malic acid, (+)-benzoyltartaric acid, and (+)-camphorsulfonic acid. Although crystalline salts were obtained, the isolated amine was inactive.

Experimental Section[6]

3-Methyl-3-heptanol.—This alcohol was prepared in 60–70% yields by treating 2-pentanone with ethylmagnesium bromide: bp 138–142°, $n^{25}D$ 1.4203 (lit. bp 141°,[7] $n^{20}D$ 1.4231[8]).

3-Amino-3-methylhexane.—The procedure for the conversion of a tertiary alcohol to a *t*-alkylamine as developed by Ritter and Kalish[2] was adapted as follows. A solution of 375 g of sulfuric acid in 200 ml of glacial acetic acid was added slowly to a stirred solution containing 172 g of 3-methyl-3-hexanol (1.5 moles) and 82.5 g (1.5 formula wt) of 90% sodium cyanide in 190 ml of glacial acetic acid. The reaction was maintained 40–60° by the use of an ice–water bath. After remaining for 48 hr at room temperature, a solution containing 600 g of sodium hydroxide dissolved in 800 ml of water was added and the mixture was refluxed for 4 hr. The amine was removed by steam distillation and the distillate was made strongly alkaline with concentrated sodium hydroxide solution. The amine was separated and the aqueous layer was extracted three times with 50-ml portions of pentane. The combined organic portions were dried with anhydrous potassium carbonate and 133 g of colorless amine was isolated by fractional distillation using a 31 × 0.5 cm tantalum wire spiral column: bp 129–130°, $n^{25}D$ 1.4171, d^{25}_4 0.919.

Anal. Calcd for $C_7H_{17}N$: C, 72.96; H, 14.88; N, 12.16. Found: C, 73.16; H, 14.88; N, 12.12.

The nmr spectra indicated no tertiary hydrogen signal (1.6 ppm downfield from TMS).

Resolution of 3-Amino-3-methylhexane.—Over a period of 1 hr, 460 g (4.0 moles) of racemic 3-amino-3-methylhexane was added to a solution of 600 g (5.2 moles) of (+)-tartaric acid dissolved in 2000 ml of water. The mixture was heated over a steam bath for a period of 1 hr and allowed to cool to room temperature. The solution was stored overnight in a refrigerator and yielded 400 g of white, crystalline tartrate salt: mp 115–116°, $[\alpha]^{25}D$ 15.1° (*c* 4, *l* = 2 dm, water).

Anal. Calcd for $C_{11}H_{23}NO_6$: C, 49.80; H, 8.74. Found: C, 49.73; H, 8.65.

The amine was recovered from the amine (+)-tartaric acid salt by the following procedure. The tartrate salt (172 g, 0.65 mole) was dissolved in about 200 ml of water. The solution was made alkaline (with cooling) by adding a solution of 56 g of potassium hydroxide dissolved in 100 ml of water. On standing the mixture separated into two layers. The water layer was extracted with three 20-ml portions of pentane. The extracts were combined with the organic layer, dried over anhydrous potassium carbonate, and distilled through the tantalum wire spiral column. The distillation gave 72.2 g (94% recovery) of the *t*-alkylamine: $[\alpha]^{25}D$ −0.032°, bp 129.5–131.5°.

Anal. Calcd for $C_7H_{17}N$: C, 72.96; H, 14.88; N, 12.16. Found: C, 72.85; H, 14.69; N, 12.10.

After three successive recrystallizations, the above amine (+)-tartrate salt gave the following properties: mp 114–116°, $[\alpha]^{25}D$ 14.8°. However, the specific rotation of the amine liberated from this salt was $[\alpha]^{25}D$ −0.096° (*l* = 4 dm, neat).

(+)-3-Methyleneamino-3-methylhexane.[9]—In 1.5 hr, 150 ml (1.25 moles) of 40% formalin was added with stirring and cooling to 144 g (1.25 moles) of active 3-amino-3-methylhexane ($[\alpha]^{25}D$ −0.032°). After stirring for 1 hr the reaction mixture separated into two layers. The mixture was made alkaline with potassium hydroxide solution and extracted with three 20-ml portions of pentane. The extracts were combined with the organic layer and dried over potassium hydroxide pellets. Distillation through the tantalum wire spiral column gave 137 g (86%) of clear, lachrymatory liquid: bp 141–145°, $n^{25}D$ 1.4318, $[\alpha]^{25}D$ +0.59° (*l* = 2 dm, neat).

Anal. Calcd for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.33; H, 13.34; N, 11.10.

(+)-3-Methylamino-3-methylhexane.[9]—A solution containing 137 g of (+)-3-methyleneamino-3-methylhexane ($[\alpha]^{25}D$ +0.59°) dissolved in 150 ml of methanol was reduced with hydrogen over 0.05 g of platinium oxide catalyst in a Parr low-pressure apparatus. Fractional distillation afforded 127 g (92%) of the secondary amine: bp 152–155°, $n^{25}D$ 1.4218, $[\alpha]^{25}D$ +0.16° (*l* 2 dm, d^{25} 0.924, neat).

Anal. Calcd for $C_8H_{19}N$: C, 74.34; H, 14.82; N, 10.84. Found: C, 74.54; H, 15.00; N, 10.78.

Registry No.—3-Amino-3-methylhexane, 7687-23-2; 3-amino-3-methylhexane tartrate, 7687-24-3; (+)-3-methyleneamino-3-methylhexane, 7687-25-4; (+)-3-methylamino-3-methylhexane, 7687-26-5.

(6) Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Optical activity was measured with a Rudolph Model 62 polarimeter.

(7) P. M. Ginnings and M. Hauser, *J. Am. Chem. Soc.*, **60**, 2581 (1938).

(8) F. C. Whitmore and D. E. Badertscher, *ibid.*, **55**, 1561 (1933).

(9) Corresponding physical properties and satisfactory elemental analyses were obtained for the racemic compound prepared from inactive amine.

Cyanide-Catalyzed Fragmentation of Triketone Monoximes[1]

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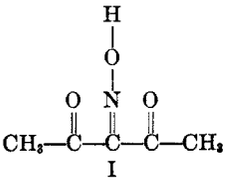
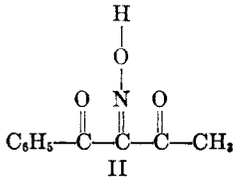
Reaction of acylating agents with triketone monoximes is reported to be complicated. Green and Saville[2] found that the reaction of acylating agents with 2,3,4-pentanetrione 3-oxime (I) leads to the pro-



I



II

duction of over 6 moles of acid and the consumption of 3 moles of oxime per mole of acylating agent. One would have expected 3 moles of acid and the consumption of 1 mole of oxime as the result of acylation, fragmentation, and hydrolysis. Compound I itself slowly decomposed in neutral, aqueous solution. Pyruvic acid was found among the decomposition products but the mechanism was considered obscure and was not investigated further.

Analogous properties have been observed for 1-phenyl-1,2,3-butanetrione 2-oxime (II).[3] Hydrogen cyanide is one of the products from reaction of II with reagents such as acetic anhydride or benzenesulfonyl chloride which are known to bring about Beckmann fragmentation of α-oximino ketones. The hydrogen cyanide produced by spontaneous decomposition of the oxime increased to a maximum, then decreased after a few hours to a plateau. An explanation offered for the decrease and leveling off of cyanide concentration was that hydrogen cyanide reacts with the remaining excess II to form a cyanohydrin, but no effort was made to isolate products.[3]

This paper concerns itself with elucidating the mechanism of cyanide reaction with the triketone monoxime (II). This is of particular current interest because II

(1) The work was presented in part at the Meeting in Miniature of the Maryland–Washington, D. C., sections of the American Chemical Society, University of Maryland, May 1966.

(2) A. L. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956).

(3) W. J. Barrett and E. B. Dismukes, Southern Research Institute, Birmingham, Ala. 35205.

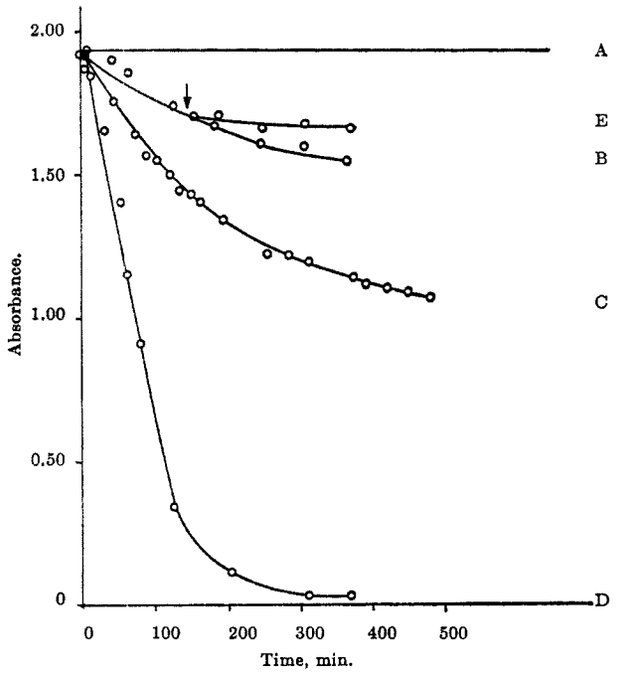
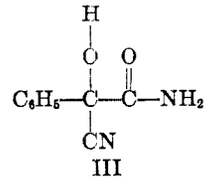


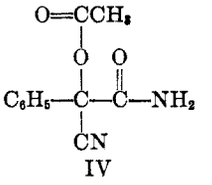
Figure 1.—Catalytic effect of cyanide on the decomposition of 1-phenyl-1,2,3-butanetrione 2-oxime (II) in pH 9.4 borate buffer. Potassium cyanide concentrations were 0 (curve A), 4×10^{-4} *M* (curve B), 4×10^{-3} *M* (curve C), and 4×10^{-2} *M* (curve D). Curve E represents a change in rate of decomposition of II when 2-phenylglyoxylamide was added (arrow; molar ratio KCN/II/2-phenylglyoxylamide = 1:100:100). Absorbance was measured at 405 mμ. The slope of line A represents the rate of decomposition of II measured at intervals over a 6-day period.

has been used to increase sensitivity of the *o*-dinitrobenzene–*p*-nitrobenzaldehyde reaction for cyanide.[4] Detailed assessment of the present work in relation to di- (and mono-) ketone monoxime research can best be performed by reading reviews by Heldt and Donaruma,[5] and Smith.[6]

The reaction of II was carried out with a twofold excess of potassium cyanide in 50% aqueous methanol solution at 10–20°. After the reaction mixture was acidified, small amounts of benzoic acid and methyl benzoate were isolated.[7] The major product, a colorless solid, was identified as 2-hydroxy-2-cyanophenylacetamide (III) by its analysis, infrared and nmr spectra, and the ready evolution of ammonia from strongly basic solutions. The identification was confirmed by synthesis from 2-phenylglyoxylamide. Acetylation of III produced 2-acetoxy-2-cyano-2-phenylacetamide (IV).

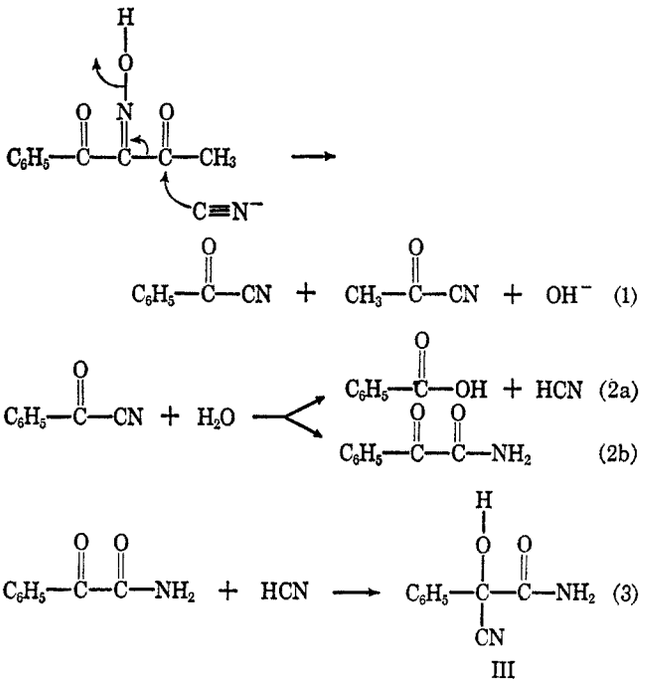


III



IV

Reaction Mechanism.—Undoubtedly benzoyl cyanide and pyruvonitrile form by fragmentation of II, perhaps in a concerted reaction involving nucleophilic attack by cyanide ion (eq 1). Hydrolysis of benzoyl cyanide gives either benzoic acid and hydrogen cyanide,



III

or 2-phenylglyoxylamide (eq 2a and 2b). Addition of hydrogen cyanide to 2-phenylglyoxylamide yields the cyanohydrin, III (eq 3). Corresponding reactions may be written for pyruvonitrile.

There is considerable analogy for the mechanism which is presented in eq 1–3. Fragmentation reactions of aromatic α-diketones and α-oximino ketones have been known for many years. Jourdan[8] reported in 1883 that benzil is cleaved with potassium cyanide to benzaldehyde and benzoic acid. Kwart and Baevsky[9] studied kinetics of the cyanide ion catalyzed cleavage of aromatic α-diketones. Werner and his collaborators[10] established that α-oximino ketones possessing the anti or α configuration behave differently from simple oximes when treated with an acylating agent or benzenesulfonyl chloride and base, in that they are fragmented to a carboxylic acid and a nitrile instead of giving the normal amide product of the Beckmann rearrangement. This cleavage reaction has been called a second-order Beckmann rearrangement, an abnormal Beckmann rearrangement, a Beckmann fission, or a Beckmann fragmentation. Blatt and Barnes[11] discovered that not only is Beckmann fragmentation confined to oximes derived from ketones which are themselves subject to cleavage, but in certain cases the same reagent, potassium cyanide, which effects cleavage of a ketone will bring about a fragmentation of its oxime. In many cases of Beckmann fragmentation, unsubstituted amides are formed instead of nitriles, probably from hydrolysis of nitriles first formed.[5,6] The hydrolysis of benzoyl cyanide in strongly acidic solution produces 2-phenylglyoxylamide and phenylglyoxylic acid,[12] while in alkaline solution benzoic acid and cyanide ion are produced.[13]

Cyanide Catalysis of Decomposition.—Reaction of equimolar amounts of cyanide and II may produce 2

(4) G. Guilbault and D. N. Kramer, *Anal. Chem.*, **38**, 834 (1966).
(5) W. Z. Heldt and L. G. Donaruma, *Org. Reactions*, **11**, 1 (1960).
(6) P. A. Smith in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 8, p 483.
(7) No attempt was made to isolate low molecular weight fragments.
(8) F. Jourdan, *Ber.*, **16**, 659 (1883).
(9) H. Kwart and M. M. Baevsky, *J. Am. Chem. Soc.*, **80**, 580 (1958).
(10) A. Werner and A. Piguet, *Ber.*, **37**, 4295 (1904).
(11) A. H. Blatt and R. P. Barnes, *J. Am. Chem. Soc.*, **56**, 1148 (1934).
(12) L. Claisen, *Ber.*, **12**, 633 (1879).
(13) H. V. Kolbe, *Ann.*, **90**, 62 (1854).

moles of cyanide from hydrolysis of benzoyl cyanide and pyruvonitrile. A spectrophotometric study of the decomposition of II[14] in the presence of various concentrations of cyanide (Figure 1) indicates that cleavage is catalyzed by cyanide. This catalysis is especially demonstrated by an experiment in which 4×10^{-4} mole of potassium cyanide was added to 4×10^{-2} mole of II. At 6 hr, when the experiment was stopped, 1 equiv of cyanide had induced the decomposition of nearly 20 molecular equiv of II. Very slow decomposition occurs in the absence of cyanide.

It is possible to inhibit the decomposition of II by adding 2-phenylglyoxylamide as a cyanide scavenger (cyanohydrin formation). Most pronounced effects are noticed when *excess* 2-phenylglyoxylamide is added to solutions containing small amounts of cyanide (Figure 1, curve E). Leveling-off effects in rate of decomposition of II such as illustrated in Figure 1 may be at least partly explained by the cyanohydrin formation.

Experimental Section

Reaction of 1-Phenyl-1,2,3-butanetrione 2-Oxime (II) with Potassium Cyanide.—A solution of 14.3 g (0.22 mole) of potassium cyanide in 100 ml of distilled water was added dropwise during a 1-hr period to a stirred and cooled solution of 19.0 g (0.1 mole) of II in 100 ml of methanol. The temperature was maintained at 10–20° throughout the reaction and work-up. After 1 hr the clear, yellow solution was slowly acidified (pH 2) with 40% sulfuric acid; a heavy, white precipitate resulted. Products were obtained by either method described below.

Method 1.—The entire reaction mixture was extracted with three 150-ml portions of ether. The ether extracts were dried with anhydrous sodium sulfate and the ether was evaporated. The residue was 20.5 g of light yellow, waxy solid. Repeated washing with benzene gave 8.5 g of white solid, mp 91–92°.

Method 2.—The acidified reaction mixture was first extracted with three 150-ml portions of benzene; the benzene extract was separately investigated. The aqueous residue was next extracted with ether. The ether extract was dried with sodium sulfate and the ether was removed *in vacuo* to give 13.9 g of light yellow solid. Washing with benzene left 8.5 g of white crystals, mp 91–92° (48.2% of theoretical for 2-hydroxy-2-cyano-2-phenylacetamide); recrystallization from ether–petroleum ether (bp 30–60°) (1:1) gave mp 91.5–93°. The infrared spectrum was identical with that of the product isolated by method 1, and with that published[15] for 2-cyano-2-hydroxy-2-phenylacetamide. The nmr spectrum (measured in acetone-d_6 and D_2O with TMS as an internal standard) showed a multiplet at δ = 7.4–7.8 ppm (five aromatic H) and a singlet at δ = 4.0 ppm (three exchangeable H).

Anal. Calcd for $C_9H_8N_2O_2$: C, 70.57; H, 5.92. Found: C, 70.4; H, 5.9.

A mixture of benzoic acid, methyl benzoate, and II was recovered from the benzene solution. These products were separated on the basis of solubility in aqueous sodium bicarbonate and sodium hydroxide. Benzoic acid and unreacted II were each recrystallized from hot water and identified by melting point and infrared spectra. Methyl benzoate was distilled under reduced pressure (24 mm) and identified by odor, infrared spectrum (identical with Sadtler Spectrum No. 1052)[16] and elemental analysis.

The following yields, calculated for the purified products, are minimum yields because of separation difficulties: 2-hydroxy-2-cyano-2-phenylacetamide, 8.5 g (48.3%); benzoic acid, 2.3 g (18.8%); methyl benzoate, 0.5 g (3.6%); unreacted II 3.0 g (15.8%).

2-Acetoxy-2-cyano-2-phenylacetamide (IV).—The cyanohydrin of 2-phenylglyoxylamide was prepared by reaction with potassium cyanide, using the reaction conditions described for the II–cyanide reaction. Acetylation of the cyanohydrin with acetic anhydride and pyridine gave IV in good yield as white crystals (from benzene), mp 163–164°. The structure was confirmed by infrared and nmr spectra.

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.62. Found: C, 60.06; H, 4.6.

Catalysis of Decomposition of II by Cyanide.—Experiments were performed with 4×10^{-2} *M* solutions of II in borate buffer (2.6×10^{-2} *M* tetraborate, adjusted to pH 9.4 with potassium hydroxide). Potassium cyanide concentrations were 4×10^{-2} *M*, 4×10^{-3} *M*, 4×10^{-4} *M*, and zero. The solutions were kept in glass-stoppered flasks in a 50° bath. Samples were removed at timed intervals for the measurement of the absorption at 405 mμ, using a Beckman DK-2A spectrophotometer. Experimental data are illustrated in Figure 1. A linear relationship was demonstrated between concentration of II (up to at least 10^{-2} *M*) and absorbance.

Inhibition of the II–Cyanide Reaction by 2-Phenylglyoxylamide.—After 150 min at 50°, a solution 4×10^{-2} *M* in II and 4×10^{-4} *M* in potassium cyanide was made 4×10^{-2} *M* in benzoylformamide. The disappearance of the 405-mμ absorbance was followed concurrently for the solutions with and without 2-phenylglyoxylamide. At these relative concentrations, the decomposition of II was almost completely halted.

In another experiment 2-phenylglyoxylamide was added to a solution of II and potassium cyanide to give a solution 4×10^{-2} *M* in each of the three reagents. The 2-phenylglyoxylamide was added at the beginning of the experiment. With equivalent amounts of II, potassium cyanide, and benzoylformamide the rate of decomposition of II was only slightly decreased (Figure 1, curves D, E).

Registry No.—II, 6797-44-0; III, 7616-87-7; IV, 7616-88-8.

Acknowledgment.—The authors thank Mr. Harold Klapper, Physical Chemistry Department, for the determination and interpretation of nmr spectra, and Frederick Baldauf, Donald Behringer, and Robert Moll for their cooperation in providing useful information. Elemental analyses were performed by the Analytical Research Department, Edgewood Arsenal.

(14) The decomposition of II was followed spectrophotometrically by the decrease in the absorbance at 405 mμ. This is a shoulder in the absorption spectrum of II for which a linear relationship between optical density and concentration, in the range under study, was demonstrated.

(15) A. Nenz, L. Marangoni, E. Gallinella, and A. Iliceto, *Chem. Ind.* (Milan), **46**, 509 (1964).

(16) Published by Sadtler Research Laboratories, Philadelphia, Pa.

Organoboron Compounds. XX. Trineopentylborane from the Neopentyl Grignard Reagent[1]

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Trineopentylborane, $[(CH_3)_3CCH_2]_3B$, previously unknown, is of considerable interest in mechanistic studies of organoboron chemistry because it is the simplest trialkylborane which is sterically crowded and restrained, cannot be made by hydroboration, and cannot participate in any reaction where direct elimination of olefin is mechanistically involved.[1] Thus the facile formation of intermediate BH species *via* elimination is not expected in trineopentylborane reactions. Furthermore, since the reaction of *t*-

(1) Previous paper: F. M. Rossi, P. A. McCusker, and G. F. Hennion, *J. Org. Chem.*, **32**, 450 (1967).

(2) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is Atomic Energy Commission Document COO-38-520.