[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Synthesis and Some Derivatives of 3-Butenenitrile

JOHN W. LYNN, RICHARD L. ROBERTS, AND JOHN R. KILSHEIMER

Received May 11, 1961

Catalytic liquid and vapor phase processes for the preparation of 3-butenenitrile from allyl chloride and hydrogen cyanide are described. Various sulfides were prepared by the free radical-catalyzed addition of thiols to 3-butenenitrile, 3-butenoic acid and esters, and were oxidized to the respective sulfones. Relative rates of isomerization of 3-butenenitrile to 2-butenenitrile using various amine catalysts were determined.

The preparation of 3-butenenitrile (allyl cyanide) by the metathetical reaction of allyl bromide with cuprous cyanide was reported by Bruylants[1] in 1922. In general, this method has been followed by subsequent workers,[2,3] though in some cases allyl chloride[4,5] was employed. We have found that the cuprous chloride-catalyzed aqueous reaction of hydrogen cyanide with allylic halides, such as 1,4-dichloro-2-butene[6] and 1,6-dichloro-5-ethoxy-2-hexene[7] in the presence of calcium carbonate, provides a facile method for the preparation of 3-butenenitrile and 3-methyl-3-butenenitrile in high yield (*ca.* 90%) and purity from allyl chloride and methallyl chloride, respectively.

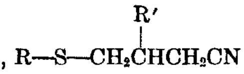
$$2CH_2{=}CHCH_2Cl + 2HCN + CaCO_3 \longrightarrow 2CH_2{=}CHCH_2CN + CaCl_2 + CO_2 + H_2O$$

We have also employed a vapor phase process which does not require the use of a hydrogen chloride acceptor. By this method a mixture of allyl chloride and hydrogen cyanide is passed over a copper–aluminum oxide catalyst at about 150° to give 3-butenenitrile (34% yield), 3-chlorobutyronitrile (21% yield) and hydrogen chloride.

The isomerization of 3-butenenitrile to conjugated 2-butenenitrile (crotononitrile) by bases[3,8,9] is well known. We have made a brief study of the relative rates of isomerization catalyzed by various amines. These data (Fig. 1) indicate triethylamine to be very effective for this transformation giving an equilibrium mixture of 98% 2-butenenitrile and 3% 3-butenenitrile after five hours at 120°. Selective bromination of nonconjugated 3-butenenitrile was used to determine analytically the relative concentration of 2- and 3-butenenitriles.

Hydrolysis of 3-butenenitrile to 3-butenoic acid by mineral acid has been reported.[5,10] We have modified the described method slightly to take advantage of the ease of conversion of nitriles to amides in concentrated acid and ease of hydrolysis of amides to acids in dilute acid.[11,12] Thus, ex-

TABLE I



ALKYL 3-CYANOALKYL SULFIDES, $R{-}S{-}CH_2\overset{\overset{R'}{|}}{C}HCH_2CN$

R	R′	Formula	B.P.	Mm.	n_D^{30}	d_{20}^{20}	Yield, %	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
C_2H_5	H	$C_6H_{11}NS$	69	2.0	1.4737	0.9718	87	55.76	8.58	10.84	56.14	8.43	10.96
i-C_3H_7	H	$C_7H_{13}NS$	73	1.2	1.4689	0.9479	91	58.68	9.15	9.78	58.98	9.18	10.03
n-C_4H_9	H	$C_8H_{15}NS$	94	1.5	1.4708	0.9423	69	61.09	9.61	8.91	60.91	9.04	8.89
i-C_4H_9	H	$C_8H_{15}NS$	101	3.5	1.4175	0.9475	77	61.09	9.61	8.91	61.47	9.33	8.98
t-C_4H_9	H	$C_8H_{15}NS$	83	2.0	1.4677	0.9351	44	61.09	9.61	8.91	61.32	9.43	9.08
n-C_5H_{11}	H	$C_9H_{17}NS$	100–108	1.5	1.4700	0.9326	66	63.10	10.00	8.18	63.28	9.70	8.20
C_6H_5	H	$C_{10}H_{11}NS$	133	2.0	1.5640	1.0919	70	67.75	6.26	7.90	68.33	5.91	7.42
$C_6H_5CH_2$	H	$C_{11}H_{13}NS$	145	2.0	1.5577	1.0715	58	69.06	6.85	7.32	69.43	6.78	7.21
n-$C_{12}H_{25}$	H	$C_{16}H_{31}NS$	165–175	1.0	1.4695	0.8965	87	71.31	11.60	5.20	69.86	11.25	5.20
$C_2H_5O_2CCH_2$[a]	H	$C_8H_{13}NO_2S$	148	6.0	1.4770	1.1030	[b]	51.31	7.00	7.48	51.26	6.70	7.09
$HOCH_2CH_2$	H	$C_6H_{11}NOS$	140	2.0	1.5034	1.100	37	49.62	7.64	9.65	48.88	7.44	9.27
$HOCH_2CH_2$	CH_3	$C_7H_{13}NOS$	146	2.0	1.4972	1.0735	85	52.79	8.23	8.80	52.21	8.20	8.80
n-C_3H_7	CH_3	$C_8H_{15}NS$	73	0.5	1.4665	0.9354	90	61.09	9.61	8.94	60.96	9.56	8.45

[a] Prepared as free acid, but isolated as ester. [b] Yield to residue product acid, 87.2%; to distilled ester, 42.7% (dec.).

---

[1] P. Bruylants, *Bull. soc. chim. Belges*, **31**, 175 (1922).

[2] J. V. Supniewski and P. L. Salzberg, *Org. Syntheses*, **8**, 4 (1928).

[3] R. A. Letch and R. P. Linstead, *J. Chem. Soc.*, 443 (1932).

[4] R. Breckpot, *Bull. soc. chim. Belges*, **39**, 462 (1930).

[5] E. Rietz, *Org. Syntheses*, **24**, 97 (1944).

[6] M. W. Farlow, U. S. Patent **2,518,608** (E. I. du Pont Co.).

[7] G. E. Tabet, U. S. Patent **2,570,886** (E. I. du Pont Co.).

[8] J. E. Mahan, U. S. Patent **2,384,630** (Phillips Petroleum Co.).

[9] P. Bruylants, *Bull. soc. chim. Belges*, **33**, 331 (1924).

[10] R. P. Linstead, E. G. Noble, and E. J. Boorman, *J. Chem. Soc.*, 557 (1933).

[11] J. D. McLean, B. S. Rabinowitch, and C. A. Winkler, *Can. J. Res.*, **20B**, 168 (1942).

[12] V. K. Krieble and C. I. Noll, *J. Am. Chem. Soc.*, **61**, 560 (1939).

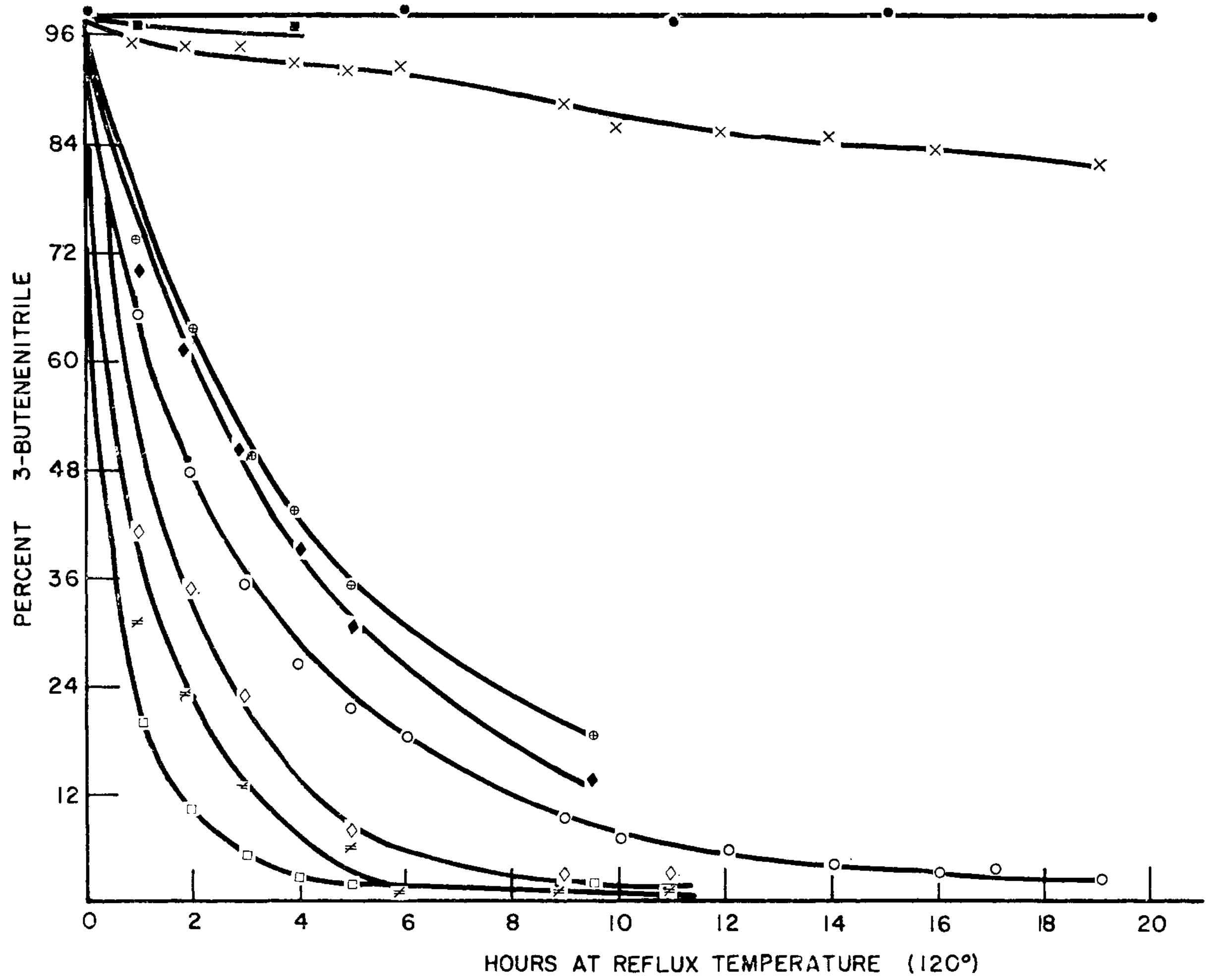


Fig. 1. Isomerization of 3-butenenitrile to 2-butenenitrile

Catalysts 1% by weight

○ Tributylamine
◆ Tripropylamine
□ Triethylamine
× γ-Picoline
● Pyridine
⊕ Morpholine
■ Ammonia
≠ *n*-Butylamine
◇ Diisopropylamine

cellent results were obtained by employing concentrated hydrochloric acid at 50° for a short period to convert nitrile to amide, then diluting with water and heating at 100° for another short period. We have found this technique to give improved hydrolyses of many other nitriles as well.

The "abnormal" addition of thiols to olefins was first reported by Posner,[13] and Kjaer, more recently, has reported[14] the preparation of 5-thiahexanonitrile by the peroxide and ultraviolet light-catalyzed addition of methanethiol to 3-butenenitrile. We have prepared a number of alkyl 3-cyanopropyl sulfides by this method (Table I) as well as several alkyl 3-carboxyalkyl sulfides (Table II).

$$RSH + CH_2{=}CHCH_2CN \xrightarrow{h\nu}$$
$$RSCH_2CH_2CH_2CN \xrightarrow{CH_3CO_3H} RSO_2CH_2CH_2CH_2CN$$

A number of the sulfides were oxidized in high yield to the sulfones[15] (Table III) using peracetic acid in ethyl acetate.[16]

EXPERIMENTAL[17]

3-Butenenitrile. Liquid phase process. A mixture of 275 g. (2.75 moles) of calcium carbonate, 8.5 g. (0.5% of total charge) of cupric sulfate, and 850 ml. of water was warmed to 40° and 421 g. (5.5 moles) of allyl chloride was added rapidly with stirring. While maintaining the mixture at 40° by external cooling, 137 g. (5.0 moles) of liquid hydrogen

---

[13] T. Posner, *Ber.*, **38**, 646 (1904).

[14] A. Kjaer and J. Conti, *Acta Chem. Scand.*, **8**, 295 (1954).

[15] V. Franzen, *Chem. Ber.*, **87**, 1478 (1954).

[16] B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

[17] All temperatures are uncorrected.

TABLE II

ALKYL 3-CARBOXYALKYL SULFIDES, $R—S—CH_2CH_2CH_2CO_2R'$

R	R′	Formula	B.P.	Mm.	n_D^{30}	d_{20}^{20}	Yield, %	Calcd., % C	Calcd., % H	Found, % C	Found, % H	Mol. Wt. Calcd.	Mol. Wt. Found
i-C_3H_7	H	$C_7H_{14}O_2S$	112	1.2	1.4742	1.0407	83	51.82	8.70	51.20	8.17	162	158[a]
n-$C_{12}H_{25}$	H	$C_{16}H_{32}O_2S$	m.p. 56–57		—	—	97	66.61	11.18	66.35	10.76	288	293[a]
n-$C_{12}H_{25}$	C_2H_5	$C_{18}H_{36}O_2S$	176–183	0.5	1.4611	0.9201	86	68.30	11.46	68.98	11.22	316	319[b]
i-C_3H_7	$—CH_2CH—C_2H_5$ | C_4H_9	$C_{15}H_{29}O_2S$	135	1.0	1.4581	0.9288	79	65.88	10.69	66.02	10.81	273	273[b]

[a] By titration with 0.1N sodium hydroxide. [b] By ebulliometry.

TABLE III

ALKYL 3-CYANOALKYL SULFONES, $R—SO_2—CH_2\overset{\overset{R'}{|}}{C}HCH_2CN$

R	R′	Formula	Yield, %	M.P.	n_D^{30}	Mol. Wt. Calcd.	Mol. Wt. Found	Calcd., % C	Calcd., % H	Calcd., % N	Calcd., % S	Found, % C	Found, % H	Found, % N	Found, % S
C_2H_5	H	$C_6H_{11}NO_2S$	98					44.7	6.8	8.7	19.8	44.72	6.67	8.73	19.2
i-C_3H_7	H	$C_7H_{13}NO_2S$	99	50							18.30				17.74
i-C_4H_9	H	$C_3H_{13}NO_2S$	99		1.4730	189	191	50.76	7.99	7.40		50.38	7.80	7.03	
t-C_4H_9	H	$C_8H_{13}NO_2S$	93								16.90				16.48
C_6H_5	H	$C_{10}H_{11}NO_2S$	96					57.4	5.26	6.7	15.3	57.65	5.27	6.66	14.9
$C_{12}H_{25}$	H	$C_{16}H_{31}NO_2S$	74	76		302	306	63.74	10.36	4.65		62.9	10.27	5.12	
$HOCH_2CH_2$	H	$C_6H_{11}NO_3S$	99		1.4800					7.9				7.89	
$HOCH_2CH_2$	CH_3	$C_7H_{13}NO_3S$	99		1.4858			44.40	6.8			44.75	6.8		
			ALKYL 3-CARBOXYALKYL SULFONES, $R—SO_2—CH_2CH_2CH_2CO_2R'$												
i-C_3H_7	H	$C_7H_{14}O_4S$	91	61–66							16.48				16.71
i-C_3H_7	$C_2H_5CHCH_2—$ | C_4H_9	$C_{15}H_{30}O_4S$	99		1.4602	305	297	58.98	9.57			57.29	9.66		

cyanide[18] was added during a 1-hr. period. After holding for an additional 4 hr. at 40°, the mixture was cooled and the layers separated. Distillation of the oil layer gave 293 g., 87.5% yield, of 3-butenenitrile (b.p. 115/atm., lit.[19] b.p. 118.6°/763 mm., n_D^{30} 1.4015, d_{20}^{20} 0.8337, 98% purity by bromine titration).

3-Butenenitrile. Vapor phase process. A mixture of 306 g. (4 moles) of allyl chloride and 84 g. (3 moles) of 97% hydrogen cyanide was vaporized at a rate of 65 ml. per hr. through a preheater held at 100° into a stainless steel tube (1.0 in. inside diameter and 70 cm. in length) containing 350 cc. of 4 × 8 mesh copper aluminum oxide catalyst held at 150°. The reaction product was distilled to give unchanged starting materials and 69 g., a 34.5% yield based on hydrogen cyanide, of allyl cyanide (b.p. 115°, n_D^{30} 1.4022). The efficiencies were 34.5% and 42.5% based on recovered hydrogen cyanide and allyl chloride, respectively. Mass spectrographic analysis of the high boilers indicated a contained yield of 21% of 3-chlorobutyronitrile was also obtained.

3-Methyl-3-butenenitrile. A mixture of 1006 g. (11 moles) of methallyl chloride and 290 g. (10 moles) of 91% hydrogen cyanide was added during a 1.5-hr. period to a stirred mixture of 45 g. of cupric sulfate, 525 g. (5.25 moles) of calcium carbonate and 2500 ml. of water while maintaining a temperature of 30–40° by external cooling. After an additional 5 hr. at 40°, the mixture was filtered and extracted with diisopropyl ether. Distillation of the extract gave 764 g., 93% yield, of 3-methyl-3-butenenitrile (b.p. 76.5°/100 mm., lit.[20] b.p. 136.2–136.4°/atm., n_D^{30} 1.4143, d_4^{25} 0.8300).

2-Butenenitrile. 3-Butenenitrile (150 g.) was heated to reflux at about 120° with 1% by weight of basic catalyst and samples were removed periodically and titrated with 0.1*N* bromine/sodium bromide reagent in aqueous acidic methanol. The titration accurately measures unchanged 3-butenenitrile since the conjugated 2-butenenitrile does not add bromine under the conditions of analysis. Distillation of the final reaction mixtures gave *cis*- and *trans*-2-butenenitrile (b.p. 109–117°, n_D^{30} 1.4142–1.4168) containing about 2% of unchanged 3-butenenitrile. (See Fig. 1.)

3-Butenoic acid. To 134 g. (2 moles) of 3-butenenitrile held at 50° there was added with stirring 386 g. (4 moles) of concd. hydrochloric acid during a 1-hr. period. Heating was continued for 1 hr. at 50° before adding 500 ml. of water and heating at reflux for 1 hr. The cooled mixture was extracted with ether and the extract distilled to furnish some unchanged nitrile and the desired acid in 80% yield and 96% efficiency (b.p. 72–77°/20 mm., lit.[5] b.p. 69–70°/12 mm., n_D^{30} 1.4204; d_{20}^{20} 1.0087, 2.8% crotonic acid by infrared analysis).

Esters of 3-butenoic acid were prepared by the conventional acid-catalyzed azeotropic water removal method.

Addition of mercaptans to 3-butenenitrile. A mixture of 3-butenenitrile (2 moles) and a mercaptan (1 mole) was heated to about 70–100° in the presence of about 0.5% by weight of benzoyl peroxide and was irradiated by a General Electric Sunlamp for about 20–40 hr. Distillation of the reaction mixture gave the desired adducts plus unchanged starting materials. (See Table I) Absence of typical —CH_3 absorption at 7.3 μ[21] in the infrared spectrum indicated only terminal addition had occurred.

General procedure for oxidation of sulfides to sulfones. A mixture of sulfide (1 mole) and acetic acid (300 ml.) was stirred at 25° during the addition of a 20% solution of peracetic acid in ethyl acetate[16] (2.5 moles) over a 1-hr. period. Stirring at 25–27° was continued for an additional 3 hr., after which the mixture was either chilled and filtered to remove solid product or evaporated to yield a residual oil.

Acknowledgment. The authors are grateful to Messrs. C. M. Lovell and H. R. Harless for spectrographic data and to Messrs. G. R. Arnold and D. F. Blackwood for technical assistance.

RESEARCH DEPARTMENT
UNION CARBIDE CHEMICALS CO.
SOUTH CHARLESTON, W. VA.

---

(18) Liquid hydrogen cyanide was stored in glass, citrate-type pressure bottles which were chilled to 0° or below prior to opening. It was fed to the reaction vessel from brine-cooled feed tanks at 0° to −10°. All reactions, material transfers, and product layer distillations were conducted in an adequate fume hood, vented to the outside air. Aqueous wastes containing hydrogen cyanide were subjected to alkaline chlorination to oxidize the cyanides first to less toxic cyanates, then to harmless nitrogen and carbon dioxide.

(19) A. Christiaen, *Bull. soc. chim. Belges*, **34**, 147 (1925).

(20) M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115–120 (1941).

(21) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, 1958, p. 13.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Some Syntheses of 1,2,4-Butanetricarboxylic Acid[1]

JOHN W. LYNN AND RICHARD L. ROBERTS

Received April 5, 1961

Several practical methods are described for the preparation of 1,2,4-butanetricarboxylic acid by nitric acid oxidation of 3-cyclohexenecarboxaldehyde and the related acid, nitrile, and ester.

The extensive use of polybasic acids in the manufacture of polymers, plasticizers, and lubricants has fostered considerable study of commercially feasible methods for their synthesis. Our studies are concerned with the oxidation of several 3-cyclohexene derivatives derived from Diels-Alder condensations[2] of butadiene with dienophiles such as acrolein, acrylic acid and acrylonitrile to give 1,2,4-butanetricarboxylic acid (V). Subsequent papers[3] describe the use of this tribasic acid in various syntheses.

The synthesis of 1,2,4-butanetricarboxylic acid

---

(1) Presented at The Gordon Research Conference, Organic Reactions and Processes, July 19, 1960.

(2) O. Diels and K. Alder, *Ann.*, **460**, 105 (1928).

(3) *J. Org. Chem.*, *in press.*