315. *The Reaction of Cyanogen and Related Nitriles with* 1 : 3-*Dienes. Part I. Thermodynamic Considerations, and a Study of the Uncatalysed Reaction of Cyanogen and Related Nitriles with* 1 : 3-*Butadiene.*

By P. J. HAWKINS and G. J. JANZ.

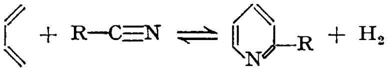
Some thermodynamic calculations and an experimental study of the reaction of butadiene with cyanogen, hydrogen cyanide, acetonitrile, and benzonitrile are reported. Although these reactions are in each case quite favoured energetically, the conversions were quite small, except in the case of cyanogen. These reactions may be considered as further examples of the Diels–Alder reaction, in which the C≡N group is the dienophilic component, and in which the intermediate 2 : 5-dihydropyridine derivatives lose hydrogen under the conditions of the reaction to form the corresponding pyridine derivatives.

REACTION of cyanogen with butadiene in the gaseous phase at moderately high temperatures leads to formation of 2-cyanopyridine (Janz, Ascah, and Keenan, *Canadian J. Res.*, 1947, **25**, **B**, 272). Further study established that this behaviour may be generalised for the simple 1 : 3-dienes such as isoprene, chloroprene, and piperylene, the product in each case being a 2-cyanopyridine derivative (Janz and Keenan, *ibid.*, p. 283). It was suggested that the reaction may be explained as proceeding by a Diels–Alder mechanism, in which the C≡N has the rôle of the dienophilic component of the dienophile, and that because the conditions are favourable for aromatisation, the reaction is accompanied by a simultaneous dehydrogenation, giving the 2-cyanopyridine. This is in accord with some observations by Alder ("Preparative Organic Chemistry," Interscience Publishers Inc., N.Y., 1948) that, when derivatives of 2 : 5-dihydropyridines are formed in the Diels–Alder reaction, the substances lose hydrogen under the normal conditions of the reactions to form the corresponding pyridine derivatives.

Further studies are now reported of the application of the diene synthesis to the formation of pyridinic nuclei, with particular reference to the use of nitriles other than cyanogen. The nitriles chosen, hydrogen cyanide, benzonitrile, and acetonitrile may be considered as members of the general class of dienophiles, R·C⋮N. Apart from the papers already mentioned, very little has been published on this class of dienophile. Dilthey *et al.* (*Ber.*, 1935, **68**, 1162) reported the synthesis of pentaphenylpyridine from benzonitrile and tetraphenyl*cyclo*pentadienone. This may be considered as a Diels–Alder reaction, accompanied by a simultaneous cleavage of carbon monoxide. The only other direct application is reported by Alder (*loc. cit.*), who used the esters of cyanoformic acid in the reaction with butadiene to form a corresponding pyridine derivative.

The thermodynamic approach was first considered in order to obtain information on the feasibility of these reactions over the temperature range to be investigated. Calculations concerning the hydrogenation of pyridine to piperidine were also undertaken to find the stability of the dihydro-intermediates with reference to the end products.

The method of calculating ΔG° and log K_p from the thermodynamic functions is well established, and ΔG° and log K_p were calculated by this method for the reactions considered except for the 2-phenylpyridine synthesis, for which, owing to lack of sufficient data to calculate the thermodynamic functions, the results were obtained by using the principles of the method of group contributions to estimate the necessary data (Andersen, Beyer, and Watson, *Nat. Pet. News*, 1944, **36**, R476). The reaction considered in each case was simply



Butadiene and Hydrogen Cyanide.—The thermodynamic functions for butadiene (Brickwedde, Moskow, and Aston, *J. Res. Nat. But. Stand.*, 1946, **37**, 263), hydrogen cyanide (Gordon, *J. Chem. Physics*, 1937, **5**, 30), pyridine (Kline and Turkevich, *ibid.*, 1944, **12**, 300), and hydrogen (Amer. Pet. Institute Project 44, Tables and Selected Values, Nat. Bur. Stand., Washington, D.C., 1946) have all been previously calculated from molecular and spectroscopic data, and were used to calculate ΔG° and log K_p for this reaction. The results are listed in Table II.

Butadiene and Acetonitrile.—The thermodynamic functions for 2-methylpyridine are listed in Table I, and are probably of sufficient accuracy for most thermodynamic calculations of the type considered. The spectroscopic frequency assignment for the calculation of the vibrational contribution to the thermodynamic function for 2-methylpyridine was made on a semi-empirical basis using the frequency assignment for pyridine (Kline and Turkevich, *loc. cit.*) as guide, and the frequencies associated with the vibrations of the methyl group. Strictly, it is incorrect to speak of the vibrations of an individual link or group, but in such a group as methyl, where a light atom moves against a much heavier residue, the vibrational frequencies associated with such vibrations are little changed from one molecule to another. By using the pyridine assignment, minus the frequencies 3054, 1061, and 747 (associated with the C–H in the 2-position of the pyridine molecule), and plus the frequencies 3000 (3), 1400 (3), 1000 (3), 1120 (2), 920 (for the methyl group in the 2-position), the vibrational contributions to the thermodynamic functions were calculated. For the rotational contribution, the product of the moments of inertia, *ABC*, for the molecule was calculated by using Kline and Turkevich's parameters for the pyridine nucleus and 1·40 and 1·087 A. for the C–C and C–H bond lengths, respectively, of the methyl group in the 2-position. *ABC* was thus found to be $1{\cdot}8722 \times 10^{-113}$. The heat of formation of 2-methylpyridine, $\Delta H^\circ_{298\cdot1(g)} = 21{\cdot}5$ kcals./mol., was calculated from the heat of combustion (Int. Critical Tables, Vol. 5) and the latest thermal data for carbon dioxide and water (Amer. Pet. Inst. Project 44, *loc. cit.*). By using the data for acetonitrile (Thompson, *Trans. Faraday Soc.*, 1941, **37**, 344), butadiene, and hydrogen, together with the above data, the ΔG° and log K_p values (Table II) were calculated.

Butadiene and Cyanogen.—The thermodynamic functions for 2-cyanopyridine have been calculated from molecular and spectroscopic data, as for 2-methylpyridine, and are listed in Table I. For the calculation of the vibrational contribution, the frequencies associated with the vibrations of the cyano-group in the 2-position, 300 (2), 380 (2), 900, 2245, were used in conjunction with the assignment for pyridine (Kline and Turkevich, *loc. cit.*), minus the frequencies associated with the C–H vibrations in the 2-position. The cyano-group has vibrational frequencies which generally remain fairly constant from one molecule to another, being sometimes slightly affected by neighbouring groups or electronic influences such as conjugation, and the values above were chosen from a consideration of the assignments made for other nitriles (Herzberg, "Infra-Red and Raman Spectra," D. Van Nostrand Co. Inc., N.Y., 1945; Kohlrausch, "Der Smekal–Raman Effekt," Julius Springer, Berlin, 1938). By using 1·15 A. for the C≡N bond length and the same parameters as for 2-methylpyridine, the product of the moments of inertia, *ABC*, was found to be $4{\cdot}402 \times 10^{-113}$. The heat of formation of 2-cyanopyridine was estimated by using 2-methylpyridine as the parent, and the increment for the change of cyano- for methyl in the molecule. This gave $\Delta H^\circ_{298\cdot1(g)} = 60{\cdot}59$ kcals./mol., and this value is recommended in preference to that reported in the earlier calculations for this compound (Janz, *Canadian J. Res.*, 1947, **25**, **B**, 331). The values of ΔG° and log K_p were calculated from these data, together with those for butadiene, hydrogen, and cyanogen (Thompson, *loc. cit.*) and are listed in Table II.

TABLE I.

Thermodynamic functions for 2-methylpyridine and 2-cyanopyridine.

Function. $T°$, K.	298·1.	300.	400.	500.	600.	700.	800.	900.	1000.	1200.
$-(G° - E_0°/T)$										
2-Methylpyridine	59·65	59·87	63·61	67·93	71·93	75·84	80·55	83·56	85·63	90·95
2-Cyanopyridine	62·52	62·75	68·05	72·30	76·76	80·98	86·19	88·84	91·08	96·30
$(H° - E_0°)$										
2-Methylpyridine	3·52	3·70	6·13	9·99	14·23	19·03	23·16	29·84	34·29	48·21
2-Cyanopyridine	4·36	4·54	7·32	11·35	15·59	20·21	24·07	30·32	34·27	46·97
$C_p°$.										
2-Methylpyridine	21·11	22·70	29·81	39·24	45·36	50·27	52·36	57·28	58·62	64·57
2-Cyanopyridine	26·50	27·10	32·46	39·96	44·41	47·88	48·81	52·73	53·24	57·74

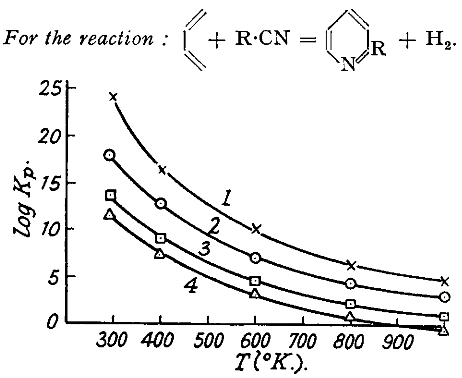
TABLE II.

Free-energy change and log K_p *for some reactions of butadiene and organic nitriles.*

Reaction.	$T°$, K.	298·1.	400.	600.	800.	1000.
(i) $C_4H_6 + HCN = C_5H_5N + H_2$	$-(\Delta G°)$	−24·56	−22·97	−19·80	−16·73	−13·71
	log K_p	18·0	12·6	7·2	4·6	3·0
(ii) $C_4H_6 + CH_3{\cdot}CN = C_5H_4N{\cdot}CH_3 + H_2$	$-(\Delta G°)$	−18·77	−16·48	−12·26	− 8·49	− 2·47
	log K_p	13·8	9·0	4·5	2·3	0·5
(iii) $C_4H_6 + (CN)_2 = C_5H_4N{\cdot}CN + H_2$	$-(\Delta G°)$	−33·15	−31·76	−28·70	−27·02	−22·12
	log K_p	24·3	17·4	10·5	7·4	4·8
(iv) $C_4H_6 + C_6H_5{\cdot}CN = C_5H_4N{\cdot}C_6H_5 + H_2$ ...	$-(\Delta G°)$	−13·55	−13·91	− 9·37	− 3·83	0·99
	log K_p	11·9	7·6	3·4	1·05	− 0·2

Butadiene and Benzonitrile.—The thermal data for benzonitrile and 2-phenylpyridine have been estimated by the method of group contributions (Andersen, Beyer, and Watson, *loc. cit.*). For benzonitrile the parent hydrocarbon chosen was toluene, for which accurate thermal data are available (Amer. Pet. Inst. Project 44, *loc. cit.*). The increment due to cyano- for methyl was estimated by comparing the data for 2-methylpyridine and 2-cyanopyridine. Thus for benzonitrile, $\Delta H°_{298\cdot1(g)} = 50\cdot85$, $S°_{298\cdot1} = 82\cdot12$, and $C_p° = 3\cdot12 + 84\cdot59 \times 10^{-3}\ T - 30\cdot75 \times 10^{-6}\ T^2$. In a similar manner the thermal data for 2-phenylpyridine were estimated by using the increment due to substitution of phenyl for methyl as given by Andersen *et al.*, together with 2-methylpyridine as the reference compound. This gives for 2-phenylpyridine, $\Delta H°_{298\cdot1\ (g)} = 53\cdot89$ kcals., $S°_{298\cdot1} = 93\cdot12$ cals. deg.$^{-1}$ mol.$^{-1}$, and $C_p° = -12\cdot55 + 178\cdot33 \times 10^{-3}\ T - 71\cdot15 \times 10^{-6}\ T^2$. The log K_p and $\Delta G°$ calculated from these data are listed in Table II. These values are of necessity a rougher approximation than those calculated for the other examples, but they should serve for indicating the general trend in this series.

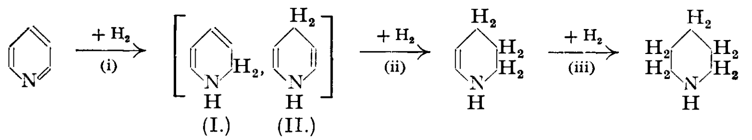
FIG. 1.


For the reaction : + R·CN = R + H$_2$.

(1) R = CN; (2) R = H;
(3) R = CH_3; (4) R = C_6H_5.

It is seen in Fig. 1 that log K_p decreases as the temperature increases in each example considered. It would be preferable to study the reactions at the lower temperatures where the thermodynamic conditions are more favourable. Over the whole temperature range considered, the free-energy change for the reaction (*i.e.*, thermodynamic stability with reference to the reactants) is greatest for the case of cyanogen, and decreases for hydrogen cyanide, acetonitrile, and benzonitrile, in that order. Temperatures higher than 800° K. are predicted to be not very favourable for the reaction involving benzonitrile (*i.e.*, log. $K_p \leq 0$).

Hydrogenation of Pyridine.—A consideration of the thermodynamics of the hydrogenation of benzene (unpublished) established that the dihydro- and tetrahydro-intermediates were thermodynamically unstable with reference to benzene and *cyclo*hexane. A similar result may be expected in the case of pyridine. The following steps have been considered in the hydrogenation of pyridine:



As well as the 1 : 2-dihydropyridine (I), the 1 : 4-dihydro-intermediate was considered, since there is evidence that under suitable conditions the hydrogenation will proceed by this path (Shaw, *J.*, 1924, **125**, 1930; 1925, **127**, 215; 1937, 300). The free-energy change was calculated from the relationship $\Delta G = \Delta H - T\Delta S$, where ΔH is the heat of hydrogenation, and ΔS the corresponding entropy change. The heats of hydrogenation and entropy changes for the separate steps are listed in Table III. The heat of hydrogenation of pyridine to piperidine was calculated from the heats of formation based on the thermal data for these compounds (Int. Critical Tables) and for carbon dioxide and water (Amer. Pet. Inst. Project 44, *loc. cit.*). The heat of hydrogenation for the double bond in tetrahydro- and 1 : 4-dihydro-pyridine was assumed to be the same as that for a true olefinic linkage (*idem, ibid.*) since no resonance energy change is involved. This value was corrected for the change in resonance energy, 1·8 kcals., in the hydrogenation of 1 : 2-dihydropyridine, where it was assumed that the resonance is the same as in *cyclo*hexa-1 : 3-diene (Wheland, " The Theory of Resonance," J. Wiley & Sons Inc., N.Y., 1944). The value for the first step was then calculated by difference. A reasonable approximation of the entropy of hydrogenation of pyridine to piperidine is obtainable from a consideration of the difference in entropy between benzene and *cyclo*hexane, and the entropy of formation of hydrogen (Amer. Pet. Inst. Project 44, *loc. cit.*). This gave $\Delta S = 86{\cdot}7$ cals. deg.$^{-1}$ mol.$^{-1}$ for this hydrogenation. The values for the free-energy change for each step calculated from these data (Table III) are plotted in Fig. 2 to show the thermodynamic stability of the intermediates with reference to the end products. In this calculation, because of the absence of values for the intermediate stages, it was assumed that the total entropy change is evenly divided over the three stages. It is seen that both the dihydro- and the tetrahydro-pyridine are thermodynamically unstable with reference to pyridine and piperidine, and even in the limits where it would be assumed that ΔS is zero or equal to $-86{\cdot}7$ cals. deg.$^{-1}$ mol.$^{-1}$ in the first step of the hydrogenation, the calculation predicts the dihydropyridine to be thermodynamically unstable relative to the other substances. Although only approximate, the results are of interest in view of the experimental observations concerning the present research, and the generalisation made by Alder (*loc. cit.*). If either of these intermediates was formed under conditions favouring aromatisation, one would expect it to pass over into pyridine.

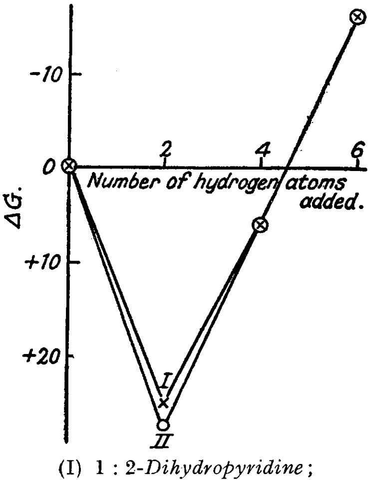
TABLE III.

The hydrogenation of pyridine to piperidine.

Reaction.	$\Delta H_{298\cdot 1}$, kcals.	$\Delta G_{298\cdot 1}$, kcals.
Pyridine to 1 : 2-dihydropyridine	16·7	25·3
Pyridine to 1 : 4-dihydropyridine	18·5	27·1
1 : 2-Dihydro- to tetrahydro-pyridine	−28·2	−19·6
1 : 4-Dihydro- to tetrahydro-pyridine	−30·0	−21·4
Tetrahydropyridine to piperidine	−30·0	−20·0
Pyridine to piperidine	−40·1	−14·3

FIG. 2.

Hydrogenation of pyridine to piperidine.



(I) 1 : 2-*Dihydropyridine*; (II) 1 : 4-*dihydropyridine.*

These reactions were studied over the temperature range 400—600° and for various reaction contact times in an unpacked vessel. The catalysis of these reactions is described in Part II (following paper). The data and results for the uncatalysed reactions are summarised in Table IV. It was found that when the reaction of butadiene with hydrogen cyanide, acetonitrile, benzonitrile, or cyanogen is carried out in this temperature range and at atmospheric pressure, the pyridinic product, *i.e.*, pyridine, or 2-methyl-, 2-phenyl-, or 2-cyano-pyridine, respectively, is formed in each case.

The space-time yields (mols. × 10^{-4} of pyridinic product/hr./100 c.c. reaction vessel volume) for these reactions are listed below. These results are for runs at 400° using comparable space velocities (0·3—0·5 l./hr./c.c. at 0° and 760 mm.) and molar ratios of nitrile to diene (approx. 3 : 1).

	Reaction of butadiene with :			
	Benzonitrile.	Acetonitrile.	Hydrogen cyanide.	Cyanogen.
Product	2-Phenylpyridine	2-Methylpyridine	Pyridine	2-Cyanopyridine
Space-time yield (mols. × 10^{-4}/hr./100 c.c.)	1·45	1·88	3·0	16·7

The space-time yields are quite small, indicating that the reaction velocities are low. The relatively larger yield for the cyanogen–butadiene reaction is probably partly accounted for by the fact that the effective concentration of the cyano-group for this nitrile is double that for the same concentration of the other nitriles. The above results indicate that the reactions do not have very convenient velocities, and in view of the thermodynamic calculations predicting a very favourable free-energy change in this temperature range, a search for a catalyst to promote the reaction was undertaken (see Part II).

The space-time yield in the benzonitrile–butadiene reaction when the vessel was packed with Pyrex-glass chips was found to be about the same as when the unpacked reactor was used (cf. runs 24 and 6, Table IV, *d*). The reaction seems to be essentially homogeneous.

In the temperature range investigated, 400—600°, the conversions of butadiene into pyridinic product were all low (1% or less) when hydrogen cyanide, acetonitrile, and benzonitrile were used in the reaction. As a novel route to the synthesis of pyridine and 2-substituted pyridines other than 2-cyanopyridine (Janz, Ascah, and Keenan, *loc. cit.*) the uncatalysed reaction of butadiene with organic nitriles would not seem to be of much interest.

EXPERIMENTAL.

Materials.—Butadiene and hydrogen cyanide were samples from Imperial Chemical Industries Limited. The hydrogen cyanide was normally stored in glacial acetic acid solution (Krieble and Snellie, *J. Amer. Chem. Soc.*, 1945, **67**, 690), and freshly distilled before use. Cyanogen was prepared by the copper sulphate–sodium cyanide method (Janz, Ascah, and Keenan, *loc. cit.*). Acetonitrile (Hopkin and Williams) and benzonitrile (B.D.H.) were dried over phosphoric oxide and redistilled before use.

Flow Apparatus.—The design of the flow apparatus was essentially that described in the butadiene–cyanogen work (*idem, ibid.*). The reactors were of Pyrex glass or silica, and of the design described by Farkas and Melville ("Experimental Methods in Gas Reactions," MacMillan Co. Ltd., London, 1939, p. 302), and the liquid flow-meters were a refinement of spiral type described by Fabris and Peacock (*Canadian Chem. & Process Ind.*, Feb., 1947), modified only to give fine control and very steady rates of feed. As well as "Drikold", liquid-air traps were used in the line after the reactor to assist in recovery of products.

Methods of Analysis.—(*a*) *Combined nitrogen.* The normal Kjeldahl method was used for the determination of recovery of total nitrogen and of nitrile, the ammonia being absorbed in saturated boric acid solution, and titrated with methyl-red as indicator (Mecker and Wagner, *Ind. Eng. Chem. Anal.*, 1933, **5**, 396). The accuracy was within 1—2%.

(*b*) *Pyridine, 2-methylpyridine, and 2-phenylpyridine.* The method of analysis used was a slight modification of that described by Ladd (*Ind. Eng. Chem.*, 1919, **11**, 522). The steam-distillate containing the pyridinic product was made up to an appropriate volume with a suitable amount of N/5-hydrochloric acid. Aliquots were titrated to (i) methyl-orange/methylene-blue, (ii) phenolphthalein. The difference in titrations calculated to the original volume gave the amount of pyridinic product. In the absence of large amounts of ammonia the method was sensitive to about 0·005 g. of pyridinic compound.

(*c*) *2-Cyanopyridine.* This was determined by hydrolysis by excess of 10% sulphuric acid to ammonia (2—3 hrs.' refluxing), which was estimated as above.

(*d*) *Cyanogen and hydrogen cyanide.* For cyanogen, Ricca's method of analysis was used (*Ann. Chim. appl.*, 1926, **16**, 83). The accuracy was about 1%. The hydrogen cyanide was determined by absorption in sodium hydroxide solution and titration of aliquot samples with silver nitrate as in the method for cyanogen.

Characterisation of Pyridinic Product.—The physical constants and analyses by means of which the pyridinic products were identified were as follows : (*a*) Pyridine; picrate, m. p. and mixed m. p. 164—165° (lit., 167°) (Found : C, 42·25; H, 2·3; N, 18·9. Calc. : C, 42·9; H, 2·6; N, 18·2%). (*b*) 2-Methylpyridine; picrate, m. p. and mixed m. p. 165—167° (lit., 167—169°) (Found : C, 44·8; H, 3·4; N, 17·3. Calc. : C, 44·7; H, 3·1; N, 17·4%). (*c*) 2-Phenylpyridine; b. p. 134—138°/10 mm., $n_D^{25°}$ 1·6170 (Found :

C, 84·1; H, 6·1; N, 9·4. Calc.: C, 85·1; H, 5·1; N, 9·0%); picrate, m. p. 168—170° (lit., 169—170°) (Found: C, 53·2; H, 3·2; N, 14·4. Calc.: C, 53·1; H, 3·15; N, 14·7%).

Results.—The data and results for each run are summarised in Table IV. The material recoveries and nitrogen balances, as well as the yields of pyridinic product calculated on the nitrile " conversion," are listed in Table V. These yields are undoubtedly low since the nitrile conversion includes any losses

TABLE IV.

Summary of experimental data and results.

Run.	T°, c.	Space velocity, l./hr./c.c.	Mol. ratio $\frac{R\cdot CN}{C_4H_6}$.	C_4H_6 input rate, mol./hr.	Duration, hrs.	Pyridinic product (total), mols. × 10^{-4}.	C_4H_6 conversion into pyridinic product (mols. %).	Space-time yield of pyridinic product, mols. × 10^{-4}/hr./100 c.c.
(*a*) Butadiene and cyanogen. 2-Cyanopyridine.								
1	400	0·0874	2·5	0·060	7·0	533	12·8	—
2	400	0·307	3·0	0·047	5·0	11·5	0·49	16·7
(*b*) Butadiene and hydrogen cyanide. Pyridine.								
6	404	0·278	3·6	0·215	1·0	2·41	0·11	3·0
2	597	0·036$_3$	1·0	0·320	7·5	334	1·39	
3	595	0·038$_1$	1·1	0·320	5·0	181	1·14	
(*c*) Butadiene and acetonitrile. 2-Methylpyridine.								
8	395	0·342	2·8	0·056	5·0	1·30	0·04$_6$	1·88
11	400	0·057$_1$	3·1	0·051	5·0	1·40	0·05$_5$	
7A	599	0·057$_8$	1·7$_2$	0·250	4·0	96·8	0·97	
7B	597	0·108	10·1	0·176	2·0	27·0	0·74	
(*d*) Butadiene and benzonitrile. 2-Phenylpyridine.								
6	393	0·531	3·0	0·083	3·0	0·60	0·02$_4$	1·45
24 *	400	0·182	3·3	0·094	2·75	2·49	0·09$_6$	1·80
4	400	0·015$_2$	2·7	0·073	4·8	2·66	0·07$_8$	
5	402	0·004$_7$	3·2	0·020	12·0	2·56	0·106	
3	495	0·014$_6$	3·3	0·061	5·0	7·75	0·25$_8$	
1	530	0·019	1·4	0·142	9·7	19·3	0·15$_2$	
2A	591	0·036	1·7	0·244	3·0	25·8	0·35$_2$	
2B	590	0·072	6·0	0·188	2·3	21·9	0·51$_5$	

* Reaction chamber packed with Pyrex-glass chips.

TABLE V.

Summary of data in total material and nitrile recoveries.

Run.	Material recovery (total), % of input.	Combined N recovery (total), % of input.	Nitrile " conversion," % of nitrile input.	Yield of pyridinic product, % on conversion.
(*a*) Butadiene and cyanogen.				
1	98·0	—	15·0	34·0
2	95·4	—	30·5	0·63
(*b*) Butadiene and hydrogen cyanide.				
6	100	—	3·2	0·93
2	94·0	—	26·0	6·0
3	79·0	—	18·5	5·4
(*c*) Butadiene and acetonitrile.				
8	89·2	91·0	18·2	0·1
11	90·0	90·5	18·0	0·1
7A	94·0	97·0	10·0	5·6
7B	97·5	97·0	7·0	1·0
(*d*) Butadiene and benzonitrile.				
6	96·5	100	5·5	0·1$_4$
24	100	96·5	4·5	0·7$_2$
4	95·5	101	4·0	0·6$_5$
5	93·0	98·5	5·0	0·7$_3$
3	97·5	99·1	2·0	3·0
1	93·5	96·0	4·0	2·6
2A	95·0	100	1·5	10—20
2B	97·0	96·5	2·5	1—3

incurred in the experimental recovery procedure which involved several operations, *i.e.*, distillations and ether extractions. The space velocity is expressed in l. of flow per hr. per c.c. of reactor volume, and the space-time yield as moles × 10^{-4} of pyridinic product per hr. per 100 c.c. of reactor volume. The conversion of butadiene into pyridinic product, calculated as % of the butadiene input, is a sufficient criterion of the extent of the reaction per pass.

The data in Table V show that with the exception of the benzonitrile–butadiene reaction, the nitrile conversions are all high per pass, and the resulting yield of pyridinic product correspondingly low. Some of this conversion is undoubtedly accounted for by side reactions, such as polymerisation (*e.g.*, to paracyanogen), decomposition (*e.g.*, to nitrogen and carbonaceous residues), and reduction to amines and ammonia (detected, but not estimated), but this aspect of the work was not followed.

The authors wish to thank Imperial Chemical Industries Limited for gifts of chemicals, the Chemical Society for a grant, the University of London for the award of an I.C.I. Fellowship to one of them (G. J. J.), and Professor C. K. Ingold, F.R.S., and Dr. Albert Wassermann for continued interest in this work.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C. 1.
[*Received, October 29th,* 1948.]