to the Grignard reagent prepared from 71 g. (0.5 mole) of methyl iodide with 12 g. (0.5 g. atom) of magnesium in 125 ml. of ether was followed by stirring at 28° for 16 hr. and standing for 24 hr. at 28°. The mixture was poured into a mixture of 200 g. of ice and a solution of 30 g. of ammonium chloride in 60 ml. of water. Separation of the layers was followed by ether extraction. The extracts were combined, dried and distilled to give 26 g. (88%) of alcohol IV, b.p. 86–88° (30 mm.), freezing point *ca.* 29°. Beckmann, *et al.*,[6] report this product as an oil, b.p. 83° (20 mm.).

Dehydration of 2-*exo*Methyl-2-*endo*hydroxynorbornane (IV). a. Phosphoryl Chloride–Pyridine.—Five grams (0.04 mole) of alcohol IV in 50 ml. of pyridine was treated with 16 ml. (0.175 mole) of phosphoryl chloride over 1 hr. The temperature was allowed to rise to 52°. After cooling, the reaction mixture was quenched to give 1.7 g. (40%) of olefins. Analysis of the mixture by gas chromatography on a dimethyl sulfolane–Celite column gave the values 80% VIII and 20% IX. Less than 1% of a more volatile material was present; λ_{max}^{film} 11.35(s) and 12.4(w) μ.

b. *p*-Toluenesulfonic Acid.—Distillation of 1 g. of alcohol IV over a few crystals of *p*-toluenesulfonic acid gave 0.6 g. of olefin which gave the following analysis: 80% VIII, 15% IX and 5% of the more volatile component.

c. Phthalic Anhydride.—Distillation of 3 g. of IV over 3 g. of phthalic anhydride[6] gave 61% VIII and 39% IX.

Dehydration of 2-*exo*Hydroxy-2-*endo*methylnorcamphane (III). a. Phosphoryl Chloride–Pyridine.—Ten ml. (0.11

mole) of phosphoryl chloride was added to a solution of 5 g. (0.04 mole) of alcohol III in 50 ml. of pyridine. The solution was allowed to warm to 75° and then was kept at 27° for 2 hr. After heating to reflux the mixture was cooled and poured onto ice-water. The olefin mixture (1.2 g., 28%) contained 69% VIII, 31% IX and less than 1% of a more volatile component; λ_{max}^{film} 11.35(s) and 12.4(w) μ.

b. *p*-Toluenesulfonic Acid.—Distillation of 1 g. of III over a few crystals of *p*-toluenesulfonic acid gave 0.5 g. of olefins containing 71% VIII, 27% IX and 2% of the more volatile component.

2-Methylenenorcamphane (VIII).—The adduct from itaconic acid and cyclopentadiene[11] was crystallized once from benzene and hydrogenated over platinum in ethanol. A mixture of 25 g. of diacids XIa and XIb with 60 g. of powdered Pyrex and 60 g. of lead dioxide (Baker analyzed) was slowly heated to 210°. A mixture of water and methylenenorcamphane gradually distilled. The phases were separated and the organic layer was dried over sodium sulfate and distilled to give 2.35 g. (17%) of VIII, $n^{24.5}$D 1.4710 (lit.[8] n^{25}D 1.4719). Gas chromatographic analysis indicated that about 2% of IX were present; λ_{max}^{film} 11.35 μ (C=CH₂).

2-Methyl-2-norbornene(IX) was prepared according to Beckmann, *et al.*,[8] and had n^{25}D 1.4616 (lit.[19] n^{20}D 1.4621); λ_{max}^{film} 12.4 μ (C=C—H).

(19) K. Alder, R. Hartmann and W. Rath, *Ann.*, **613**, 6 (1958).

NEW BRUNSWICK, N. J.

The Decomposition of α,α'-Azoisobutyronitrile in Liquid Bromine

BY ORLIN D. TRAPP AND GEORGE S. HAMMOND[1]

The decomposition of α,α'-azoisobutyronitrile in liquid bromine gives no tetramethylsuccinonitrile. Since the decomposition is no more than a factor of two faster than in other media the spontaneous decomposition is involved. It is concluded that any dinitrile formed in the inefficient decomposition in other solvents must arise from recombination of radicals in the solvent cage and not from non-radical reactions.

It has been suggested that the inefficiency of α,α'-azoisobutyronitrile (ABN), a polymerization and oxidation initiator, is due to primary recombination of the radical pair produced in the first decomposition step.[2–4] One is hard pressed to devise tests which provide rigorous distinction between radical recombination in the solvent cage and various non-radical side reactions. One possible approach to the problem is the study of the products of decomposition carried out in the presence of high concentrations of very reactive free radical scavengers. Under such conditions one might expect that reactions of the type

$$\overline{2R\cdot} + M \longrightarrow \text{products}$$

will intervene and alter the course of the reaction whereas there should be no interference with non-radical processes.

Such considerations prompted us to study the decomposition of ABN in liquid bromine. At the outset we were most concerned with the determination of the yield of tetramethylsuccinonitrile (RR), the product of symmetrical coupling of cyanopropyl
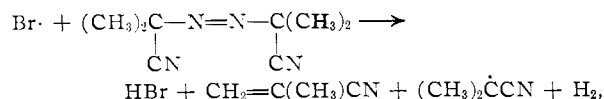
(1) Division of Chemistry, California Institute of Technology, Pasadena, Calif.

(2) J. C. Bevington, J. H. Bradbury and G. M. Burnett, *J. Polymer Sci.*, **12**, 469 (1954); J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955); J. C. Bevington, *J. Chem. Soc.*, 3707 (1954).

(3) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 74 ff.

radicals. Careful examination of reaction mixtures showed that the yield of the dinitrile is vanishingly small. In order to ascertain that the usual, unimolecular decomposition of ABN was actually under observation it was necessary to demonstrate that the decomposition was not greatly accelerated in bromine. Kinetic measurements by the usual techniques are not applicable to the bromine system but an estimate of the decomposition rate was obtained by interrupting reactions, removing the bromine and determining the residual ABN by ultraviolet absorption of a benzene solution of the residue. Results showed that ABN was certainly present although an absorbing by-product was also present which obscured the short wave-length minimum in the ABN spectrum. Figure 1 shows the resolution of the experimental spectrum to obtain an analysis for the azo compound. The rate constants calculated from two such experiments were 4.6 and 5.3 × 10⁻⁴ sec.⁻¹ at 80.9°. While the rates are faster by a factor of two or more than rates in other solvents at the same temperature we can be assured that at least a considerable amount of decomposition must have occurred by the usual path of decomposition.

The actual reaction products are unknown except that trace amounts of liquid were obtained which distilled near the boiling point of α-bromoisobutyronitrile. Much more of the ABN decomposed may have reacted to give the bromonitrile since it

was found that the latter compound does not survive heating in bromine. Since R–R is the only one of the usual decomposition products which is not destroyed by bromine we can only conclude that the dinitrile is produced only from precursors which are scavenged by bromine. In all probability the small amount of dinitrile formed directly from ABN in the normal decomposition is produced by way of free radicals which undergo primary recombination before they diffuse apart. The only possible bearing which our results have on the mechanism of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine, the principal product of inefficient decomposition in the usual type of scavenging experiment,[5] derives from the relatively fast rate of decomposition in bromine. Three acceptable explanations for this phenomenon come immediately to mind: (1) There may be some direct reaction between bromine and ABN; (2) induced reactions such as

$$Br\cdot + (CH_3)_2C-N=N-C(CH_3)_2 \longrightarrow$$
$$\begin{array}{cc} | & | \\ CN & CN \end{array}$$
$$HBr + CH_2=C(CH_3)CN + (CH_3)_2\dot{C}CN + H_2,$$

may occur to a limited extent; and (3) the primary recombination of R· and RN₂· may occur in most solvents and be suppressed by immediate reaction with bromine. The last of the three possibilities would require that the decomposition of ABN should be stepwise, contrary to commonly held views.[7]

Experimental

Decomposition of ABN in Bromine.—A 2.32-g. sample of ABN was heated in 46 g. of bromine at 62° for 7 days. The tube was opened and the bulk of the bromine was removed by vacuum distillation at room temperature. The distillation was discontinued after a final period of pumping for one hour at 5 mm. The pot residue was a dark orange sirup. Other experiments had shown that the higher boiling fractions removed by such a distillation contained the hydrogen bromide–water azeotrope and organic oils. No more than a trace boiled between 130–140° (α-bromoisobutyronitrile).

Ethylene was passed slowly through the residue to react with excess bromine. The residue was then heated gently *in vacuo* in an attempt to sublime out tetramethylsuccinonitrile. A small amount of oil and a few crystals, m.p. 78–90°, were collected on the cold finger.

All fractions were extracted with ether, a good solvent for the extraction of R–R. The combined extracts were dried and the ether was removed by evaporation. Heating the residue *in vacuo* gave about 0.03 g. of solid sublimate, m.p. 128–138°. Comparison of the infrared spectrum of the material in carbon tetrachloride with that of tetramethylsuccinonitrile in the same solvent showed that the unknown material contained no detectable amount of the dinitrile.

Seven other runs were done using similar amounts of bromine and ABN. The others were worked up by various distillation techniques and the residues were variously distilled, fractionated from solvents and subjected to hydrolysis. In no case was any weighable amount of material with a spectrum similar to the dinitrile isolated.

Rate of Decomposition of ABN in Bromine.—Weighed samples of about 1.5 g. of ABN were heated in 5 ml. of bromine for periods of 30 and 72 minutes at 80.8°. The tubes then were opened and the bromine was removed by

(5) This is demonstrated by studies of the rates of formation of R–R′ from ABN and a study of the decomposition of R–R′. The decomposition study is reported in an accompanying paper[6] and application of the results in interpretation of ABN decomposition will be the subject of a future publication.

(6) G. S. Hammond, O. D. Trapp, R. T. Keys and D. L. Neff, This Journal, **81**, 4878 (1959).
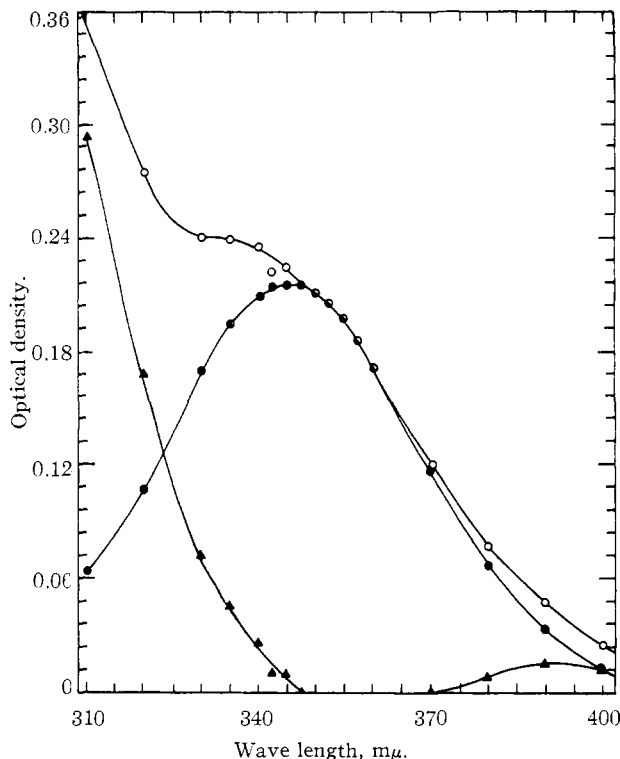
(7) C. Walling, ref. 4, p. 511.

Fig. 1.—Resolution of the spectrum of the mixture obtained by heating ABN in bromine for 72 minutes: O—O, readings observed; ●—●, absorbance calculated for assigned concentration of ABN; ▲—▲, difference assigned to reaction products.

vacuum distillation below 50°. All but a trace of the residue was benzene soluble. Phenol was added to the benzene solution until the bromine color disappeared. The phenols were then, at least partially, removed by washing with 5% aqueous sodium hydroxide. The benzene solution was washed thoroughly with distilled water and dried over Drierite. The solution was diluted to 250 ml. and samples were taken for ultraviolet spectra, which were determined in a Beckman DU instrument. The short wave length side of the ABN absorption band was obscured by absorption which was due to an interfering species, perhaps unremoved tribromophenol. However, Fig. 1 shows that the spectrum could be adequately fitted using the assumption that the absorption above 3500 Å. was due exclusively to ABN. First-order rate constants were calculated using these assumptions.

Recovery of Tetramethylsuccinonitrile (R–R).—A sample of 2.45 g. of R–R was heated in 15 ml. of bromine at 62.5° for 7 days. The flask was opened. The bromine was removed by codistillation with carbon tetrachloride *in vacuo*. Fifty ml. of carbon tetrachloride was added initially followed by successive 25-ml. portions. During the process a small portion of the reaction mixture was siphoned into the first trap. The residue in the flask was 2.19 g. and that in the trap was 0.14 g. giving a total of 2.33 g. recovered dinitrile (95%), m.p. 166–168°; m.p. of original charge, 169.5–171°.

α-Bromoisobutyronitrile in Bromine.—A 2.63-g. sample of the bromonitrile was heated in 45 g. of bromine at 61° for 7 days. The flask was opened and bromine was pumped off at about 90 mm. until the boiling point of the residue seemed to be increased. The receiver (a Dry Ice trap) was changed and the distillation was continued with the pressure being gradually lowered to 5 mm. The distillate was taken up in ether to give a colorless solution which was washed with saturated aqueous sodium bisulfite. The solution was dried and after distillation of the ether there was less than 0.5 ml. of higher boiling liquid. The residue from the original distillation was also taken up in ether and an insoluble precipitate was removed by filtration. The pre-

cipitate weighed 31 mg. and melted above 230°. The ether extract was distilled, the residue being heated at 100° at 5 mm. A small amount of oil was collected in the trap and a few crystals collected in the condenser. Further attempts to isolate pure products were unsuccessful but it is certain that no more than a trace of the bromonitrile survived the experiment.
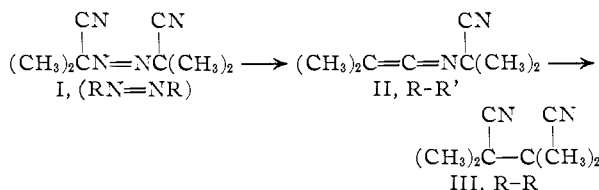

Isolation and Study of the Intermediate [Dimethyl-N-(2-cyano-2-propyl)-ketenimine] Formed in the Decomposition of α,α'-Azoisobutyronitrile

BY GEORGE S. HAMMOND,[1] ORLIN D. TRAPP, RICHARD T. KEYS AND DAVID L. NEFF

Dimethyl-N-(2-cyano-2-propyl)-ketenimine (R–R') has been isolated and characterized. The ketenimine reacts with halogens, water and butyl mercaptan. Decomposition of the compound, which produces tetramethylsuccinonitrile in the absence of free radical scavengers, follows first-order kinetics. Involvement of free radicals is demonstrated by the ability of the compound to initiate autoxidation of cumene and polymerization of styrene. The efficiency of R–R' as an initiator is less than that of α,α'-azoisobutyronitrile (ABN). The results are best accommodated by a free radical mechanism with a substantial cage effect.

Talât-Erben and Bywater[2] have shown that dimethyl-N-(2-cyano-2-propyl)-ketenimine (II) is an intermediate in the decomposition of α,α'-azoisobutyronitrile (ABN),[3] I. The ketenimine itself isomerizes forming tetramethylsuccinonitrile (III) which was previously known to be the principal end-product of ABN decomposition.[5–7] The ketenimine henceforth will be referred to as R–R' and the isomeric dinitrile will be called R–R.

$$\underset{\text{I, (RN=NR)}}{(CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}N=N\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2} \longrightarrow \underset{\text{II, R–R'}}{(CH_3)_2C=C=N\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2} \longrightarrow$$

$$\underset{\text{III, R–R}}{(CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}-\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2}$$

Since the decomposition of ABN is known to involve free radicals it was of interest to study the isomerization of R–R'. If the reaction also involves a free radical mechanism it would provide an excellent case for the study of cage effects.

Results and Discussion

Since R–R' is a liquid which is very soluble in petroleum solvents, in which ABN and R–R are sparingly soluble, we were able to develop a convenient preparative method for R–R'. ABN was decomposed by heating it in the presence of refluxing cyclohexane. After an appropriate time interval, the solids were removed by filtration and nearly pure R–R' was recovered by concentration of the filtration and nearly pure R–R' was recovered by concentration of the filtrate. The product was

further purified by distillation *in vacuo*. The ketenimine reacts with water as previously reported[2] and reacts rapidly with iodine, bromine and concentrated solutions of butyl mercaptan. Direct titration with bromine in carbon tetrachloride was finally adopted as the best criterion of purity and was used as a basis for standardization of ultraviolet and infrared methods of analysis. The infrared band at 2020 cm.$^{-1}$ and the ultraviolet band having a maximum at 2900 Å. follow Beer's law except that the ultraviolet absorption is appreciably affected by oxygen.

Measurement of the rate of decomposition of R–R' was carried out using the infrared analysis. Runs were made at three temperatures, in several solvents, and in the presence of oxygen, both with and without anti-oxidants. The data give a good fit to the first-order law and are summarized in Table I. The rate of decomposition is increased substantially in the presence of oxygen.

Since the decomposition of R–R' initiates the autoxidation of cumene and the polymerization of styrene, it is virtually certain that decomposition of the ketenimine produces free radicals.

Acceleration by oxygen cannot be attributed to a direct reaction of oxygen with R–R' since the inclusion of a small amount of an antioxidant removes the effect completely. The most acceptable explanation of the results is found in the assumption that peroxy radicals are formed in the presence of oxygen and attack the ketenimine unless they are scavenged rapidly by an antioxidant. Study of the phenomenon is being continued. The scheme (1) to (9) probably represents the decomposition mechanism. Primary decomposition products which are still resident in the same solvent cage are represented by $\overline{2R\cdot}$.

$$R–R' \longrightarrow \overline{2R\cdot} \tag{1}$$

$$\overline{2R\cdot} \longrightarrow R–R \tag{2}$$

$$\overline{2R\cdot} \longrightarrow 2R\cdot \tag{3}$$

$$2R\cdot \longrightarrow R–R \tag{4}$$

$$2R\cdot \longrightarrow R–R' \tag{5}$$

(1) Division of Chemistry, California Institute of Technology, Pasadena, Calif.

(2) M. Talât-Erben and S. Bywater, THIS JOURNAL, **77**, 3244 (1955).

(3) We have previously referred to this compound as AIBN but suggest the adoption of ABN as a designation in conformity with the terminology of Mayo.[4]

(4) F. R. Mayo, THIS JOURNAL, **80**, 2465 (1958).

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

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

(7) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).