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The Thermal Decomposition of 2,2'-Azo-bis-isobutyronitrile. Part I. Products of the Reaction

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The isolation and identification of hydrolysis products from an intermediate formed in the decomposition of 2,2'-azo-bis-isobutyronitrile is described. Evidence is given that the intermediate is dimethylketenecyanisopropylimine.

2,2'-Azo-bis-isobutyronitrile was first prepared by Thiele and Heuser[2] who found that the main product of thermal decomposition was tetramethylsuccinodinitrile. A more exhaustive study by Bickel and Waters[3] showed the final products to be tetramethylsuccinodinitrile (I) (84%), isobutyronitrile (II) (3.5%) and 2,3,5-tricyanohexane (III) (9%). The yields of I and III have been confirmed by the present authors. A reaction scheme was postulated to explain these products based on the decomposition of the azonitrile to give free cyanisopropyl radicals which dimerized to give I, disproportionated to give II and methacrylonitrile; the latter reacted with further radicals to give III.

Rate studies on this reaction, using ultraviolet spectroscopy, showed (Part II) the formation of a strongly absorbing unstable intermediate. The identification of this intermediate is the subject of the present paper.

The cooled reaction mixture was extracted with dilute hydrochloric acid and then water, at the time when the ultraviolet absorption showed the intermediate to be at a maximum concentration. From the aqueous layers, N-isobutyryl-α-aminoisobutyric acid (IV) and N-isobutyryl-α-aminoisobutyramide (V) were isolated. Further correlation of these products with the strongly absorbing intermediate was indicated by carrying out the extraction on (a) a solution of the azonitrile which had been heated several hours at 80°, (b) a solution of the azonitrile and tetramethylsuccinodinitrile. In both cases the amount of material in the aqueous layers was negligible; crystalline material was only extracted from the reaction mixture while the azonitrile was decomposing.

The decomposition of the azonitrile as shown by Overberger and Berenbaum[4] would be expected to lead to the formation of cyanisopropyl radicals in a free state. The $-CONH_2$ and $-COOH$ groups of the isolated products were clearly existent as a $-CN$ group in the original intermediate. When this substitution is made, the skeletons of two cyanisopropyl radicals are evident in these molecules. This suggests that the intermediate is dimethylketenecyanisopropylimine (VI) which on mild hydrolysis gives the two compounds isolated.

$$\underset{\text{VI}}{(CH_3)_2C{=}C{=}N{\cdot}C(CH_3)_2CN} \xrightarrow{H_2O} \underset{\text{V}}{(CH_3)_2CH{\cdot}CO{\cdot}NH{\cdot}C(CH_3)_2CONH_2} \xrightarrow{H_2O} \underset{\text{IV}}{(CH_3)_2CH{\cdot}CO{\cdot}NH{\cdot}C(CH_3)_2COOH}$$

Some support for this viewpoint comes from the isolation of an oily fraction which had a strong infrared absorption at 4.96 μ corresponding to the presence of a 1:2 diene structure.

Ketenimines have been prepared by Staudinger,[5] Stevens and French,[6] and Dykstra and Backer.[7] These authors showed that ketenimines are in general much more stable than the parent ketenes. In particular, they are only slowly attacked by water, but are hydrolyzed rapidly by dilute acids to the corresponding substituted amides.

From the skeletons of the isolated products it seems that the intermediate is formed by the abnormal recombination of two cyanisopropyl radicals. It is known that these radicals are resonance stabilized since they are comparatively unreactive. No evidence in this work, for instance, was ever found for the presence of dibenzyl in the reaction products, a compound easily detected by ultraviolet absorption measurements. Its presence would have been noted with only a small attack of the radicals on the toluene. Thus the electron density on the nitrogen atom of the cyanisopropyl radical due to resonance must be sufficiently great that a direct

$$(CH_3)_2\dot{C}{\cdot}CN \longleftrightarrow (CH_3)_2C{=}C{=}N{\cdot}$$

recombination reaction linking this atom to the carbon atom carrying the free valence electron of another radical is possible.

The normal recombination reaction giving tetramethylsuccinodinitrile occurs more readily. About 11–12 mole % of ketenimine derivatives were isolated, and it can be shown (Part II) that this corresponds to about 33% total formation over the whole reaction. Thus about 66% of the radicals must combine directly in the normal manner. Recombination of two radicals at the two nitrogen atoms would be correspondingly more rare. No products corresponding to this reaction were found.

Experimental

1. Decomposition of 2,2'-Azo-bis-isobutyronitrile.—This compound was obtained from Westville Laboratories, Monroe, Connecticut, and recrystallized from benzene to m.p. 101° dec. Thermal decomposition was carried out at 80.4° in C.P. grade toluene while nitrogen was bubbled

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(2) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(3) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

(4) C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **73**, 4883 (1951).

(5) H. Staudinger, *Ber.*, **53**, 72 (1920).

(6) C. Stevens and J. C. French, THIS JOURNAL, **75**, 657 (1953); **76**, 4398 (1954).

(7) R. Dykstra and H. J. Backer, *Proc. Acad. Sci. Amsterdam*, **B55**, 382 (1952).

through the solution. This was purified by bubbling through Fieser's solution, then passing it up a tower containing finely divided copper[8] and finally dried. Ultraviolet absorption measurements at 320 mμ showed that the intermediate was at maximum concentration after 110 minutes. Reaction was stopped at this point by cooling rapidly to room temperature. The toluene solution was extracted with 1 *N* hydrochloric acid followed by distilled water. The ultraviolet absorption of the toluene layer was decreased to a low value by this treatment. The aqueous layers were separately evaporated to dryness under reduced pressure below 50° yielding crystalline products. The product from the water extraction was recrystallized from alcohol, to a m.p. of 190° (V), and that from the hydrochloric acid was dissolved in alcohol, and freed from ammonium chloride by precipitation with ether. It was finally recrystallized from ether to a m.p. of 150–151° (IV). In a typical experiment 98 g. of the azonitrile heated in 700 ml. of toluene yielded 1.8 g. of ammonium chloride, 7.2 g. of IV and 4.7 g. of V.

2. **Identification of IV.**—This compound had an acid reaction and when titrated potentiometrically against 0.1 *N* caustic soda yielded an equivalent weight of 173; pK = 4.35.

The compound was recovered unchanged after refluxing with aqueous alkali. Hydrolysis by refluxing with 40% sulfuric acid for several hours followed by extraction with ether gave an 80% yield of isobutyric acid, b.p. 153–154°, $n^{18}D$ 1.3927; ethyl ester b.p. 111–112°, $n^{18}D$ 1.3875.[9] The residual sulfuric acid was neutralized with barium carbonate and an amino acid was isolated (ninhydrin test) from this solution using the method described by Buckley, Heath and Rose.[10] This sublimed at ~280°, gave an identical ultraviolet spectrum in presence of formaldehyde to that produced by an authentic specimen of α-aminoisobutyric acid. The equivalent weight by titration against 0.1 *N* caustic soda in presence of formaldehyde according to the method described by Sørensen[11] was 104; theoretical for α-aminoisobutyric acid 104; yield in the hydrolysis, 72%.

A mixed melting point on compound IV with a specimen of N-isobutyryl-α-aminoisobutyric acid prepared as below, showed no depression.

Anal. Calcd. for $C_8H_{15}O_3N$: C, 55.46; H, 8.73; N, 8.09. Found: C, 55.85; H, 9.01; N, 8.30.

3. **Synthesis of N-Isobutyryl-α-aminoisobutyric Acid.**—Methyl α-aminoisobutyrate was prepared from α-aminoisobutyric acid, b.p. 135–136°.[12] Isobutyric anhydride, b.p. 180–183°, was prepared from sodium isobutyrate and isobutyryl chloride.[13] The two were condensed and the product was warmed with 2 *N* caustic soda until it dissolved. Isobutyric acid separated on acidification and was removed. Further isobutyric acid was removed by shaking with petroleum ether. The aqueous layer was evaporated to dryness and the residue crystallized from ether. The crystals were washed with benzene several times and recrystallized from ether; yield 50%, m.p. 150–151°. Titration against 0.1 *N* caustic soda gave an equivalent weight of 173, pK = 4.33.

This compound was also prepared by condensing α-aminoisobutyronitrile with isobutyryl chloride, followed by hydrolysis of the nitrile group as described under (1) with dilute hydrochloric acid; m.p. 150–151°, over-all yield 75%.

4. **Identification of V.**—This compound was heated with aqueous caustic soda and yielded one equivalent of ammonia. A larger quantity was hydrolyzed, the solution acidified, extracted with ether and the extract concentrated. Crystals were obtained which after recrystallization from alcohol melted at 150–151° and showed no melting point depression when mixed with IV. V must be N-isobutyryl-α-aminoisobutyramide.

Anal. Calcd. for $C_8H_{16}O_2N_2$: C, 55.81; H, 9.37; N, 16.28. Found: C, 55.95; H, 9.31; N, 16.13.

5. **Isolation of an Oily Fraction Containing the Intermediate.**—Decomposition of the azonitrile was carried out as in (1) and stopped at the same point. The toluene was evaporated at low temperature leaving a mass of crystals covered with an oily substance. The latter was pressed off the crystals with absorbent paper which was then extracted with benzene. After concentration, a viscous oil remained which slowly deposited crystals on cooling to 5°. The crystals (m.p. 168°) were presumably tetramethylsuccinodinitrile. The oil therefore still contained tetramethylsuccinodinitrile and perhaps the original azo compound. Physical methods failed to effect a separation. The oil had a strong ultraviolet absorption with a maximum at 287 mμ ($E_{\max}$ 135 assuming a mol. wt. of 136), very near to the wave length of maximum absorption (294 mμ) found by Stevens and French[6] for the compound ethyl-*n*-butylketene-*n*-butylimine. It also showed a strong infrared absorption band at 4.96 μ.

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