was heated under a 100-cm. Vigreux column at reflux temperature until acetone stopped distilling. The excess alcohol was removed by distillation and the residue poured into a mixture of 2.5 kg. of ice and 800 ml. of concentrated hydrochloric acid. The resultant slurry was warmed to 50° and extracted with chloroform. After washing with water, sodium carbonate and hydrochloric acid solutions, the extract was distilled to give 150 g. of product boiling at 107–135° (13 mm.). The distillate solidified and was recrystallized from dilute ethanol to give 159 g. (52%) of the desired lactone, m.p. 51–52°. Hill and Cornelison[4] report m.p. 50–51°.

An attempt to prepare this compound from isopropyl mucochlorate using a smaller excess of aluminum isopropoxide gave only a 16% yield of lactone.

4,5-Dichloro-3-pyridazone (II, R = H).—Solutions of 126 g. (0.75 mole) of mucochloric acid, 84 g. (0.75 mole) of semicarbazide hydrochloride and 52 g. (0.375 mole) of potassium carbonate in 50% ethanol were mixed. The resultant precipitate was filtered after three hours and the product, 164 g. (89% yield), was recrystallized from ethanol. The semicarbazone melted at 183° with decomposition.

Anal. Calcd. for $C_5H_4O_3N_3Cl_2$: N, 18.74; Cl, 32.2. Found: N, 18.49; Cl, 32.13.

Eighty-four grams of this material was added slowly to 300 ml. of glacial acetic acid at 100–110° with stirring to facilitate evolution of carbon dioxide. The solution was diluted with water and cooled to give 42 g. (69% yield) of 4,5-dichloro-3-pyridazone, m.p. 202°.

Anal. Calcd. for $C_4H_2ON_2Cl_2$: C, 29.3; H, 1.22; N, 17.08; Cl, 43.2. Found: C, 29.28; H, 1.24; N, 16.90; Cl, 43.17.

This method is analogous to that used for the corresponding dibromo derivative prepared by Bistrzycki.[8] An attempt to prepare the azine from two moles of mucochloric acid and one mole of hydrazine using an adaptation of the method described by Hatt for benzalazine[9] gave the above pyridazone in 92% yield.

4,5-Dichloro-2-phenyl-3-pyridazone (II, R = C_6H_5).—A solution of 126 g. of mucochloric acid and 40 g. of anhydrous

(8) A. Bistrzycki and C. Herbst, *Ber.*, **34**, 1014 (1901).

(9) H. H. Hatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 395.

sodium carbonate in 1 l. of cold water was mixed with a cold solution of 108 g. of phenylhydrazine hydrochloride in 1 l. of water. After 1 hour, the yellow solid which formed in quantitative yield was filtered and recrystallized from dilute ethanol. The phenylhydrazone melted at 124–125° (dec.).

Anal. Calcd. for $C_{10}H_8O_2N_2Cl_2$: C, 46.4; H, 3.09; N, 10.80. Found: C, 46.31; H, 2.93; N, 10.81.

Forty grams of mucochloric acid phenylhydrazone was dissolved in 300 cc. of glacial acetic acid and heated to boiling for 15 minutes. A small amount of water was then added to the hot solution. On cooling this deposited 34 g. (90% yield) of crystals of the nearly pure pyridazone. After recrystallization from 90% ethanol, the glistening white prisms melted at 163–164°.

Anal. Calcd. for $C_{10}H_6ON_2Cl_2$: C, 49.8; H, 2.49; N, 11.61. Found: C, 49.65; H, 2.55; N, 11.60.

α-Aryloxy-β-chloro-β-formylacrylic Acids.—To a solution of 31 g. (0.25 mole) of hydroquinone monomethyl ether and 30 g. (0.55 mole) of potassium hydroxide at 5° was added 42 g. (0.25 mole) of mucochloric acid. The solution was stirred and cooled by the addition of crushed ice. After standing at 5–15° for one hour, the solution was poured into a cold solution of 70 ml. of concentrated hydrochloric acid in 100 ml. of water. The oil which precipitated was washed with water and crystallized on standing. Recrystallization from a mixture of benzene and hexane gave 40 g. (62%) of β-chloro-β-formyl-α-(p-methoxyphenyl)-acrylic acid, m.p. 105°.

Anal. Calcd. for $C_{11}H_9O_5Cl$: C, 51.5; H, 3.53. Found: C, 51.41; H, 3.54.

By a similar method using p-chlorophenol there was obtained a 69% yield of β-chloro-α-(p-chlorophenyl)-β-formylacrylic acid, m.p. 55°.

Anal. Calcd. for $C_{10}H_6O_4Cl_2·H_2O$: C, 43.1; H, 2.89. Found: C, 43.17; H, 2.89.

In analogous fashion, β-naphthol was converted in 44% yield to β-chloro-β-formyl-α-(2-naphthoxy)-acrylic acid, m.p. 156–157°.

Anal. Calcd. for $C_{14}H_9O_4Cl$: C, 60.8; H, 3.28. Found: C, 61.04; H, 3.55.

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[CONTRIBUTION FROM THE WALKER LABORATORY, DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. IV. Propionitrile and Butadiene[1]

BY G. J. JANZ AND R. E. MYERS

In the presence of a chromium oxide catalyst at 420° and atmospheric pressure, propionitrile and butadiene react to form 2-ethylpyridine and aniline. Using a catalyst containing 4% Cr_2O_3, and 4 seconds reaction time, 34 mole per cent. of the nitrile converted is accounted for as a basic product, containing ethylpyridine and aniline in nearly equimolar ratio. The reactivity of propionitrile in the pyridinic synthesis is found to be the same order as that previously found for acetonitrile, hydrogen cyanide and benzonitrile.

This communication reports an investigation of the reactions of propionitrile and butadiene over a chromium oxide–aluminum oxide catalyst at atmospheric pressure in the temperature range of 400°. The reaction conditions were selected to gain results comparable with those reported for butadiene and organic nitriles in Parts I and II of this series.[2] The addition of propionitrile to butadiene at somewhat higher temperatures (600°) and in the homogeneous gas phase has been reported in a recent paper.[3] As well as ethylpyridine in small amounts, larger amounts of aniline were obtained under these reaction conditions. As a guide to the present investigation the thermodynamics for the formation of ethylpyridine and aniline from these reactants were considered. The free energy changes were calculated at 700° and 900°K., respectively (*i.e.*, approx. 400° and 600°C.), using conventional methods.[4] At 700°K., the free energy changes were −13 and −21 kcal./mole, and at 900°K., −6

(1) Abstracted in part from the thesis submitted by R. E. Myers in partial fulfillment of the requirements for the degree of Bachelor of Science (Chemical Engineering) at Rensselaer Polytechnic Institute, Troy, N. Y.

(2) G. J. Janz and P. J. Hawkins, *Nature*, **162**, 28 (1948); *J. Chem. Soc.*, 1479, 1485 (1949).

(3) C. S. Marvel and J. C. H. Hwa, *J. Org. Chem.*, **15**, 525 (1950).

(4) O. A. Hougen and K. M. Watson, "Chemical Process Principles," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948; J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947); J. G. M. Bremner and G. D. Thomas, *Trans. Faraday Soc.*, **43**, 779 (1947).

<div align="center">TABLE I</div>

MATERIAL BALANCE, CONVERSIONS AND YIELDS FOR THE REACTION OF PROPIONITRILE AND BUTADIENE AT 420° OVER A
4% Cr_2O_3–96% Al_2O_3 CATALYST AT 4 SECONDS

Reactant	Total input, mole	Un-reacted	Ethyl-pyridine	Aniline	Ammonia	Ethyl-benzene	Polymers	Volatiles	Catalysts deposit	Total
			Recovery, mole per cent. of input							
Propionitrile	0.935	92.7	1.2	1.3	1.9	...	0.5	1.9	0.5	100
Butadiene	0.937	77.9	1.2	1.3	..	1.4	3.0	0.7	14.5	100
			Yields, mole per cent. calcd. on conversion							
Propionitrile			16.2	17.7	26.5	...	7.3	26.5	5.8	100
Butadiene			5.3	5.8	..	6.3	13.5	3.4	65.7	100

and −17 kcal./mole for the ethylpyridine and aniline reactions, respectively. Thus at both the temperatures in question these reactions are thermodynamically feasible. The driving force $(-\Delta F^0)$ favoring ethylpyridine formation is greater at 700°K. than at 900°K. The lower temperature is thus more favorable for this reaction. The large negative free energy changes for the aniline reaction detract from the use of this system for preparation of 2-ethylpyridine unless a catalyst selective to the pyridinic reaction is used. At 600°, Marvel and Hwa found that the yield of aniline was eight times that of ethylpyridine for the uncatalyzed reactions.[3] In the present investigation the results of a catalyst search[5] for the pyridinic cyclization–dehydrogenation were used to select the most promising catalysts for this reaction.

Experimental

Propionitrile (Eastman Organic Chemicals, practical grade) was redistilled in a packed column and dried over anhydrous $CaSO_4$ before use (obsd. b.p. 97.2° (760 mm.), $n^{25}D$ 1.3642, lit. b.p. 97.1° (760 mm.), $n^{25}D$ 1.3640). The butadiene was a C.P. grade (Matheson Co.) and was used without purification. Two catalysts were used: 12% Cr_2O_3, 88% Al_2O_3, and 4% Cr_2O_3, 96% Cr_2O_3. The former was the type used in the work with the other nitriles and butadiene,[2] and the latter had been found a very promising catalyst for this process. The preparation of the catalysts and the continuous flow apparatus have been described elsewhere.[5] The reaction was first investigated using the 12% Cr_2O_3 catalyst for product analyses, identification and yields for comparison with the previous work,[2] and subsequently with the 4% Cr_2O_3 catalyst to gain a material balance, conversions and yields for the process using a more promising catalyst.

(i) **Reaction over 12% Cr_2O_3, 88% Al_2O_3.**—Preliminary work showed that the catalyst activity decreased rapidly with time, i.e., during a 12-hr. experiment the butadiene conversions were 4, 1 and 0.5 mole per cent. for each 4-hr. increment of this period. Accordingly the catalyst was used only for 2 hours before reactivation.[5] A series of 14 such runs were made to accumulate 1207 g. of crude product for investigation. The reaction conditions were in each case: temperature, 425 ± 10°, contact time, 20 sec., equimolar ratio of butadiene and propionitrile in feed. The separation and method of analysis for the basic products was as in the previous work.[2] From the reaction of propionitrile and butadiene, the basic product was a mixture of ethylpyridine and aniline.[3] The composition of the product at 400° from the catalyzed reaction, was determined refractometrically after the ethylpyridine–aniline mixture had been isolated by distillation (ethylpyridine, $n^{25}D$ 1.4948; aniline, $n^{25}D$ 1.5815). In the present work also, the identity of these products was confirmed (i) by comparison of the infrared spectra with those for the authentic specimens, and (ii) melting point and X-ray diffraction data for the picrate derivatives. From the nonbasic liquid product, a fraction was isolated in appreciable

(5) G. J. Janz, W. J. G. McCulloch and E. F. Timpane, Ind. Eng. Chem., in publication.

amounts, having a characteristic aromatic odor. It was identified as ethylbenzene from its physical properties (obsd. b.p. 54° (40 mm.), 135.9° (760 mm.), $n^{25}D$ 1.4889; lit., b.p. 53° (40 mm.), 136° (760 mm.), $n^{25}D$ 1.4933) and by the close correspondence of its infrared absorption spectrum with that for an authentic specimen.

The yields for this experiment were: ethylpyridine and aniline, 2.3 and 2.5 mole per cent., respectively (calcd. on propionitrile conversion), and ethylbenzene, 15.4 mole per cent. (on butadiene conversion).

The formation of ethylbenzene can be explained by a reaction of butadiene occurring simultaneously in this system. An experiment using butadiene only over the 12% Cr_2O_3 catalyst at 420° at 20-second contact time and atmospheric pressure, gave a 21 mole per cent. yield of ethylbenzene. A small amount of vinylcyclohexene (less than 1%) was also found. Of the butadiene converted per pass, 52 mole per cent. was accounted for as a gain in weight of the catalyst bed for a two-hour experiment.

(ii) **Reaction over 4% Cr_2O_3, 96% Al_2O_3.**—This catalyst had been found to have a relative activity about 30 times that of the 12% Cr_2O_3 catalyst in the phenylpyridine synthesis from butadiene and benzonitrile.[5] The reaction conditions for the run using this catalyst with propionitrile and butadiene were: temperature, 420 ± 5°; contact time, 4 seconds; equimolar ratio of propionitrile and butadiene in feed, duration of run, 2 hours. The crude product was worked up as in the previous case to obtain the material balance, conversions and yields. These data are summarized in Table I. In the first two hours, using a freshly activated catalyst, the gain in weight of the catalyst bed is quite appreciable, and can be attributed largely due to butadiene. This is in accord with the results observed using butadiene only in the presence of this catalyst system. The yield of ethylbenzene, however, is only 6.3 mole per cent. at this shorter reaction time. The volatiles (not condensed at −80°) and polymers (high boiling residues) were not investigated since the primary interest was in the yields of basic products. A total of 34 mole per cent. of the nitrile converted per pass is accounted for as ethylpyridine and aniline, the yields being 16.2 and 17.7 mole per cent., respectively.

Discussion

The reaction of propionitrile with butadiene at 400° in the presence of a chromia–alumina catalyst is more complex than with the nitriles previously studied[2] under these conditions, since aniline as well as ethylpyridine is formed. The space-time yield of ethylpyridine in the presence of a catalyst containing 12% Cr_2O_3 may be compared with the results reported for cyanogen, hydrogen cyanide, acetonitrile and benzonitrile (Table II). The space-time yield (moles of pyridinic product per hour per 100 cc. catalyst bed) is in the first approximation a measure of the rate of reaction. The comparison thus leads to the interesting observation that, with the exception of cyanogen, the reactivities of the nitriles are all of the same order of magnitude. The energy of activation is not appreciably influenced by the changes in structure of the group attached to the (C≡N) group. It is evident

that the influence of internal electronic polarizability within the nitriles is not very great in the reaction mechanism. The high space-time yield found with cyanogen is difficult to interpret. It may be accounted for in part by the fact that there are two potential reaction centers present per molecule, and that the delocalization energy within each (C≡N) group is considerably greater than for the cyano groups of the other nitriles in this series.

TABLE II

SPACE-TIME YIELDS FOR THE REACTION OF SOME ORGANIC NITRILES WITH BUTADIENE AT 400° OVER A 12% CHROMIUM OXIDE–ALUMINUM OXIDE CATALYST

Nitrile	Product	Space-time yield,[a] × 10[4]	Reference
NC–CN	2-Cyanopyridine	150	2
H–CN	Pyridine	11	2
CH₃–CN	2-Methylpyridine	16	2
CH₃CH₂–CN	2-Ethylpyridine	7	This work
C₆H₅–CN	2-Phenylpyridine	16	2

[a] Defined as moles of product per hr. per 100 cc. catalyst bed.

As well as the pyridinic product, aniline and ethylbenzene were isolated. The latter is accounted for by the thermal dimerization of butadiene followed by rearrangement to the final product. Shorter reaction times serve to decrease the yield of this simultaneous reaction. This is in accord with the results of related studies using nitriles other than propionitrile. At very short reaction times little or no ethylbenzene was found.

The formation of aniline is understood if there is a rearrangement of the nitrile

$$CH_3—CH_2—CN \longrightarrow CH_3—CH=C=NH$$
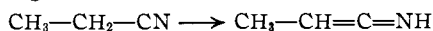
with subsequent cyclization and rearrangement as postulated by Marvel and Hwa.[3] The dissociation energy of the C–H methylene bond is 21 kcal. less than the C–H bond in the methyl group.[6] The thermal stability of propionitrile is thus less than that of acetonitrile.

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(6) M. Szwarc, Chem. Revs., 47, 168 (1950).

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The Diene Synthesis with Unsymmetrical Butadienes and β-Nitrostyrenes[1]

BY W. C. WILDMAN, R. B. WILDMAN, W. T. NORTON AND J. B. FINE[2]

The diene synthesis with unsymmetrical butadienes and β-nitrostyrenes has been studied. The adduct formed from 2-ethoxybutadiene and β-nitrostyrene proved to be 1-ethoxy-4-nitro-5-phenylcyclohexene. β-Nitrostyrene and 4-methoxy-β-nitrostyrene each formed two adducts with isoprene. The isomer that possessed the methyl group para to the nitro group was present in the larger amount in each case. Piperylene and β-nitrostyrene formed both possible structural isomers; the isomer in which the methyl group was ortho to the nitro group was predominant.

The diene synthesis with unsymmetrical butadienes and olefins has been studied recently to determine whether any general rules can be formulated for the mode of addition of the components. As a corollary to this type of study, further insight into the mechanism of the Diels–Alder reaction should be gained. These studies have been confined largely to 1- and 2-substituted butadienes and monosubstituted ethylenes. This paper extends the information to include the condensation of a disubstituted olefin, β-nitrostyrene, or its 4-methoxy derivative, with the unsymmetrical dienes, piperylene, isoprene and 2-ethoxybutadiene. The adducts formed in this work are also of value in the projected syntheses of several natural products.

Of the three dienes studied, only 2-ethoxybutadiene formed a single pure adduct with β-nitrostyrene. This adduct possessed the structure IIa. This orientation is in accord with that found for the addition of 2-ethoxybutadiene to methyl 3,4-dihydro-1-naphthoate[3] and to 2,3-dimethoxy-β-

nitrostyrene,[4] although no structure proof of the latter adduct was offered.

The condensations with isoprene and piperylene gave high yields of isomeric mixtures of I and II. Only Ic and IIc were completely separable. In series b and d, the isomer ratio could be approximated by the relative amounts of certain transformation products. It is interesting to note that the ratio of Ib to IIb is almost the same as Ic to IIc, indicating that the presence of a 4-methoxyl group does not change the course of addition of isoprene significantly.

Proof that the condensation of 2-ethoxybutadiene and β-nitrostyrene formed IIa involved acid hydrolysis of the enol ether and conversion of the nitroketone to a diketone by the Nef reaction. While the ultraviolet absorption spectrum of this compound was compatible with that of a 1,4-diketone, further proof of structure was offered by conversion to phenylquinone.

In a previous paper it was shown that certain 4-nitro-5-phenylcyclohexenes, prepared from *symmetrical* butadienes and β-nitrostyrenes, could be converted by the Nef reaction to 6-phenyl-3-cyclohexen-1-ones and then to 6-phenyl-2-cyclohexen-1-

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1952.

(2) Abstracted in part from a thesis submitted by J. B. Fine in partial fulfillment of the requirements for the degree of Bachelor of Arts, Princeton University, May, 1952.

(3) H. L. Holmes and K. M. Mann, THIS JOURNAL, 69, 2000 (1947).

(4) J. A. Barltrop and J. S. Nicholson, J. Chem. Soc., 2524 (1951).