer equipped with a leveling bulb. To the top of the eudiometer was sealed a stopcock carrying a standard taper joint for connection to gas sample tubes. The reaction flask was heated in a Wood metal-bath which was in turn heated by a Glascol heating mantle.

Approximately 10 ml. of the appropriate benzothiazoline was placed in the reaction flask and the system was sealed by filling the eudiometer with fresh water. The Wood metal-bath was heated at a rate of one to two degrees per minute. The volume increments of evolved gas per unit time were noted and the temperature at which a steady marked evolution of gas occurred was taken to represent the initial gas evolution temperature.

The collected gas was then transferred to an evacuated gas sample tube, one end of which was fitted with a rubber serum cap. The gas was then injected by means of a hypodermic syringe into a vapor phase chromatography unit for identification.

The residue in the pyrolysis flask was cooled and vacuum distilled in most cases. When a solid benzothiazole was to be expected, the residue from the pyrolysis was triturated with cold absolute ether or absolute ethanol to remove tarry contaminants. Recrystallization from suitable solvents gave the pure benzothiazoles.

Identification of the benzothiazoles when these had been previously described was on the basis of mixture melting points and comparison of infrared spectra with those of samples prepared by alternate methods. Details of the decompositions will be given only for those which presented special features.

The vapor phase chromatography equipment was the same as that used previously.[2] The support in the columns was Johns–Manville C-22 fire-brick crushed to 30–60 mesh. The liquid phases were either Dow–Corning Hi-Vac 550 silicone grease alone or preceded by approximately 20% of the column length by a liquid phase consisting of a saturated solution of silver nitrate in ethylene glycol. Helium was the sweep gas. The columns were calibrated at 25° and a standard rate of helium flow with pure hydrocarbons obtained from Phillips Petroleum Co. or Shell Oil Co.

Pyrolysis of 2-Methyl-2-isobutenylbenzothiazoline.—A mixture of 30 g. of o-aminobenzenethiol and 64.4 g. of mesityl oxide was refluxed for 24 hr. Excess ketone and water were stripped from the mixture under reduced pressure. Vacuum distillation gave 13.3 g. (27%) of a pale yellow oil, b.p. 135–137° (3.5 mm.). Due to the extreme instability of the benzothiazoline a satisfactory analysis could not be obtained.

Five grams of the above compound was thermally decomposed and the initial gas evolution temperature was 212°. Vacuum distillation of the residue gave 1.5 g. (41%) of a colorless oil, b.p. 65–70° (1 mm.). This was identified as 2-methylbenzothiazole by conversion to the picrate, m.p. and mixture m.p. with an authentic sample 153–155°, and by infrared. Vapor phase chromatography of the gas evolved on the silver nitrate–ethylene glycol–silicone grease column indicated the presence of only methane.

This experience paralleled that with the corresponding benzimidazoline.[3] Apparently the isobutenyl side chain underwent cleavage at some stage of the procedure.

Pyrolysis of 2-Ethyl-2-(n-butyl)-benzothiazoline.—When 10 g. of the benzothiazoline was pyrolyzed the initial gas evolution temperature was 240°. Vacuum distillation of the residue gave a yellow oil, b.p. 92–94° (2 mm.), picrate m.p. 136–138°; and a colorless oil, b.p. 122° (2 mm.), picrate m.p. 126–128°. These were identified as 2-ethyl- and 2-(n-butyl)-benzothiazole, respectively, by comparison with authentic samples. The yields were 3.81 g. (44%) of the 2-ethyl compound and 3.96 g. (40%) of the 2-(n-butyl) compound.

Vapor phase chromatography showed the presence of two gases in about equal amounts. These were identified as ethane and butane by retention times.

Pyrolysis of 2,2-Tetramethylenebenzothiazoline.—Five grams of the benzothiazoline was heated at 260° for 4 hr. No gas was evolved and the mixture darkened considerably. On distillation, the residue gave 1.5 g. (30%) of a colorless oil, b.p. 114–116° (1.5 mm.). The picrate, m.p. 126–128°, was identical with a known sample of the picrate of 2-(n-butyl)-benzothiazole.

Anal. Calcd. for $C_{17}H_{16}N_4O_7S$: C, 48.6; H, 3.8. Found: C, 48.6; H, 3.8.

Pyrolysis of 2,2-Pentamethylenebenzothiazoline.—Pyrolysis of 5 g. of the benzothiazoline at 270° for 15 hr. liberated no gas and gave 2 g. (40%) of a colorless oil, b.p. 138–140° (2 mm.). The picrate, m.p. and mixture m.p. with an authentic sample of the picrate of 2-(n-amyl)-benzothiazole, 105-107°, was prepared.

Anal. Calcd. for $C_{18}H_{18}N_4O_7S$: C, 49.8; H, 4.2; N, 12.9. Found: C, 49.6; H, 4.2; N, 13.0.

Pyrolysis of 2,2-(2′-Methylpentamethylene)-benzothiazoline.—Pyrolysis of 8.7 g. of the benzothiazoline at 270° for 20 hr. gave 5.4 g. (62%) of clear oil, b.p. 140–144° (2.5 mm.). The picrate melted at 97–98° after several recrystallizations from ethanol. The m.p. was not depressed on mixture with a picrate of 2-(n-hexyl)-benzothiazole prepared from o-aminobenzenethiol and n-heptanoyl chloride. 2-Isohexylbenzothiazole has been reported,[20] but appears to have been misnamed. In all probability this compound was also 2-(n-hexyl)-benzothiazole.

Anal. Calcd. for $C_{19}H_{20}N_4O_7S$: C, 50.9; H, 4.5. Found: C, 50.9; H, 4.5.

Isolation of the above benzothiazole does not preclude the simultaneous formation of the isomeric 2-(1-methylpentyl)-benzothiazole which may have been lost in the purification procedure.

Base Catalysis of the Decomposition of 2-Methyl-2-(t-butyl)-benzothiazoline.—A solution of 0.5 g. of the benzothiazoline in 10 ml. of 1-octanol to which had been added 0.5 g. of sodium was slowly heated. The initial gas evolution temperature was 145°. Isobutane was evolved in 88% yield. The residue was not examined.

Rate Measurements.—The apparatus consisted of a graduated gas buret connected to the top of a water-cooled condenser which was in turn fitted to a 3-necked 100-ml. flask. The flask was equipped with a thermometer projecting to its bottom, a magnetic stirring bar and a standard taper adapter fitted with a rubber serum cap. Heat was supplied by a Glascol heating mantle. When the flask was wrapped with glass wool temperatures in the 200–300° region could easily be maintained to within one degree.

Solvents in which the decompositions were carried out were redistilled diphenyl ether for the lower temperatures or Dow–Corning 550 silicone oil for the higher. There was no difference between the rate in one solvent and that in the other.

The solvent was heated to the desired temperature which was maintained for 30 min. before starting a run. One ml. of the benzothiazoline was injected into the flask through the serum cap with a hypodermic syringe. The volume of the gas evolved, temperature and time were noted over a period approximately 10–80% completion of the reaction. Gas volume was corrected to atmospheric pressure. The

(20) C. Courtot and S. Tschelitcheff, *Compt. rend.*, **217**, 231 (1943).

final data were taken in the range of 25–80% completion of the reaction. Variation in temperature before attainment of equilibrium was thereby eliminated. The rate curves obtained are shown in Fig. 1 and the rate constants and approxiate energies of activation are given in Table III.

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The Mechanism of Dye Formation in Color Photography. VII. Intermediate Bases in the Deamination of Quinonediimines[1]

BY L. K. J. TONG, M. CAROLYN GLESMANN AND R. L. BENT

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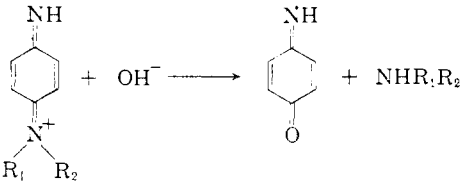
The deamination of certain oxidized derivatives of *p*-phenylenediamines in aqueous solutions proceeds through stable intermediates which have been postulated as the addition products with OH^-. Some equilibrium constants for this reaction were measured spectrophotometrically. The addition compounds appear to be inert in the formation of indoaniline dyes.

It has been shown earlier in this series[2,3] that quinonediimines, formed by oxidation of *p*-amino-N,N-dialkylanilines, undergo a deamination of the substituted amino group to form quinonemonoimines according to the equation



In the cases reported earlier, the rate of this reaction was a linear function of the OH^- concentration. Certain amines containing hydroxyalkyl substituents on the tertiary nitrogen, however, follow a more complicated rate law. The analysis of this rate law has led to a more detailed understanding of the SN2 deamination reaction and is reported in the present paper.

As before, the reaction rates are measured by determination of the yields at various times of the indoaniline dye and the indophenol dye which are formed by coupling of the quinonediimine or the quinonemonoimine, respectively, with α-naphthol, depending on whether or not deamination takes place. The deaminations of the quinonediimines derived from the amines in Table I, like those of the four compounds discussed earlier,[2] are directly proportional to the OH^- concentration over the whole measured range from *p*H 8.0 to 12.0. The rates are given in Table I as log $k_1/(OH^-)$, *i.e.*, deamination rates for unit OH^- activity. The values of the earlier measurements are repeated, in italics, for comparison.

The deamination rates of quinonediimines derived from the amines listed in Table II when plotted against *p*H, Fig. 1, tend toward limiting values and actually reach these in several cases. Then even drastic increases in *p*H up to 0.375 *N* KOH do not further raise the deamination rate. Such changes in dependence are often indicative of the formation of more or less stable intermediates, but diamines with high oxidation potentials might exhibit a non-linear log *k* *vs.* *p*H plot because of

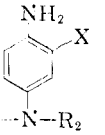
(1) For Part VI, see L. K. J. Tong and M. Carolyn Glesmann, THIS JOURNAL, **79**, 4310 (1957).

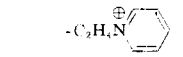
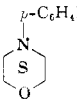
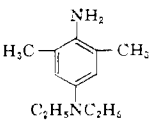
(2) L. K. J. Tong, *J. Phys. Chem.*, **58**, 1090 (1954).

(3) L. K. J. Tong and M. Carolyn Glesmann, THIS JOURNAL, **78**, 5827 (1956).

TABLE I

SECOND-ORDER RATE CONSTANTS $k_1/(OH^-)$ FOR ELIMINATION OF THE DIALKYLAMINE



Number	Compound X	R1	R2	log $k_1/(OH^-)$
1	CH_3	C_2H_5		5.35
2	H	C_2H_5	$-C_2H_4SO_3^\ominus$	4.51
3	H	C_2H_5	$-C_2H_4NHCOCH_3$	4.42
4	H	CH_3	$-CH_3$	4.40
5	Cl	C_2H_5	$-C_2H_5$	*4.34*
6	H	C_2H_5	$-C_2H_4OCH_3$	*4.30*
7	H	C_2H_5	$-C_2H_5NHSO_2CH_3$[a]	4.30
8	H	C_2H_5	$-C_2H_5$	*3.99*
9	CH_3	C_2H_5	$-C_2H_4SO_3^\ominus$	*3.83*
10	CH_3	C_2H_5	$-C_2H_4NSO_2CH_3$ (CH3 on N)	*3.78*
11	CH_3	C_2H_5	$-C_2H_4NHSO_2CH_3$[a]	*3.64*
12	CH_3	C_2H_5	$-C_3H_6SO_3^\ominus$	3.46
13	C_2H_4OH	C_2H_5	$-C_2H_5$	3.36
14	CH_3	C_2H_5	$-CH_2COO^\ominus$	3.35
15	CH_3	$-CH_2COO^\ominus$	$-CH_2COO^\ominus$	3.24
16	CH_3	C_2H_5	$-C_2H_5$	*3.22*
17	CH_3	C_2H_5	$-C_2H_4NSO_2CH_3$[a] ($\ominus$ on N)	*2.48*
18	H	C_2H_5	$-C_2H_4NSO_2CH_3$[a] ($\ominus$ on N)	*2.34*
19	$-OCH_3$	C_2H_5	$-C_2H_5$	2.03
20				5.00
21				4.10
22				3.78
23				2.34

[a] Data from references 2 and 3 are included for comparison. Compounds 17 and 18 are the same as compounds 11 and 7 after ionization.