

olefin by one carbon atom only is based on the decomposition of Zeise's salt to produce acetaldehyde, but no symmetrically substituted ethanes.¹¹ The mechanism of decomposition for a symmetrically coordinated olefin might well cause the formation of unsymmetrical products if the reaction involves attack on one carbon.

Similar resonance structures could be written for an end-on association between the olefin and the platinum, but the number of resonance structures would be smaller.

(11) J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

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α -(N-Alkylamino)-nitriles

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RECEIVED MAY 7, 1953

The preparation of α -N-substituted aminonitriles is common in the literature.¹ No extensive study of the α -N-monoalkylaminonitriles has been made, nor have preparative methods been described which involve the use of anhydrous hydrogen cyanide or those cyanhydrins which are now commercially available. Methods which utilize these common reagents have now been studied and a number of new α -N-alkylaminonitriles have been prepared. In addition physical data, which are often lacking on previous preparations of members of this series, have been obtained.

or their equivalent combinations, usually in equimolar amounts. Thus, anhydrous hydrogen cyanide may be added as a liquid to the imine or trimer formed by the combination of amine and carbonyl compound. The addition of the amine to commercially available 50 or 70% aqueous glycolonitrile, lactonitrile or acetone cyanohydrin is a convenient and satisfactory alternative.² Since the reactions are exothermic, temperatures are held below about 40°. Catalysts are not required, since the amine will promote cyanohydrin formation, if this is necessary to the selected route.

The expected side-reaction of bis-cyanoalkylation is a minor one, particularly as the molecular weight of any component increases, and is of no consequence when a ketone reactant is involved. This is probably because of the much reduced basicity which obtains when one cyanoalkyl group is introduced into the amine, so that the product does not compete successfully with the more basic starting amine for the other reactants.

Lower yields in the accompanying table mainly reflect either difficulty of isolation or some decomposition on distillation at higher temperatures. The products are stable to storage, particularly at refrigerator temperatures, although some darkening may occur due to the formation of hydrogen cyanide polymers.

Experimental

The two examples illustrate the procedures used. Analysis for nitrogen was by the Kjeldahl method. Neutralization equivalents were measured by titration in acetic acid with standard perchloric acid-acetic acid.³

α -N-Methylaminoisobutyronitrile.—Methylamine was bubbled rapidly into acetone cyanohydrin (722 g., 8.5

α -(N-ALKYLAMINO)-NITRILES

Compound	Empirical formula	Yield, %	°C.	B.p.		n_D^{20}	d_{4}^{25}	Nitrogen, %		Neut. equiv.	
				Mm.	n_D^{20}			Calcd.	Found	Calcd.	Found
CH ₃ NHCH ₂ CN	C ₃ H ₆ N ₂	58	65-67 ^a	23	1.4184	0.9171	40.0	39.5	70	72	
CH ₂ =CHCH ₂ NHCH ₂ CN	C ₆ H ₈ N ₂	67	74-76 ^b	12	1.4484	.9188	29.1	28.9	96	96	
<i>n</i> -C ₃ H ₇ NHCH ₂ CN	C ₆ H ₁₀ N ₂	40	65	15	1.4289	.8858	28.5	28.0	98	99	
CH ₃ NHCH(C ₂ H ₅)CN	C ₆ H ₁₀ N ₂	91	66	15	1.4258	.8860	28.5	28.0	98	98	
CH ₃ NHC(CH ₃) ₂ CN	C ₅ H ₁₀ N ₂	93	60 ^c	24	1.4174	.8600	28.5	28.1	98	99	
<i>n</i> -C ₄ H ₉ NHCH ₂ CN	C ₈ H ₁₂ N ₂	70	105-110 ^d	29	1.4311	.8818	25.0	25.1	112	114	
(CH ₃) ₃ CNHCCH ₂ CN	C ₆ H ₁₂ N ₂	71	90-99 ^e	22	1.4294	.8756	25.0	24.8	112	113	
CH ₃ NHC(CH ₃)(C ₂ H ₅)CN	C ₆ H ₁₂ N ₂	68	75-77 ^f	28	1.4270	.8698	25.0	24.6	112	112	
CH ₂ =CHCH ₂ NHC(CH ₃) ₂ CN	C ₇ H ₁₂ N ₂	77	80-82	30	1.4393	.8766	22.6	22.3	124	125	
<i>n</i> -C ₄ H ₉ NHCH(CH ₃)CN	C ₇ H ₁₄ N ₂	90	95-97	31	1.4286	.8589	22.0	21.7	126	128	
Cyclohexyl NHCH ₂ CN	C ₈ H ₁₄ N ₂	66	77-82 ^{d,g}	1	1.4735	.9657	20.2	20.2	138	140	
<i>n</i> -C ₄ H ₉ NHC(CH ₃) ₂ CN	C ₈ H ₁₆ N ₂	87	86-88	28	1.4262	.8483	20.0	19.5	140	141	
Cyclohexyl NHC(CH ₃) ₂ CN	C ₁₀ H ₁₈ N ₂	77	M.p. 56-57 ^h	^h			16.9	16.8	166	166	
<i>n</i> -C ₈ H ₁₇ NHCH ₂ CN	C ₁₀ H ₂₀ N ₂	66	120-125	2	1.4425	.8611	16.7	16.2	168	170	
C ₄ H ₉ CH(C ₂ H ₅)CH ₂ NHCH ₂ CN	C ₁₀ H ₂₀ N ₂	75	99-101	1.5	1.4448	.8667	16.7	16.0	168	168	
1,1,3,3-(CH ₃) ₄ C ₄ H ₈ NHCH ₂ CN	C ₁₀ H ₂₀ N ₂	91	99-102 ^e	5	1.4509	.8808	16.7	16.4	168	167	
3,5,5-(CH ₃) ₃ C ₆ H ₁₀ NHCH ₂ CN	C ₁₁ H ₂₂ N ₂	74	92	0.6	1.4453	.8561	15.4	15.5	182	182	

^a A. H. Cook and S. F. Cox, *J. Chem. Soc.*, 2334 (1949), b.p. 65° at 20 mm. ^b H. Z. Lecher and R. S. Long, Can. Pat. 477,792, b.p. 60° at 15 mm. ^c N. J. Leonard and E. Barthel, *THIS JOURNAL*, 72, 3632 (1950), b.p. 54° at 18 mm., n_D^{20} 1.4176. ^d Mentioned but not described by N. C. Throdahl and M. W. Harman, *Ind. Eng. Chem.*, 43, 421 (1951); Monsanto Chemical Co., Brit. pat. 640,158, b.p. 77-80° at 6 mm. ^e L. S. Luskin, *et al.*, paper in preparation. ^f Ref. b, b.p. 66-68° at 17 mm., n_D^{20} 1.4282. ^g R. A. Jeffreys and E. B. Knott, *J. Chem. Soc.*, 4632 (1952), b.p. 74-76° at 1 mm., m.p. 18°. We found m.p. 24°. ^h A. D. Ainley and W. A. Sexton, *Biochem. J.*, 43, 468 (1948), m.p. 52-53. We recrystallized the crude solid product from Skellysolve A.

The compounds which are listed in the accompanying table, have been prepared by the reaction of amines, carbonyl compounds and hydrogen cyanide,

(1) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," A.C.S. Monograph Series No. 105, Reinhold Publ. Corp., New York, N. Y., 1947, pp. 198-215.

moles) which was stirred and cooled to maintain the temperature between 23 and 32°. In 75 minutes, the absorp-

(2) Glycolonitrile and acetone cyanohydrin are commercial products of the Rohm and Haas Co. Lactonitrile was obtained from the American Cyanamid Co.

(3) P. C. Markunas and J. A. Riddick, *Anal. Chem.*, 23, 337 (1951).

tion was 380 g. (12.3 moles). The solution was refrigerated overnight. Distillation at reduced pressure through a column 45 cm. long packed with Berl saddles gave 675 g. (81%) of a colorless liquid, collected at 66–68° (50 mm.). The foreruns were refluxed under a water separator with 200 ml. of benzene to give 159 ml. of water. By distillation, an additional 96 g. (11.5%) of product was obtained.

α -Allylaminoacetonitrile.—Commercial formalin (249 g., 36.2%, 3 moles) was added to aqueous allylamine (419 g., 40%, 3 moles) at 15–20° in 30 minutes. After stirring one hour, hydrogen cyanide (81 g., 3 moles) was added at 20°. The mixture was stirred for three hours, then saturated with salt. The oil layer was separated and the brine layer was extracted with benzene. The combined extract and oil were distilled to give 147 g. of a faintly yellow liquid, b.p. 97–108° (30 mm.), n_D^{20} 1.4503, d_4^{20} 0.9221. Further distillation gave 35 g. of somewhat less pure material.

Acknowledgments.—Robert W. Faulkner, Jr., and Rita Cerruti assisted in much of the experimental work. Individual experiments were provided by Martin J. Culver, Gerard E. Gantert and John O. Van Hook. Analyses were performed under the direction of Thomas Callan.

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The Reaction of N-Bromosuccinimide with 2-Heptene

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RECEIVED MARCH 6, 1953

In their classic paper on allylic bromination by the use of N-bromosuccinimide (NBS) Ziegler, *et al.*,¹ made the statement that an allylic methylene group undergoes substitution much more readily than an allylic methyl group. The evidence for this statement was that 2-methyl-2-hexene reacted with NBS much more rapidly than did 2-methyl-2-butene, and that 1,1-diphenyl-1-butene reacted much more rapidly than 1,1-diphenyl-1-propene. The alkenes were prepared by dehydration of tertiary alcohols, and no structure work was carried out with the bromides resulting from the NBS reactions. The above conclusion on the relative reactivity of allylic methylene and allylic methyl groups may not be justified. The observed results may be due to individual differences in the various compounds. That this could be the case is suggested by the finding of Bateman and Cunneen² that 1-octene reacted with NBS much more readily than did 1,5-hexadiene. Also, in the present work it was found that the reaction of NBS and 2-heptene was unsuccessful in the absence of benzoyl peroxide.

Instances in the literature of the reaction of NBS with compounds containing both allylic methylene and methyl groups and where structure work was carried out on the reaction product are rather few. Buu-Hoi, *et al.*,³ have compared the monobromopinene from the pinene-NBS reaction with the bromide resulting from the reaction of 1-myrtanol with phosphorus tribromide. The physical constants of the two compounds were quite similar and the ultraviolet spectra were similar, but not identical.

(1) K. Ziegler, A. Spaeth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

(2) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 941 (1950).

(3) Buu-Hoi, Hiong-Ki-Wei, J. Lecomte and R. Royer, *Bull. soc. chim. France*, **148** (1948).

They concluded the monobromopinene had the structure of myrtenyl bromide. Mousseron, *et al.*,⁴ have reported on the reaction of some methylcyclohexenes and methylcyclopentenes with NBS. The products of these reactions on oxidation by a method used by Courtot and Pierron⁵ gave ketones, and hence it was concluded that bromination had occurred in the ring. Bateman, *et al.*,⁶ have found 2,6-dimethyl-2,6-octadiene to give a complex mixture of isomeric bromides.

The work of Buchman and Howton⁷ and of Bateman and Cunneen² indicates that one cannot neglect the possibility of allylic rearrangement in NBS reactions. There is disagreement between Bateman⁸ and Karrer⁹ as to the occurrence of an allylic rearrangement in the reaction of 1,5-hexadiene with NBS.

4-Bromo-2-heptene was desired for some synthetic work, and the synthesis of this compound by the reaction of 2-heptene with NBS was proposed. This reaction presented a clear case to test the relative reactivity of allylic methylene and methyl groups. The product of the reaction would also indicate whether or not allylic rearrangement had occurred during the reaction. 2-Heptene was prepared by a Boord-type synthesis, and this was reacted with NBS in the presence of benzoyl peroxide. The product was distilled *in vacuo* and had an amazingly narrow boiling range (0.5°). Analysis of the material showed it to be monobromoheptene. The infrared curves of the 2-heptene and monobromoheptene were quite similar, and in neither curve was there any indication of terminal carbon-carbon unsaturation. 1-Bromo-2-heptene has been prepared by Young, *et al.*,¹⁰ and found to have n_D^{26} 1.4745. Our bromoheptene had n_D^{26} 1.4712. Young, *et al.*,¹¹ have shown that allylic halides can be ozonized without rearrangement, and this method of structure proof was chosen for the bromoheptene. The bromoheptene was carefully ozonized and the ozonide decomposed with hydrogen peroxide. Acetic acid was isolated in nearly quantitative yield from the decomposition mixture, and α -bromovaleric acid was also isolated. These data would indicate that in the reaction of 2-heptene with NBS the allylic methylene group does react in preference to the allylic methyl group, that there is no significant allylic rearrangement and that the product is 4-bromo-2-heptene.

Experimental

Chemicals.—For exploratory experiments 2-heptene (pure grade, Phillips Petroleum Company, Bartlesville, Oklahoma) was used. The material was distilled through a Fenske column (18 theoretical plates) and practically all of the

(4) M. Mousseron, F. Winternitz and R. Jacquin, *Compt. rend.*, **224**, 1062 (1947).

(5) C. Courtot and J. Pierron, *Bull. soc. chim. France*, [4] **45**, 286 (1929).

(6) L. Bateman, J. I. Cunneen and H. P. Koch, *J. Chem. Soc.*, 3045 (1950).

(7) E. R. Buchman and D. R. Howton, *THIS JOURNAL*, **70**, 2517 (1948).

(8) L. Bateman, J. I. Cunneen, J. M. Fabran and H. P. Koch, *J. Chem. Soc.*, 936 (1950).

(9) P. Karrer and S. Perl, *Helv. Chim. Acta*, **33**, 36 (1950).

(10) W. G. Young, L. Richards and J. Azorlosa, *THIS JOURNAL*, **61**, 3070 (1939).

(11) W. G. Young, A. C. McKinnis, J. D. Webb and J. D. Roberts, *ibid.*, **68**, 293 (1946).