The Course of the Alkyl Nitrate Nitration with Isopropylpyridines. Formation of 2,3-Bis(pyridyl)-2,3-dimethylbutanes[1]

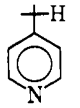
H. FEUER,* J. DOTY, AND J. P. LAWRENCE

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received July 31, 1972

The alkyl nitrate nitration of 4-isopropylpyridine (**1**) and 2-isopropylpyridine (**2**) does not afford the tertiary 2-nitro-2-(4-pyridyl)propane (**5**) and 2-nitro-2-(2-pyridyl)propane (**6**) but instead leads to dimers, 2,3-bis(4-pyridyl)-2,3-dimethylbutane (**3**) and 2,3-bis(2-pyridyl)-2,3-dimethylbutane (**4**), respectively. On the other hand, 3-isopropylpyridine (**7**) is recovered unchanged. The tertiary nitro compounds **5**, **6**, and 2-nitro-2-(3-pyridyl)propane (**8**) prepared by an alternate route are converted, respectively, to dimers **3**, **4**, and 2,3-bis(3-pyridyl)-2,3-dimethylbutane (**9**) under the conditions of the alkyl nitration. Compounds **5** and **6** are considered intermediates in the dimerization reactions which very likely proceed by an electron-transfer process. The intermediacy of the nitro compounds is established by the fact that both **5** and dimer **3** are obtained when the anion of **1** is added to the nitrate ester in liquid ammonia (inverse addition).

Recently, we reported on the successful application of the alkyl nitrate nitration to the preparation of primary and secondary α-nitroalkyl heterocyclic compounds.[1] We are now reporting the results of the reaction with tertiary alkyl heterocyclics, which were found to take a different course.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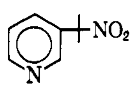
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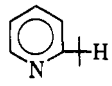
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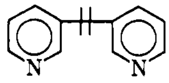
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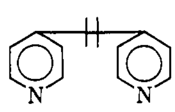
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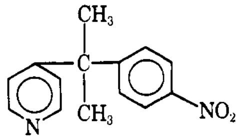
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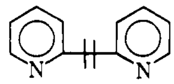
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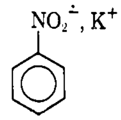
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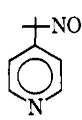
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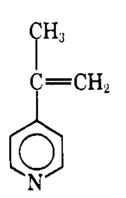
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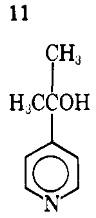
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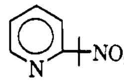
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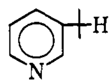
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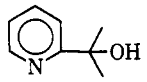
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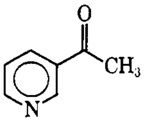
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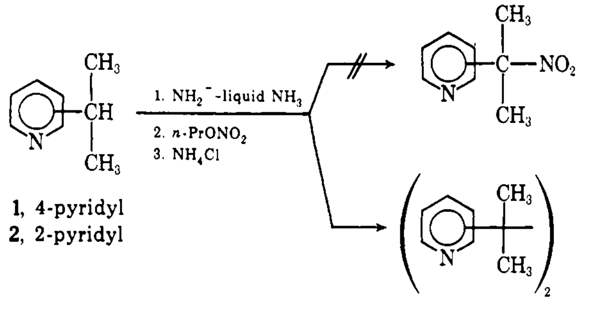
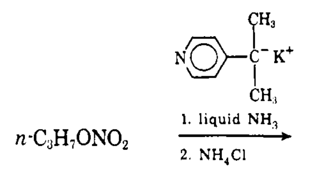
When 4-isopropylpyridine (**1**) was subjected to the alkyl nitrate nitration under the standard conditions (*vide infra*, Experimental Section) in the sodium amide–liquid ammonia system (A) or in the potassium amide–liquid ammonia system (B), 2,3-bis(4-pyridyl)-2,3-dimethylbutane (**3**) was obtained in 88% yield, instead of the expected tertiary nitro compound 2-nitro-2-(4-pyridyl)propane (**5**) (eq 1). Similarly, 2-isopropylpyridine (**2**) was converted to 2,3-bis(2-pyridyl)-2,3-dimethylbutane (**4**) in 90% yield in system B when the nitration time was 60 min. After the usual nitration time of 15 min, the yield was only 42%, and 47% of **2** was recovered. When the reaction was carried out in system A, no dimer was formed and compound **2** was recovered unchanged. Apparently, in sodium amide, compound **2** was converted to its anion at a much slower rate than the 4 isomer **1**. Similar results have been observed in alkylations of these compounds.[2]



3, 4-pyridyl
4, 2-pyridyl

(1)

In a control test, it was established that the alkyl nitrate[3] was necessary for the dimerization to occur. Moreover, good evidence was obtained that the tertiary nitro compounds 2-nitro-2-(4-pyridyl)propane (**5**) and 2-nitro-2-(2-pyridyl)propane (**6**) were very likely intermediates in the formation of the dimers **3** and **4**. For example, both **5** and **3** were obtained in yields of 60 and 32%, respectively, when, in an inverse addition, the anion of **1**, generated in system B, was added to *n*-propyl nitrate in liquid ammonia (eq 2). In system B the tertiary nitro compounds **5** and **6** (*vide infra* for their preparation) were converted in yields



$$n\text{-}C_3H_7ONO_2 \xrightarrow[\text{2. } NH_4Cl]{\text{1. liquid } NH_3} 3 + 5 \qquad (2)$$

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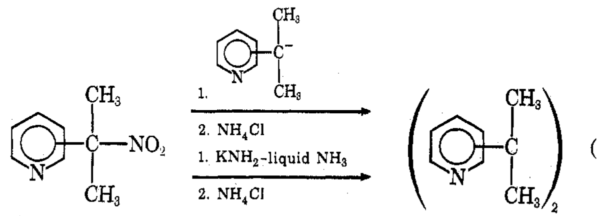
[1] Alkyl Nitrate Nitration of Active Methylene Compounds. X. For paper IX see H. Feuer and J. P. Lawrence, *J. Org. Chem.*, **37**, 3662 (1972).

[2] H. C. Brown and W. A. Murphy, *J. Amer. Chem. Soc.*, **73**, 3308 (1951).

[3] Dimer **3** was obtained in 50% yield when instead of *n*-propyl nitrate an alkyl nitrite, isoamyl nitrite, was employed.

of 70% to dimers **3** and **4**, respectively (eq 3). Also, these dimers were formed when **5** and **6**, respectively, were added to equimolar amounts of the carbanions of **1** and **2**, generated in system A and B (eq 3).

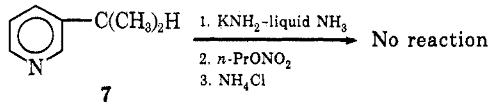


(3)

5, 4-pyridyl
6, 2-pyridyl
7, 3-pyridyl

3, 4-pyridyl
4, 2-pyridyl
9, 3-pyridyl

The intermediacy of the tertiary nitroisopropylpyridines in the dimerization reaction was firmly established in experiments with 3-isopropylpyridine (**7**), which was recovered unchanged when subjected to the alkyl nitrate nitration in system B. No trace of the expected dimer or nitro compound was obtained (eq 4). The failure of **7** to undergo dimerization or nitration cannot be attributed to lack of carbanion formation, for it has been shown to alkylate in system B to give 3-*tert*-butylpyridine.[2,4] Deuterium exchange reactions (see Experimental Section) have shown that **1**, **2**, and **7** incorporated 65, 9, and 4% deuterium, respectively. However, as indicated, **2** gave dimer **4** in 90% yield when the nitration time was extended from 15 to 60 min. On the other hand, no reaction occurred when **7** was subjected to a nitration time of 2 hr or when the nitrate ester was added slowly (4 hr). *n*-Propyl nitrate and **7** were recovered to the extent of 20 and 90%, respectively.



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(4)

On the other hand, the reaction of 2-nitro-2-(3-pyridyl)propane (**8**), which was prepared by an alternate route (*vide infra*), with the carbanion of **7** generated in system B gave the dimer 2,3-bis(3-pyridyl)-2,3-dimethylbutane (**9**) in 84% yield (eq 3). Also **8** underwent dimerization directly in system B to give **9** in nearly quantitative yield (eq 3).

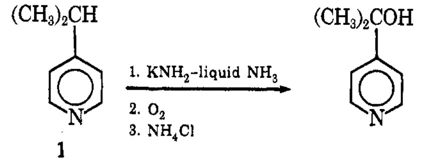
The structures of dimers **3**, **4**, and **9** were established by their infrared and nmr spectra, and also by their conversion to the corresponding dipicrates.

Discussion

Regarding the formation of dimers **3**, **4**, and **9**, steric considerations would seem to eliminate the possibility of a direct displacement of the tertiary nitro group in **5**, **6**, and **8** by the tertiary carbanion of **1**, **2**, and **7**. It is proposed that these dimerizations occur by electron-transfer processes related to reactions reported by Kornblum in which the tertiary nitro group of α,p-dinitrocumene was readily replaced by a variety of anions.[5]

Evidence that isopropylpyridines can participate in electron-transfer processes in the amide–liquid ammonia system was obtained in two experiments.

In system B, **1** was converted in the presence of oxygen to 2-(4-pyridyl)-2-propanol in 73% yield (eq 5).



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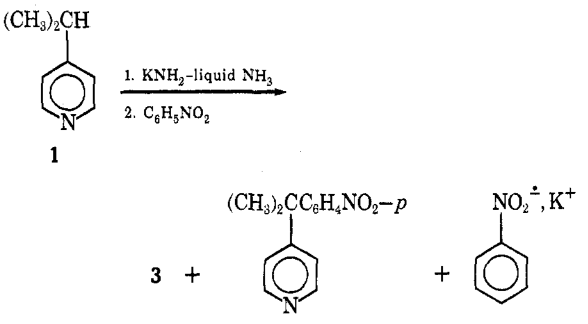
(5)

A study of the oxygenation of carbanions has shown that the reaction involves a radical–radical anion mechanism, and Russell has reported that *p*-nitrocumene was converted to *p*-nitrocumyl alcohol in the presence of base and oxygen.[6]

The reaction of **1** with nitrobenzene in system B gave 53% of dimer **3** and 10% of 2-(4-nitrophenyl)-2-(4-pyridyl)propane[7] (**10**) (eq 6). There was also obtained a red-brown solid believed to be potassium nitrobenzenide[8] (**11**). On addition of water, it decomposed to nitrobenzene. Russell has discussed many examples of electron-transfer processes.[9] The formations of **3**, **10**, and **11** in liquid ammonia are also believed to be initiated by a one-electron transfer between the carbanion of **1** and the electron acceptor nitrobenzene.



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10 **11**

(6)

By using the formation of dimer **3** as an example, the essential steps leading to dimerization are presented in Scheme I. The reaction is initiated by an electron transfer from the anion **1a** of **1** to compound **5** to form the radical anion A and isopropylpyridine radical B. A then collapses into nitrite ion and radical B (step 2), which then couples with **1a** to generate the radical anion C of dimer **3** (step 3). In the final step, the radical chain[10] is propagated by transfer of the odd electron from C to compound **5**, thereby forming **3** and regenerating A.[11]

The proposed scheme indicates that in the alkyl nitration of isopropylpyridines 0.5 equiv of the alkyl nitrate should be sufficient to obtain optimum yields

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[4] Similarly, 3-methylpyridine does not undergo the alkyl nitrate nitration in systems A or B.[1]

[5] N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *J. Amer. Chem. Soc.*, **89**, 5714 (1967).

[6] G. A. Russell, E. H. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and T. Strom, "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, Chapter 10.

[7] The scope of this reaction is being investigated.

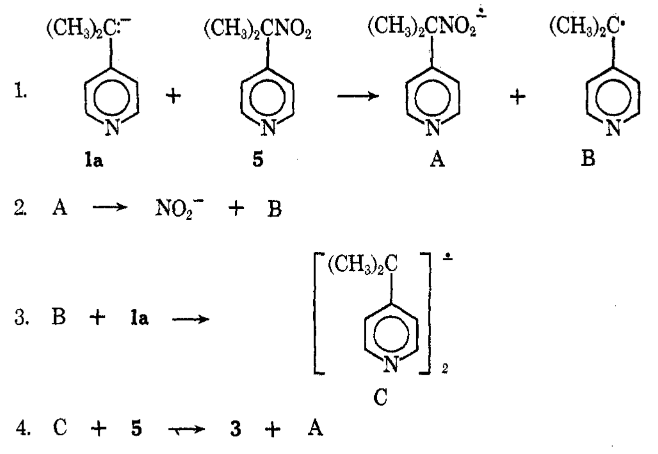
[8] G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

[9] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

[10] It is realized that dimer **3** could also form by the combination of radicals B. However, this process would be less favorable in the highly diluted solution in which the experiments were performed.

[11] A referee has pointed out that dimerization could occur by an anionic mechanism involving a front-side, four-centered mechanism; *e.g.*, attack of **1a** on **5** would give **3**.

Scheme I



of dimer, and also that acidification is unnecessary. The data presented in Table I bear this out.

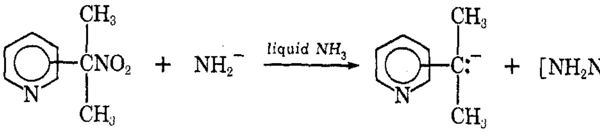
Table I

Alkyl Nitrate Nitration of 4-Isopropylpyridine[a] (1)

KNH$_2$, *M*	*n*-PrONO$_2$, *M*	NH$_4$Cl, *M*	Dimer 3, yield, %	Recovered 1, yield, %
2.0	2.5	2.0	71	
1.0	1.0	1.0	88	6
1.0	1.0		83	6
1.0	0.5		81	11

[a] In all experiments, 1 mol of 1 was used. The time for anion formation was 15 min and the total nitration time was 15 min.

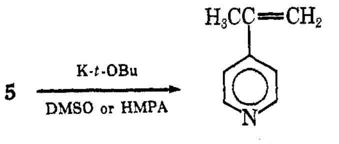
The direct formation of dimers from *tert*-nitroisopropylpyridines on treatment with amide in liquid ammonia requires an additional explanation. It is believed that the isopropylpyridine anion (the electron donor) is generated by displacement of the nitro group by amide ion (eq 7). An excess of base had to



(7)

be used to obtain maximum yields of dimer. For example, in the reaction of equimolar amounts of 5 and sodium amide, there was isolated in addition to 33% of dimer 3 and 42% of recovered 5, 1 in 12% yield. Apparently, the carbanion of 1 was protonated at some stage of the reaction (perhaps by the nitramide) and the excess base is necessary to regenerate the carbanion.

It should be pointed out that the base-solvent system is rather critical for the success of the dimerization. The reaction of 5 with potassium methoxide in methanol at reflux temperature led only to recovered starting material. A reaction did occur when 5 was treated with potassium methoxide in DMSO at 75° and at ambient temperatures with potassium *tert*-butoxide in DMSO or HMPA. However, the product of these reactions was not the dimer 3 but the olefin 4-isopropenylpyridine (12) arising from the loss of nitrous acid (eq 8).



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(8)

Synthesis of Nitroisopropylpyridines.—The synthesis of the nitroisopropylpyridines 5, 6, and 8 was achieved by direct nitration of the respective isopropylpyridines with 90% nitric acid. The results of various reaction conditions are presented in Table II. The data indicate that highest yields were obtained when reactions were carried out for 24 hr in sealed tubes at 100°. Under these reaction conditions there were also formed the tertiary alcohols 2 -(4-pyridyl)-2-propanol (13) and 2-(2-pyridyl)-2-propanol (14) from the nitration of 1 and 2, respectively, and 3-acetylpyridine (15) from the nitration of 7. It is obvious that reactions should be carried out in an autoclave. However, only a Hastelloy steel autoclave was available (composition, 60% Ni, 20% Fe, and 20% Mo) which was attacked by the nitric acid. Large amounts of nickel hydroxide were formed and the material balance was low owing to considerable decomposition of the starting material (see Table II).

Table II

Nitration of Isopropylpyridines with 90% Nitric Acid[a]

Reaction conditions: Time, hr	Reaction conditions: Temp, °C	Nitro compounds, yield, %: 5	Nitro compounds, yield, %: 6	Nitro compounds, yield, %: 8	Tertiary alcohols, yield, %: 13	Tertiary alcohols, yield, %: 14	Ketone, yield, %: 15
			Ambient Pressure				
26	100	56			2		
96	100		14			8	
48	100			15			17
			Sealed Tube				
24	100	70	55	35	5	30	31
24	75	32[b]	*c*		16		
24	50			*d*			
			Autoclave[e]				
24	100	58	17		7	12	

[a] The mole ratio of isopropylpyridine to nitric acid was 1:9. [b] About 42% of 1 was recovered. [c] No reaction occurred and 90% of 2 was recovered. [d] No reaction occurred and 98% of 7 was recovered. [e] Substantial amounts of Ni(OH)$_2$ were present. The material balance was low owing to considerable decomposition of the starting materials.

The structures of the nitroisopropylpyridines were established by their nmr spectra and also by their conversion into the respective picrates.

Experimental Section

Equipment.—All infrared spectra were taken with a Perkin-Elmer recording spectrophotometer, Models 21 and 421. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 analytical nmr spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph A-90S using either SF-96, SE-30, or DC-200 on Chromosorb P or Chromosorb W 4-ft columns. Solvents were evaporated on a Buchler flash evaporator.

Apparatus.—Reactions were performed in an oven-dried 500-ml four-necked flask equipped with a mechanical stirrer, Dry Ice condenser, thermometer, and pressure-equalizing addition funnel.

Materials.—*n*-Propyl nitrate of Eastman White Label grade, and nitric acid (90%), Baker Analyzed, were used as received. 4-Isopropylpyridine from Reilly Tar and Chemical Co. was distilled before use. 2- and 3-isopropylpyridines were prepared by the method of Brown and Murphy.[2]

2,3-Bis(4-pyridyl)-2,3-dimethylbutane (3). A. From 4-Isopropylpyridine (1).—To a freshly prepared solution of sodium amide (0.10 mol) in 300 ml of liquid ammonia was added 4-isopropylpyridine (12.0 g, 0.1 mol) at −35°. After the solution was stirred for 10 min, *n*-propyl nitrate (10.7 g, 0.10 mol) was added as rapidly as possible while the temperature was kept below −33°.[12] The mixture was then cooled to −50° and acidified with ammonium chloride (5.5 g, 0.11 mol), the ammonia was gradually replaced with absolute ether, and the reaction mixture was filtered after attaining room temperature (3-4 hr). The solid was stirred in 100 ml of methylene chloride and filtered. The combined ethereal and methylene chloride filtrates were concentrated *in vacuo* and the residue was recrystallized from 95% ethanol to give 10.5 g (88%) of 2,3-bis(4-pyridyl)-2,3-dimethylbutane (**3**): mp 205°; ir (KBr) 1600 cm^{-1} (C=N); nmr ($CDCl_3$) δ 8.5 (m, 4, N=CH), 7.0 (m, 4, N=CHCH), and 1.4 (s, 12, CH_3).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 79.85; H, 8.32; N, 11.52.

The combined alcohol filtrates were concentrated *in vacuo* to give 0.77 g (6%) of **1**. Its glpc retention time was identical with that of an authentic sample.

2,3-Bis(4-pyridyl)-2,3-dimethylbutane dipicrate was prepared in the usual manner,[13] mp 269° dec (95% EtOH).

Anal. Calcd for $C_{28}H_{26}N_8O_{14}$: C, 48.14; H, 3.72; N, 16.05. Found: C, 48.24; H, 3.95; N, 15.98.

B. From Compound 1 and 2-Nitro-2-(4-pyridyl)propane (5).—To a freshly prepared solution of sodium amide (0.057 mol) in 300 ml of liquid ammonia was added compound **1** (2.7 g, 0.023 mol). After the solution was stirred for 10 min at −33°, 2-nitro-2-(4-pyridyl)propane (**5**) (3.8 g, 0.023 mol) was added while the temperature was kept below −33°. Work-up of the reaction mixture as described in A except that 3.6 g (0.068 mol) of ammonium chloride was used gave 5.4 g (100%) of dimer **3**, mp 205° (95% EtOH). A mixture melting point determination with a sample prepared in A gave no depression.

C. From Compound 5 and Sodium Amide.—To a freshly prepared solution of sodium amide (0.065 mol) in 40 ml of liquid ammonia was added **5** (4.3 g, 0.026 mol) while the temperature was kept below −33°. The solution was stirred for 15 min, cooled to −45°, acidified with ammonium chloride (4.2 g, 0.078 mol), and worked up as described in A to yield 4.5 g (73%) of dimer **3**, mp 204° (95% EtOH).

2,3-Bis(2-pyridyl)-2,3-dimethylbutane (4). A. From 2-Isopropylpyridine (2).—The experimental procedure was similar to that described for the preparation of **3** from compound **1**, except that potassium amide (0.102 mol), 2-isopropylpyridine (**2**) (6.2 g, 0.051 mol), propyl nitrate (13.1 g, 0.128 mol), and ammonium chloride (6.0 g, 0.17 mol) were employed: and that after addition of the nitrate the reaction was continued for 60 min prior to acidification.

Recrystallization from hexane afforded 5.5 g (90%) of 2,3-bis(2-pyridyl)-2,3-dimethylbutane[14] (**4**): mp 121°; ir (KBr) 1587 cm^{-1} (C=N); nmr ($CDCl_3$) δ 8.4 (m, 2, N=CH), 6.3-7.4 (m, 6, N=CCH=CHCH), and 1.4 (s, 12, CH_3).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 79.69; H, 8.52; N, 11.80.

The combined hexane filtrates were concentrated *in vacuo* to give 0.2 g (2%) of **2**. Its glpc retention time was identical with that of an authentic sample.

2,3-Bis(2-pyridyl)-2,3-dimethylbutane dipicrate was prepared in the usual manner,[13] mp 228° dec (95% EtOH).

Anal. Calcd for $C_{28}H_{26}N_8O_{14}$: C, 48.14; H, 3.72; N, 16.05. Found: C, 48.32; H, 3.56; N, 16.05.

B. From Compound 2 and 2-Nitro-2-(2-pyridyl)propane (6).—The experimental procedure was similar to that described for the preparation of **3** from compounds **1** and **5** except that potassium amide (0.057 mol), 2-isopropylpyridine (2.3 g, 0.023 mol), 2-nitro-2-(2-pyridyl)propane (3.8 g, 0.023 mol), and ammonium chloride (3.6 g, 0.068 mol) were employed and that after addition of the nitrate the reaction was continued for 60 min prior to acidification.

Recrystallization from hexane afforded 5.2 g (95%) of dimer **4**, mp 120-121°. A mixture melting point determination with an authentic sample gave no depression.

C. From Compound 6 and Potassium Amide.—The experimental procedure was similar to that described for the preparation of **3** from compound **5** and sodium amide, except that 0.026 mol of potassium amide in 50 ml of liquid ammonia, 2.1 g (0.012 mol) of 2-nitro-2-(2-pyridyl)propane (**6**), and 1.9 g (0.035 mol) of ammonium chloride were employed and that after addition of the nitrate the reaction was continued for 60 min prior to acidification.

Recrystallization from hexane afforded 1.05 g (70%) of dimer **4**, mp 121°.

2,3-Bis(3-pyridyl)-2,3-dimethylbutane (9). A. From 3-Isopropylpyridine (7) and 2-Nitro-2-(3-pyridyl)propane (8).—The experimental procedure was similar to that described for the preparation of dimer **4** from compounds **2** and **6** except that potassium amide (0.02 mol) in 50 ml of liquid ammonia, 3-isopropylpyridine (**7**) (1.21 g, 0.01 mol), and 2-nitro-2-(3-pyridyl)propane (**8**) (1.66 g, 0.01 mol) were used.

There was obtained 2.1 g (84%) of 2,3-bis(3-pyridyl)-2,3-dimethylbutane (**9**): mp 168° (C_6H_{14}); ir (KBr) 1585 cm^{-1} (C=N); nmr ($CDCl_3$) δ 1.38 (s, 12, CH_3), 7.2 (m, 4, aromatic H), and 8.4 (m, 4, aromatic H).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.38; N, 11.66. Found: C, 79.75; H, 8.39; N, 11.71.

2,3-Bis(3-pyridyl)-2,3-dimethylbutane dipicrate was prepared in the usual manner,[13] mp 260° dec (95% EtOH).

Anal. Calcd for $C_{28}H_{26}N_8O_{14}$: C, 48.14; H, 3.72; N, 16.05. Found: C, 47.93; H, 3.92; N, 16.33.

B. From Compound 8 and Potassium Amide.—The experimental procedure was similar to that described for the preparation of **3** from **5** and sodium amide. From 0.026 mol of potassium amide in 50 ml of liquid ammonia, 1.84 g (0.011 mol) of 2-nitro-2-(3-pyridyl)propane (**8**) and 1.6 g (0.03 mol) of ammonium chloride there was obtained 1.3 g (94%) of dimer **9**, mp 168°. A mixture melting point determination with an authentic sample gave no depression.

Inverse Addition of 4-Isopropylpyridine Anion to *n*-Propyl Nitrate.—To a freshly prepared solution of potassium amide (0.05 mol) in 150 ml of liquid ammonia was added compound **1** (6.05 g, 0.05 mol) at −35°. After 15 min, the anion of **1** was added dropwise to a solution of *n*-propyl nitrate in 100 ml of ammonia at −40°. The reaction mixture was then stirred for 1 hr and acidified with ammonium chloride (2.65 g, 0.05 mol), and the ammonia was replaced by ether. Evaporation of the filtrate *in vacuo* left a suspension which was filtered to give 2.0 g (32%) of dimer **3**, mp 204° (C_6H_{14}). The filtrate was distilled to yield 5.0 g (60%) of 2-nitro-2-(4-pyridyl)propane (**5**): bp 70° (0.07 mm); $n^{20}D$ 1.5231; ir (neat) 1550 cm^{-1} (NO_2). An authentic sample (*vide infra*) had the same physical constants.

Oxidation of 4-Isopropylpyridine (1) in Liquid Ammonia.—To a freshly prepared solution of potassium amide (0.06 mol) in 200 ml of liquid ammonia was added compound **1** (7.2 g, 0.059 mol) at −35°. After 15 min of anion formation, oxygen was introduced into the ammonia solution for a period of 1 hr. The solution was cooled to −50° and acidified with ammonium chloride (3.2 g, 0.06 mol), the ammonia was replaced by ether, and the reaction mixture was filtered after room temperature was attained. The ether filtrate was concentrated *in vacuo* to yield 5.9 g (73%) of 2-(4-pyridyl)-2-propanol (**13**), mp 131° (C_6H_{14}) (lit.[15] mp 132°). A mixture melting point with an authentic sample (*vide infra*) gave no depression.

Reaction of 4-Isopropylpyridine (1) with Nitrobenzene.—To a freshly prepared solution of potassium amide (0.05 mol) in 150 ml of liquid ammonia was added compound **1** (3.02 g, 0.025 mol). The solution was stirred for 15 min at −35°, and then nitrobenzene (3.1 g, 0.025 mol) was added. The reaction mixture was stirred for 8 hr at −35° and acidified with ammonium chloride (2.65 g, 0.05 mol), the ammonia was replaced by ether (3-4 hr), and the reaction mixture was filtered after room temperature was attained. The ethereal filtrate was extracted with 3 *N* HCl, basified with 3 *N* sodium hydroxide, and again extracted with ether. The combined ethereal extracts were dried ($MgSO_4$) and concentrated *in vacuo* to yield 3.0 g of material. Column chromatography on neutral alumina yielded three components. Fraction I (hexane) was 0.5 g (8%) of 4-isopropylpyridine (**1**). Fraction II (hexane-ether, 1:1) was

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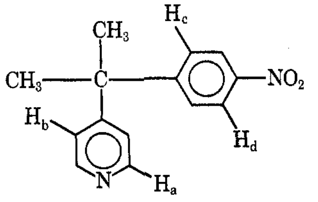
[12] *Caution!* The first few drops of alkyl nitrate should be added slowly because a considerable exotherm might develop.

[13] R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1957, p 229.

[14] G. Fraenkel and J. W. Cooper, *J. Amer. Chem. Soc.*, **93**, 7228 (1971), report mp 91° for this compound.

[15] C. R. Clemo and E. Hoggarth, *J. Chem. Soc.*, 41 (1941).

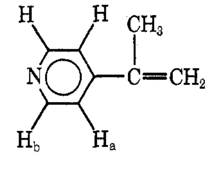
0.6 g (10%) of 2-(*p*-nitrophenyl)-2-(4-pyridyl)propane (**10**): mp 79–80° (C_6H_{14}); ir (KBr) 1595 (C=N), 1508 (NO_2), and 1340 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 1.70 (s, 6, CH_3), 7.1 (m, 2, H_b), 7.3 (m, 2, H_c), 8.1 (m, 2, H_d), and 8.6 (m, 2, H_a).



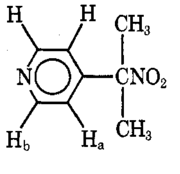
Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.42; H, 5.83; N, 11.57. Found: C, 69.16; H, 5.56; N, 11.73.

Fraction III (ether–acetone, 1:1) was 1.6 g (53%) of dimer **3**, mp 205°.

Reaction of 2-Nitro-2-(4-pyridyl)propane (5) with Potassium *tert*-Butoxide in DMSO.—To a dry 100-ml round-bottom flask flushed with nitrogen was added potassium *tert*-butoxide (2.8 g, 0.025 mol) and 50 ml of dry DMSO. The solution was degassed for 15 min and compound **5** (3.8 g, 0.0228 mol) was added by weight difference from a 5-ml syringe. After 4 hr at room temperature the reaction mixture was poured into water, extracted with 2 × 50 ml of ethyl ether, dried ($MgSO_4$), and concentrated *in vacuo* to yield 2.7 g (100%) of 4-isopropenylpyridine (**12**): n^{20}_{D} 1.5422; nmr ($CDCl_3$) δ 2.0 (s, 3, CH_3), 5.14 (s, 1, $=CH_2$), 5.50 (s, 1, $=CH_2$), 7.2 (m, 2, H_a), and 8.4 (m, 2, H_b).



2-Nitro-2-(4-pyridyl)propane (5).—The following experiment is typical of the procedure employed for the nitration of isopropylpyridines. 4-Isopropylpyridine (**1**) (12.0 g, 0.1 mol) and 90% nitric acid (35 ml) were heated at 100° in a sealed tube for 24 hr.[16] The solution was poured into 250 ml of water, basified with sodium hydroxide pellets, and extracted with ether. The combined ethereal extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Distillation of the residue and further purification of the distillate by chromatographing on alumina with ether as the eluent gave 11.6 g (70%) of 2-nitro-2-(4-pyridyl)propane (**5**): bp 70° (0.07 mm); n^{20}_{D} 1.5213; ir (neat) 1550 cm^{-1} (NO_2); nmr (CCl_4) δ 1.9 (s, 6, CH_3), 7.2 (m, 2, H_a), and 8.5 (m, 2, H_b).

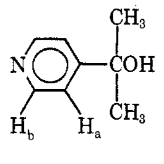


Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.83; H, 6.02; N, 16.87. Found: C, 58.04; H, 6.30; N, 17.16.

2-Nitro-2-(4-pyridyl)propane picrate was prepared in the usual manner,[13] mp 145–146° dec (95% EtOH).

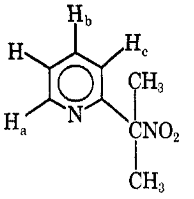
Anal. Calcd for $C_{14}H_{13}N_5O_9$: C, 42.53; H, 3.29; N, 17.72. Found: C, 42.69; H, 3.51; N, 17.51.

The aqueous solution was extracted with chloroform and dried ($MgSO_4$), and the combined extracts were concentrated *in vacuo* to give 0.7 g (5%) of 2-(4-pyridyl)-2-propanol (**13**): mp 130° (CCl_4) (lit.[15] mp 132°); nmr ($CDCl_3$) δ 1.6 (s, 6, CH_3), 4.8 (s, 1, OH), 7.4 (m, 2, H_a), and 8.4 (m, 2, H_b).



Reactions which were carried out at ambient pressures in refluxing nitric acid were worked up by a similar procedure.

2-Nitro-2-(2-pyridyl)propane (6).—2-Isopropylpyridine (**2**) (12.1 g, 0.1 mol) gave 4.2 g (30%) of 2-(2-pyridyl)-2-propanol (**14**), bp 39–40° (0.04 mm), mp 49–50° (CCl_4) (lit.[17] mp 50–51°), and 9.2 g (55%) of 2-nitro-2-(2-pyridyl)propane (**6**): bp 54–55° (0.04 mm); n^{20}_{D} 1.5163; ir (neat) 1555 cm^{-1} (NO_2); nmr (CCl_4) δ 1.9 (s, 6, CH_3) 7.0–7.8 (m, 3, H_b + H_c), and 8.3–8.5 (m, 1, H_a).

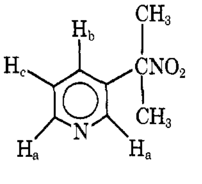


Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.83; H, 6.02; N, 16.87. Found: C, 57.70; H, 6.32; N, 17.16.

2-Nitro-2-(2-pyridyl)propane picrate was prepared in the usual manner,[13] mp 96–97° dec (95% EtOH).

Anal. Calcd for $C_{14}H_{13}N_5O_9$: C, 42.53; H, 3.29; N, 17.72. Found: C, 42.67; H, 3.57; N, 17.79.

2-Nitro-2-(3-pyridyl)propane (8).—The experimental procedure was similar to that described for the preparation of **5** except that 3-isopropylpyridine (**7**) (6.05 g, 0.05 mol) was used. After the ethereal extract was concentrated *in vacuo*, the residue was chromatographed on alumina. Elution with a 1:1 mixture of ether–hexane gave 2.8 g (35%) of 2-nitro-2-(3-pyridyl)propane (**8**): bp 89–90° (0.4 mm); n^{20}_{D} 1.5217; ir (neat) 1540 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 2.0 (s, 6, CH_3), 7.2 (m, 1, H_c), 7.8 (m, 1, H_b), and 8.6 (m, 2, H_a).

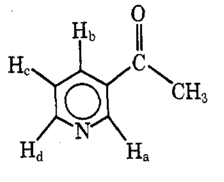


Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.83; H, 6.02; N, 16.87. Found: C, 57.90; H, 6.00; N, 16.91.

2-Nitro-2-(3-pyridyl)propane picrate was prepared in the usual manner,[13] mp 149–150° dec (95% EtOH).

Anal. Calcd for $C_{14}H_{13}N_5O_9$: C, 42.53; H, 3.29; N, 17.22. Found: C, 42.35; H, 3.46; N, 17.99.

Further elution of the column with ethyl ether gave 1.8 g (30%) of 3-acetylpyridine (**15**): nmr ($CDCl_3$) δ 2.64 (s, 3, CH_3), 7.3 (m, 1, H_c), 8.2 (m, 1, H_b), 8.7 (m, 1, H_d), and 9.1 (m, 1, H_a).



The nmr spectrum and glpc retention time were identical with those of an authentic sample.[18]

Deuteration of Isopropylpyridines.—The following experiment is typical of the procedure employed. To a freshly prepared solution of potassium amide (0.036 mol) in liquid ammonia (50 ml) was added **7** (2.18 g, 0.018 mol) at −35°. After 15 min, the ammonia was replaced by ether (30 min), and the reaction mixture was quenched with deuterium oxide (0.8 g, 0.04 mol) and filtered. The filtrates were concentrated *in vacuo* to yield 2.04 g of material. Nmr and mass spectra indicated about 4% deuterium incorporation at the tertiary carbon.

When the anion of **7** was quenched directly in the ammonia solution with deuterium oxide (tenfold excess), nmr and mass

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[16] *Caution!* The sealed tubes should be handled very carefully because of danger of explosion. Prior to opening, they should be cooled in liquid nitrogen.

[17] W. Sobecki, *Chem. Ber.*, **41**, 4103 (1908).

[18] An authentic sample of **15** was obtained from Aldrich Chemical Co.

spectra indicated about 4.5% incorporation of deuterium at the tertiary carbon.

Registry No.—**1**, 696-30-0; **2**, 644-98-4; **3**, 25128-23-8; **3** dipicrate, 25128-24-9; **4**, 25128-42-8; **4** dipicrate, 37387-92-1; **5**, 37387-93-2; **5** dipicrate, 37387-94-3; **6**, 37387-95-4; **6** picrate, 37387-96-5; **7**, 6304-18-3; **8**, 37387-98-7; **8** picrate, 37387-99-8; **9**, 37387-00-4; **9** dipicrate, 37388-01-5; **10**, 37388-02-6; **12**, 17755-30-5; **13**, 15031-78-4.

Acknowledgment.—We thank the Office of Naval Research and the Commercial Solvents Corporation for generous support. We are indebted to our colleague Professor Nathan Kornblum for helpful discussions.

Heteronuclear Stabilized Carbonium Ions. II. *N*-Aroyl- and Aryl-2-oxazolinium Cations. Intermediates in a New Class of Neighboring Group Reactions[1]

DONALD A. TOMALIA* AND JANET N. PAIGE

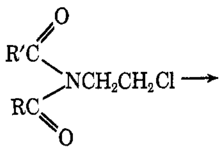
Edgar C. Britton Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

Received August 3, 1972

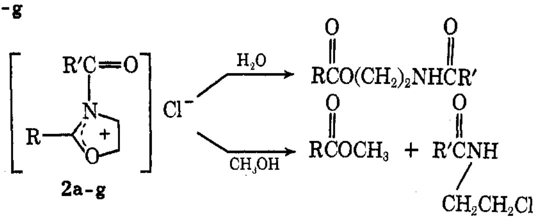
N-(2-Chloroethyl)-*N*-acyl/aroyl benzamides/acetamides were solvolyzed under several conditions: (a) in refluxing aqueous acetonitrile; (b) in aqueous acetonitrile with equimolar amounts of $AgNO_3$ (25°); and (c) in refluxing methanol. Hydrolyses produced the corresponding amido esters while methanolyses produced equimolar amounts of methyl esters and *N*-2-chloroethylamides. These solvolyses represent a new class of neighboring group reactions involving imide moiety participation, presumably *via* *N*-aroyl/acyl-2-oxazolinium cations. Several such cations were synthesized, isolated, and characterized. Evidence for the intervention of these cations in the solvolyses is presented. The preferred preparative route for the cations involved cyclization of appropriate *N*-(2-chloroethyl)imides with $AgBF_4$ or $AgSbF_6$. Selective participation of the better carbonium ion stabilizing carbonyl function was observed when cyclizing unsymmetrical imides. The ambident character of these cations was noted in that chloride ion attack occurred at the 5 position to produce *N*-(2-chloroethyl)imides; hydrolyses and methanolyses involved nucleophilic attack at the 2 position, producing, respectively, amido esters and equimolar amounts of methyl esters as well as 2-substituted 2-oxazolinium salts. Proposed solvolyses mechanisms are discussed.

Participation of amide groups *via* 2-oxazolinium salts to produce various solvolysis products is well known. These reactions have been studied extensively by Winstein,[2] Heine,[3] and others.[4,5] In some instances these 2-oxazolinium salts[2,6] have actually been isolated and characterized. Although this area has received considerable attention, to our knowledge no report of imide group participation has yet appeared in the literature.

Recently, we noted that certain imides [*i.e.*, *N*-(2-chloroethyl)-*N*-acyl/aroyl benzamides/acetamides, **1a–g**], underwent facile solvolysis reactions in aqueous acetonitrile or in methanol as shown below.



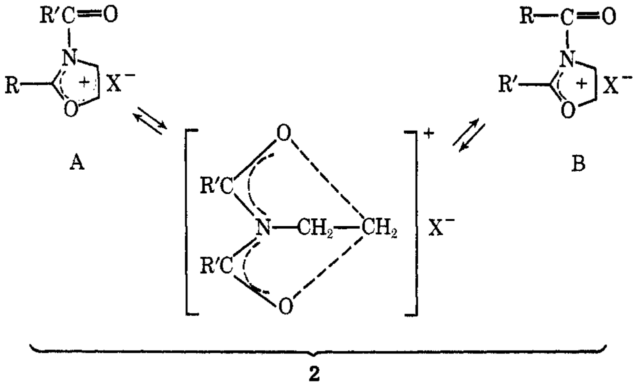
1a-g



2a-g

These transformations represent a new class of neighboring group reactions in which *N*-aroyl/acyl-2-oxazolinium cations, **2a–g**, are postulated as transient intermediates.

Fry[7] first proposed these cations as intermediates in the ring opening of 2-oxazolines with acid chlorides. More recently, Nehring and Seeliger[8] proposed these cations as intermediates in the thermal equilibration of *N*-(2-chloroethyl)-*N*-benzoyl acetamide to mixtures of the symmetrical *N*-(2-chloroethyl)-*N*-(aroyl/acyl) benzamide and acetamide.



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The unique structure of these cations offers the possibility of assessing various carbonyl participation aptitudes under equilibrating conditions as well as an opportunity to determine the effect of electronic and resonance properties of various R and R′ substituents on charge distribution in the oxazoline ring. As shown for the related 1,3-dioxolenium system,[9–11] the

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] S. Winstein, L. Goodman, and R. Boschan, *J. Amer. Chem. Soc.*, **72**, 2311 (1950).

[3] H. Heine, *ibid.*, **78**, 3708 (1956).

[4] B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

[5] S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **3**, 548 (1964).

[6] M. E. Kreling and A. G. McKay, *Can. J. Chem.*, **37**, 504 (1959).

[7] E. M. Fry, *J. Org. Chem.*, **15**, 802 (1950).

[8] R. Nehring and W. Seeliger, *Justus Liebigs Ann. Chem.*, **709**, 113 (1967).

[9] H. Hart and D. A. Tomalia, *Tetrahedron Lett.*, **No. 29**, 3383 (1966).

[10] D. A. Tomalia and H. Hart, *ibid.*, **No. 29**, 3389 (1966).

[11] H. Hart and D. A. Tomalia, *ibid.*, 1347 (1967).