total yield 7.74 g. (96.5%). This solid was extracted with hot ethanol which left behind an insoluble crystalline residue; yield 0.48 g. (6.67%). The decomposition point of this residue was raised from 223.9 to 230° by one crystallization from water. Several crystallizations from water were ineffective in increasing the decomposition point of this sample of 1-amino-2-nitraminoethane to the value of 240° reported by Hall and Wright.[14]

Anal. Calcd. for $C_2H_7N_3O_2$: C, 22.83; H, 6.66; N, 40.0. Found: C, 22.90; H, 6.72; N, 40.37.

The alcohol soluble crystalline product was purified by several crystallizations from ethanol and water. It melted at 160–161° with decomposition and gave analytical values in good agreement with bis-(β-nitraminoethyl)-urea.

Anal. Calcd. for $C_5H_{12}N_6O_5$: C, 25.41; H, 5.09; N, 35.57. Found: C, 26.01; H, 5.37; N, 35.25.

2β-Chloroethylamino-2-oxazolinium Picrate.—Bis-(β-nitraminoethyl)-urea (0.5 g., 0.002 mole) was refluxed with 10 cc. of 37% hydrochloric acid solution for 2.5 hours. The solution was evaporated to dryness and the oily residue (430 mg.) was redissolved in water (10 cc.). A picrate was formed in the usual manner, yield 445 mg. (55.6%). The melting point was raised from 184–187° to 193–194° by crystallization from water; yield 372 mg.

Anal. Calcd. for $C_{11}H_{12}ClN_5O_8$: C, 34.99; H, 3.18; N, 18.54. Found: C, 35.12; H, 2.95; N, 18.95.

Bis-(β-chloroethyl)-urea.—Bis-(β-nitraminoethyl)-urea (1.70 g., 0.072 mole) was dissolved in 8.0 cc. of concentrated hydrochloric acid. After the clear solution had remained at room temperature for six days, it was cooled to 20° and then it was carefully brought to a *p*H of 7 with 10% sodium hydroxide solution. The resulting mixture was cooled to 0° after which the white crystals were removed by filtration; yield 0.89 g. (67.3%). After one crystallization from absolute ethanol (7.9 cc./g.), the melting point was raised from 126.5–127° to 127–127.5°. Bestian[8] reports a melting point of 127° for bis-(β-chloroethyl)-urea.

Anal. Calcd. for $C_5H_{10}Cl_2N_2O$: C, 32.45; H, 5.42; Cl, 38.33; N, 15.15. Found: C, 32.67; H, 5.26; Cl, 38.00; N, 15.01.

Hydrolysis of 1-Nitro-2-nitriminoimidazolidine with Hydrochloric Acid.—Ten grams (0.057 mole) of 1-nitro-2-nitriminoimidazolidine was refluxed in 20 cc. of 20% hydrochloric acid solution until gassing ceased. The solution was concentrated to 10 cc. *in vacuo* after which crystals (m.p. 113–115°) were deposited on standing at room temperature; yield 1.27 g. (13.3%). After one crystallization from chloroform, these crystals melted at 117.5–119°. A mixed melting point determination with a sample of 1β-chloroethyl-3-nitrourea (m.p. 115–117°), kindly supplied by Dr. G. F. Wright, showed no depression.

The original filtrate was evaporated to dryness *in vacuo*. When attempts to crystallize the residual oil (5.89 g.) failed, it was dissolved in water (15 cc.) and treated with a saturated aqueous solution of picric acid and triethanolamine picrate. A yellow picrate was obtained in 19.4% yield (3.42 g.) which melted at 142–143°. This picrate did not depress the melting point of an authentic sample of β-chloroethylamine picrate (m.p. 143–144°).

Silver Salt of 1-Nitro-2-nitriminoimidazolidine.—An aqueous ethanol solution containing 1 g. of 1-nitro-2-nitriminoimidazolidine was treated with an aqueous ethanolic solution of silver nitrate. The crystalline silver salt, which formed immediately, was removed by filtration, washed and dried. It explodes when held on a spatula over an open flame.

Anal. Calcd. for $C_3H_4N_5O_4Ag$: Ag, 38.26. Found: Ag, 38.11, 38.29.

Ultraviolet Absorption Spectra.—The spectra were measured with a Beckman quartz spectrophotometer, model DU. Analytically pure samples were used to prepare the solution.

OTTAWA, ONTARIO, CANADA

(14) R. H. Hall and G. F. Wright, THIS JOURNAL, **73**, 2213 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

Mannich Bases of Nitroparaffins: Steric Effect of the Amino Groups on Carbon Alkylation

BY GRADUS L. SHOEMAKER AND ROBERT W. KEOWN

RECEIVED MARCH 25, 1954

Alkylations of active methylene compounds with the Mannich bases of nitroparaffins are shown to proceed more readily when the displaced amine has large bulky groups attached to it. The yields of the alkylation product in the reaction of the Mannich base of nitroethane with malonic, acetoacetic and acetylsuccinic esters doubled when piperidine was replaced by the more bulky diisopropylamine. In a similar manner alkylations of nitroparaffins with the diisopropylamino base were completed in a fraction of the time required for the more compact N-diethylamino-2-nitropropane.

The use of Mannich bases for carbon–carbon alkylation seems to require primarily that the tertiary Mannich base have the ability to form a conjugated unsaturated system through the displacement of the amino group.[1] The unsaturated compound thus formed then undergoes reaction with the active methylene compound by means of a Michael addition thus

$$\mathrm{RCHCH_2NR'_2} \xrightarrow[\mathrm{NO_2}]{-\mathrm{R'_2NH}} \mathrm{RC{=}CH_2} \xrightarrow[\mathrm{NO_2}]{+\ \mathrm{CH_2Z_2}} \mathrm{RCHCH_2CHZ_2} \quad (\mathrm{NO_2})$$

The structural requirements of quaternary ammonium salts for use in similar alkylations (Robinson's method) are the same with the possible exception of those compounds which contain an allylic system attached to the nitrogen atom.[1] These allylic quaternary ammonium salts appear to be the only Mannich bases which can alkylate directly through a carbonium ion without the formation of an unsaturated intermediate.

Since then most carbon–carbon alkylations with Mannich bases proceed through this elimination–addition mechanism, it would appear that the more easily the amine is displaced from the Mannich base, the more readily would the unsaturated intermediate be formed. Ease of formation of this intermediate should then facilitate the subsequent addition reaction. Although numerous papers have considered the requirements for the alkylating radical in these alkylations, there have been few reports[1] concerning the effect of the displaced amino group. In particular it would seem that steric effects of bulky alkyl groups (F-strain) attached to the amino nitrogen would increase the ease of amine displacement from the Mannich

(1) J. H. Brewster and E. L. Eliel, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 99.

base. To study these effects, the Mannich bases of nitroethane and 1-nitropropane with piperidine and diisopropylamine were prepared, and used in typical alkylations.

The steric effects of dialkylamino groups on the stability of 2-nitroalkylamines to hydrogenation and to hydrolysis in aqueous solution have already been considered by Senkus.[2] He has suggested that the more bulky the alkyl groups attached to the amino nitrogen, the less stable is the resulting 2-nitroalkylamine. This increased instability of such compounds should therefore also facilitate the formation of the conjugated olefinic compound. Since the steric effects of the two isopropyl groups in diisopropylamine are well established,[3,4] a comparison of the alkylating tendency of the Mannich bases containing this amine, and of those containing much more compact amines such as piperidine and diethylamine, was undertaken.

The formation of 1-diisopropylamino-2-nitropropane occurred readily in a 66% yield. This yield compares favorably with yields when other secondary amines are used.[5] The 1-diisopropylamino-2-nitrobutane was prepared in a similar manner. Moreover, in both cases none of the undesired di-Mannich base formed by the reaction of two moles of amine and two of formaldehyde with one of the nitroparaffin was observed. Presumably the steric effect of two isopropyl groups also prevents the reaction of a second molecule of formaldehyde and diisopropylamine with the mono-Mannich base. These Mannich bases distil readily provided they are first washed to remove the nitrous

$$CH_3CH_2NO_2 + HCHO + \left[\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\right]_2 NH \longrightarrow CH_3CHCH_2N\left[CH<\begin{matrix}CH_3\\CH_3\end{matrix}\right]_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

acid salt of diisopropylamine, the product of a side reaction[6]; if not removed these salts often cause violent decompositions during the distillation. The bases, if not used immediately after distillation, should be stored at 0° to prevent a slow decomposition.

The Mannich base of nitroethane was also made using the more compact amines, diethylamine and piperidine. The diethylamine reacted readily, but all attempts to distil the resulting base at reduced pressure resulted in rapid and complete decomposition of the reaction mixture. It should be noted that steric strain or lack of it, is not necessarily related to thermal stability. This was observed also by Senkus.[2] The piperidine base was prepared in the manner described by Blomquist[7] with minor modifications in temperature and method of addition. In contrast to the diisopropylamino base, a substantial amount of the disubstituted compound was present and this was removed completely with great difficulty.

The alkylation studies were carried out under the usual conditions for such reactions including a nitrogen atmosphere and sodium alkoxide catalyst. Three esters with active methylene groups, namely, ethyl malonate, ethyl acetoacetate and ethyl acetylsuccinate, were alkylated. Usually it is necessary to remove the displaced amine as it is formed to prevent its readdition to the olefinic bond. However, the slowness with which diisopropylamine adds to unsaturated systems[3] made this removal less important, and yields were essentially the same at temperatures where the amine was removed as compared to reactions where the amine remained in solution.

Table I shows the maximum yield obtained in the alkylation of these three esters under a variety of conditions. Use of sodium butoxide is butanol, which permitted a reflux temperature at which the eliminated diisopropylamine was volatile, gave no increase in yield over the lower boiling ethanol except for ethyl malonate. In all cases the yield of alkylated ester was more than doubled when 1-diisopropylamino-2-nitropropane was used instead of 1-piperidino-2-nitropropane. Since both of these Mannich bases give by amine displacement the same 2-nitropropene as an intermediate, it would appear that the difference in final yields must definitely be linked to ease of displacement of the amine. The amine that is thus eliminated can therefore be an important factor in these carbon–carbon alkylations.

TABLE I

ALKYLATION OF ACTIVE METHYLENE ESTERS

Mannich base	Alkylated molecule	Catalyst	Yield, %
1-Piperidino-2-nitropropane	Ethyl acetoacetate	NaOBu	17.3
	Ethyl malonate	NaOBu	12.8
	Ethyl acetylsuccinate	NaOBu	8.3
1-Diisopropylamino-2-nitropropane	Ethyl malonate	NaOEt	25.0
	Ethyl malonate	NaOBu	37.2
	Ethyl malonate	Triton B	47.0
	Ethyl acetoacetate	NaOEt or NaOBu	46.0
	Ethyl acetylsuccinate	NaOBu	27.4

To further investigate this effect on other types of compounds, the alkylation of 1- and 2-nitropropane with these Mannich bases was studied. Snyder and Hamlin[8] in the only previous report of alkylation with Mannich bases of nitroparaffins had used 1-dimethylamino- and 1-diethylamino-2-nitrobutane in the alkylation of 1- and 2-nitropropane. The dimethylamino base appeared to give slightly better yields than the diethylamino base. The use of diisopropylamine gave no greater yields (Table II) than Snyder had reported, but it did greatly decrease the reaction time for maximum yield. Particularly when used with trimethylbenzylammonium hydroxide (Triton B) as catalyst, the reaction was complete (as evidenced by lack of further amine evolution) within 30 minutes or less. Actually in one case the presence of additional catalyst other than the amine that was released was unnecessary for reaction to occur. Again it would appear that the use of an amine with large "F"-strain increases the speed of the reaction through the more facile formation of the intermediate unsaturated compound. Further work

(2) M. Senkus, THIS JOURNAL, **72**, 2069 (1950).
(3) O. Hromatka, *Ber.*, **75B**, 131 (1942).
(4) H. C. Brown and H. Pearsall, THIS JOURNAL, **67**, 1765 (1945).
(5) H. G. Johnson, *ibid.*, **68**, 12 (1946).
(6) N. J. Leonard and G. L. Shoemaker, *ibid.*, **71**, 1876 (1949).
(7) A. T. Blomquist and T. H. Shelley, *ibid.*, **70**, 147 (1948).
(8) H. R. Snyder and W. E. Hamlin, *ibid.*, **72**, 5082 (1950).

is continuing on the steric effect of the displaced amino group in these alkylations.

TABLE II

ALKYLATION OF NITROPARAFFINS

Mannich base	Alkylated molecule, propane	Catalyst	Time	Yield, %
1-Diisopropyl-	2-Nitro-	Triton B	35 min.	50
amino-2-	2-Nitro-	NaOH	3 hr.	44
nitrobutane	1-Nitro-	Triton B	15 min.	45
1-Diethyl-	1-Nitro-	NaOH	28 hr. at 90°	18[8]
amino-2-nitrobutane				
1-Dimethyl-	1-Nitro-	NaOH	8 hr. at 120°	34[8]
amino-2-	2-Nitro-	NaOH	8 hr. at 120°	55[8]
nitrobutane				
1-Diisopropyl-	2-Nitro-	Triton B	15 min.	52
amino-2-	2-Nitro-	None	1 hr.	43
nitropropane	2-Nitro-	NaOH	2.5 hr.	50
	1-Nitro-	Triton B	15 min.	33

Acknowledgment.—The authors wish to acknowledge a Frederick Gardner Cottrell grant from the Research Corporation under which most of this work was done.

Experimental

1-Diisopropylamino-2-nitropropane.—Fifteen grams (0.5 mole) of formaldehyde (as a 30% aqueous solution) was added dropwise to 50 g. of diisopropylamine, the temperature not being allowed to rise above 15°. After addition was complete, the mixture was stirred an additional hour at room temperature. This mixture was then added dropwise by means of a dropping funnel to 56 g. (0.75 mole) of nitroethane and stirred for three hours at room temperature. The organic layer was salted out, separated, washed and dried over sodium sulfate. Distillation at reduced pressure under nitrogen gave 64.0 g. of yellow-green oil, b.p. 99–103° (10 mm.), $n^{20}D$ 1.4497. This is a 66% yield. Titration with standard acid of an ethanolic solution of this oil using a Beckman *p*H meter gave a neutral equivalent of 187.8 as against a calculated value of 188.2.

Anal. Calcd. for $C_9H_{20}N_2O_2$: N, 14.90. Found: N, 15.01.

The hydrochloride salt when prepared by the usual method was a white crystalline compound, m.p. 127°.

Anal. Calcd. for $C_9H_{21}N_2O_2Cl$: Cl, 15.78. Found: Cl, 15.70.

The Mannich base is somewhat unstable and must be stored under nitrogen in a refrigerator. When allowed to stand at room temperature, a yellow solid appears which has a decomposition temperature above 200° and probably is a polymer of 2-nitropropene.

Anal. Calcd. for $(C_3H_6O_2N)_x$: N, 16.09. Found: N, 16.22.

1-Piperidino-2-nitropropane.—This base was made in a similar manner to the diisopropylamino base, first preparing the amine methylol compound in solution, and then adding the cold solution dropwise to the nitroethane, also maintained at 5–10°. After stirring at 7° for two hours, the reaction mixture was worked up as above; yield, using 0.5 molar quantities, was 45.0 g. (52.5%) of a clear oil boiling at 88–91° (3 mm.), $n^{22}D$ 1.4610.

The yield with this procedure was consistently higher than when the reverse addition[7] of the nitroparaffin in one lot to the amine methylol solution was used.

Blomquist and Shelley[7] report a boiling point of 87° at 1 mm. and of $n^{20}D$ 1.4469. Emmons[9] has reported more recently b.p. 67–68° at 1 mm., $n^{20}D$ 1.4650, which agrees very closely with our values.

1-Diisopropylamino-2-nitrobutane.—This Mannich base was prepared in the same manner as the 1-diisopropylamino-2-nitropropane using 0.5 mole of amine and of formaldehyde, and 0.75 mole of nitropropane. The 1-diisopropylamino-2-nitrobutane was obtained in 68% yield, b.p. 96–98° (3 mm.), $n^{22}D$ 1.4445.

Anal. Calcd. for $C_{10}H_{22}N_2O_2$: N, 13.85; neut. equiv., 202. Found: N, 14.05, 14.28; neut. equiv., 208.

1-Diethylamino-2-nitropropane.—This compound was prepared in a similar manner to the 1-piperidino-2-nitropropane, using one-half molar quantities of the reactants. The reaction proceeded smoothly, but all attempts to distil the product resulted in a rapid and complete decomposition.

Ethyl 2-Carbethoxy-4-nitrovalerate.—To 10 ml. of *n*-butyl alcohol was added 1.4 g. (0.06 mole) of sodium. After the sodium had reacted, 14.4 g. (0.09 mole) of ethyl malonate and 11.3 g. (0.06 mole) of 1-diisopropylamino-2-nitropropane were added and the mixture stirred rapidly. The temperature was raised to 90° and nitrogen was bubbled through the solution to expel the diisopropylamine as it was released. After 12 hours at this temperature, 25 ml. of ether was added, and the resulting solution washed with five 30-ml. portions of 10% hydrochloric acid and then twice with similar portions of water. After drying over sodium sulfate and removal of the more volatile solvents, the residue was distilled under reduced pressure. A yellow oil, 5.5 g. (37%), b.p. 125–126° (3 mm.), was obtained, $n^{20}D$ 1.4385, d^{23} 1.124.

Anal. Calcd. for $C_{10}H_{17}O_6N$: N, 5.65; *MR*, 57.30. Found: N, 5.45; *MR*, 57.66.

When the above was run using sodium ethoxide in ethanol as the catalyst, a reduced yield (25%) was obtained. In all runs there was a large, non-distillable residue of approximately 10 g. All attempts at characterizing this viscous liquid have been unsuccessful.

The replacement of 1-diisopropylamino-2-nitropropane with 1-piperidino-2-nitropropane in the above reaction, using the same conditions, yielded 1.9 g. (12.8%) of ethyl 2-carbethoxy-4-nitrovalerate, b.p. 126° (3 mm.), $n^{23}D$ 1.4390.

Ethyl 2-Acetyl-4-nitrovalerate.—This compound was prepared in the same manner as above using 50 ml. of butanol, 1.4 g. of sodium, 11.2 g. of 1-diisopropylamino-2-nitropropane and 10.0 g. of ethyl acetoacetate. This gave 6.0 g. (46% yield) of ethyl 2-acetyl-4-nitrovalerate, b.p. 128–130° (3 mm.), $n^{20}D$ 1.4858, d^{23} 1.162.

Anal. Calcd. for $C_9H_{15}O_5N$: N, 6.45; *MR*, 53.29. Found: N, 6.13; *MR*, 53.50.

Use of 0.06 mole of 1-piperidino-2-nitropropane in place of the 1-diisopropylamino-2-nitropropane gave 2.3 g. (17%) of the same ester, b.p. 128–130° (3 mm.), $n^{20}D$ 1.4832.

Ethyl 3-Acetyl-3-carbethoxy-5-nitrocaproate.—This compound was similarly prepared using 0.06 mole quantities as above with 15 g. of ethyl acetylsuccinate. This gave 5.0 g. (27%) of a yellow oil, b.p. 130° (1 mm.), $n^{23}D$ 1.4417, d^{23} 1.122.

Anal. Calcd. for $C_{13}H_{21}O_7N$: C, 51.51; H, 6.98; N, 4.63; *MR*, 71.12. Found: C, 51.25; H, 7.12; N, 4.98; *MR*, 71.5.

Again replacing the diisopropylamino base with the piperidino compound lowered the yield to 1.5 g. (8.3%), b.p. 130° (1 mm.), $n^{23}D$ 1.4430.

2,4-Dinitro-2-methylhexane.—Forty grams of 2-nitropropane, 12 g. of 1-diisopropylamino-2-nitrobutane and 10 ml. of 37% trimethylbenzylammonium hydroxide were heated at 125° until evolution of the amine ceased (35 minutes). The solution was cooled and extracted with three 25-ml. portions of ether. The ether extracts were washed twice with dilute acid, four times with water and dried over sodium sulfate. The ether and excess nitroparaffin were stripped off at reduced pressure. Fractional distillation gave 5.6 g. (49.5%) of 2,4-dinitro-2-methylhexane, b.p. 104–106° (2 mm.), $n^{20}D$ 1.4565 (lit.[8] b.p. 88–92° (0.3 mm.), $n^{20}D$ 1.4536).

Using 2.2 g. of sodium hydroxide as a catalyst in the above reaction yielded 4.5 g. (39%) of the dinitrohexane in one hour, and 5.0 g. (44%) after 3.5 hours.

3,5-Dinitroheptane.—Use of 0.06 mole of 1-diisopropylamino-2-nitrobutane, Triton B and excess 1-nitropropane as above produced in 15 minutes 5.1 g. of 3,5-dinitroheptane (45% yield); b.p. 115–116° (3 mm.), $n^{20}D$ 1.4535 (lit.[10] b.p. 115–116° (4 mm.)).

2,4-Dinitro-2-methylpentane.—Forty grams of 2-nitropropane, 11.3 g. of 1-diisopropylamino-2-nitropropane and 10 ml. of Triton B yielded 5.5 g. (52%) of 2,4-dinitro-2-methylpentane in 15 minutes, b.p. 104–106° (3 mm.), $n^{20}D$

(9) W. D. Emmons, THIS JOURNAL, **75**, 1993 (1953).

(10) C. T. Bahner and H. T. Kite, *ibid.*, **71**, 3597 (1949).

1.4525. The 4-bromo-2,4-dinitro-2-methylpentane melted at 77–79° (lit.[11] 76°).

Use of sodium hydroxide as catalyst yielded 5.3 g. (50%) after two hours reflux, b.p. 104–107° (3 mm.), $n^{20}D$ 1.4542. Use of no catalyst at all (except the released diisopropylamine) yielded 4.5 g. (44%) of the dinitropentane in one hour. However, the reaction left considerable residue, and the product was more difficult to purify than when Triton B was used.

2,4-Dinitrohexane.—Excess 1-nitropropane, 11.2 g. (0.06 mole) of 1-diisopropylamino-2-nitropropane and Triton B catalyst yielded 3.5 g. (33%) of 2,4-dinitrohexane in 15 minutes, b.p. 100–103° (3 mm.), $n^{20}D$ 1.4531.

Anal. Calcd. for $C_6H_{12}N_2O_4$: N, 15.91. Found: N, 16.13.

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(11) A. Lambert and H. A. Piggott, *J. Chem. Soc.*, 1489 (1947).

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

The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. VII. Acetonitrile

BY GEORGE J. JANZ AND SAMUEL C. WAIT, JR.

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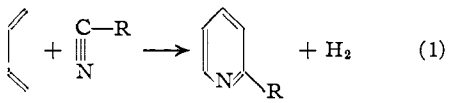
The reaction of acetonitrile with butadiene, isoprene and 2-methyl-1,3-pentadiene, at 400° yields 2-methylpyridine, 2,4-dimethylpyridine and 2,4,6-trimethylpyridine, respectively. The rate of reaction is appreciably enhanced by aluminum oxide as a catalyst. The relative reactivity of the dienes above was found to be 1:6:8, respectively, in the presence of the alumina surface. The preferential formation of one isomeric product, and the enhanced rate over the alumina are in accord with a semi-ionic Diels–Alder type reaction mechanism. Thermodynamic considerations show that the yield achieved over the alumina catalyst is approximately 8% of the value predicted for reaction equilibrium.

This communication reports the reaction of acetonitrile with butadiene, isoprene and 2-methylpentadiene-1,3 at 400°. Under comparable conditions it has been shown[1] that the (C≡N) group of organic nitriles adds to butadiene yielding 2-substituted pyridines as products. This reaction formulated as



(1)

has been demonstrated to be quite general for nitriles with R = H, CH_3, C_6H_5 and CN, respectively. With the exception of cyanogen which was more reactive, the relative reactivities of these nitriles were found to be of the same order of magnitude,[2] apparently little influenced by the internal electronic polarizability within these molecules. The present work extended these studies to determine the relative reactivities of substituted dienes in this reaction. Acetonitrile was selected as the nitrile since the reaction products, mono-, di- and trimethylpyridines are well known and can readily be characterized.

Experimental

Acetonitrile, isoprene and 2-methylpentadiene-1,3 (Eastman Organic Chemicals, Technical grade) were fractionally distilled before use. The physical constants for these were: b.p. 80–81° (1 atm.), $n^{25}D$ 1.3430; b.p. 32–33° (1 atm.), $n^{25}D$ 1.4187; b.p. 75–76° (1 atm.), $n^{25}D$ 1.4470, respectively. Butadiene was a C.P. grade (Matheson) and, after passing over anhydrous $CaCl_2$, was used without further purification. The aluminum oxide (Harshaw Chemical Co., Al-0501) had a composition of 99.5% Al_2O_3, and a surface area of 186 m.²/g. This alumina has been found[3] to have an activity almost as great as the Cr_2O_3–Al_2O_3 catalysts used in the previous investigations of this series. The continuous flow apparatus, the catalyst activation and procedure for an experiment have been described elsewhere in detail.[4] Nitrogen was used as an inert gas in the reactant feed in equimolal ratio to the diene and nitrile.

Production Separation and Identification.—The separation of 2-methylpyridine from the crude product of the butadiene–acetonitrile reaction, as well as the identification already has been described.[5] A similar procedure was followed for investigation of the crude product obtained from the isoprene–acetonitrile and methylpentadiene–acetonitrile reactions, respectively. In each case the reactants were passed over the catalyst bed at 400° using flow rates to give a 4-second contact time in the hot zone. The duration of an experiment was 2 hr. The short contact time was chosen to keep side reactions to a minimum, and the 2-hr. reaction period was selected to give results comparable with the earlier studies. It had been observed that the rate of reaction decreased rapidly if a catalyst bed was used for periods longer than 2 hr. After each 2-hr. period the catalyst was revivified by oxidation with a slow stream of oxygen at a temperature of 475° to remove the surface deposits. The experiment was then continued for another 2-hr. period. A series of such batch runs was made in each case until about 500 g. of crude product (sufficient for investigation) had been gained. The separation of the pyridinic product from the crude was as follows. The unreacted diene and nitrile were removed by distillation. The high-boiling residue in the pot was then extracted with 10% aqueous sulfuric acid to remove the pyridinic products. The latter were recovered from the aqueous acid layer by adding an excess of sodium hydroxide and steam distilling. The pyridinic products were isolated finally by ether extraction of the aqueous steam distillate, and recovered from the ether solution after drying over anhydrous sodium sulfate. For the quantitative determination of the amount of pyridinics, it was found that the non-aqueous potentiometric titration of bases[6,7] with perchloric acid in glacial acetic acid was applicable. An aliquot of the crude residue above after removal of the unreacted nitrile and diene was taken for this determination, thus avoiding the possible mechanical losses in the subsequent handling of the product during the separation of the actual pyridinic products. Picrate and picrolonate derivatives were prepared and purified by recrystallization according to Hackmann and Wibaut[8] for identification. The data are summarized in Table I. The mixed melting points were made with samples prepared from authentic samples of the 2,4- and 2,4,6-isomers. No appreciable depression was found. The composition of each product was confirmed by micro-analysis of the picrate derivatives.

Anal. of dimethylpyridine picrate. Calcd. for $C_{13}H_{12}N_4O_7$: C, 46.41; H, 3.60; N, 16.7. Found: C, 47.30;

(1) G. J. Janz and P. J. Hawkins, *Nature*, **162**, 28 (1948).

(2) G. J. Janz and R. E. Myers, Pt. IV, THIS JOURNAL, **75**, 1910 (1953).

(3) G. J. Janz and W. J. G. McCulloch, unpublished work.

(4) G. J. Janz, W. J. G. McCulloch and E. F. Timpane, *Ind. Eng. Chem.*, **45**, 1343 (1953).

(5) P. J. Hawkins and G. J. Janz, Pt. I, *J. Chem. Soc.*, 1479 (1949).

(6) J. F. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

(7) H. N. J. Wilson, *J. Soc. Chem. Ind. (London)*, **67**, 237 (1948).

(8) J. Th. Hackmann and J. P. Wibaut, *Rec. trav. chim.*, **162**, 229 (1943).