

Henry Feuer*, James K. Doty and Nathan Kornblum

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

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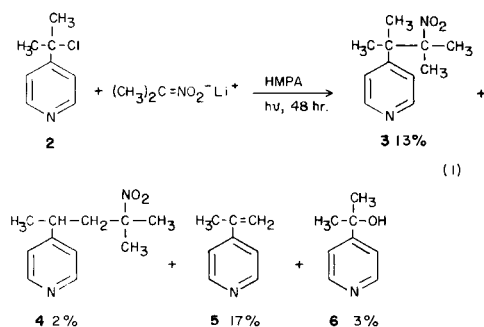
The reaction of 2-chloro-2-(4-pyridyl)propane (**2**) with lithium 2-propanenitronate affords the C-alkylation product 2-nitro-3-(4-pyridyl)-2,3-dimethylbutane (**3**), the Michael-adduct 2-nitro-2-methyl-4-(4-pyridyl)pentane (**4**), 4-isopropenylpyridine (**5**) and 2-(4-pyridyl)-2-propanol (**6**). Of these four products, only the formation of **3** is suppressed when the reaction is performed in the presence of radical inhibitors. The reaction of compound **2** with sodium azide gives the tertiary substitution product 2-azido-2-(4-pyridyl)propane (**8**). The reaction is not influenced by radical inhibitors. This is also the case in the reaction of **2** with sodium benzenethiolate, which affords 2-mercaptophenyl-2-(4-pyridyl)propane (**9**) and 1-mercaptophenyl-2-(4-pyridyl)propane (**10**). Compound **5**, the product of an E₂-type elimination is also formed in the azide and thiolate reactions. A Michael type addition of sodium benzenethiolate to **5** explains the formation of **10**. Similarly, generation of **5** in reactions of **2** with sodium methanethiolate and sodium cyanide accounts for the formation of 1-mercapto-methyl-2-(4-pyridyl)propane (**11**) and 3-(4-pyridyl)butanenitrile (**12**), respectively.

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Recently, we reported on reactions of 2-nitro-2-(4-pyridyl)propane (**1**) with nucleophiles which were found to proceed by electron transfer pathways (1). The present paper is concerned with reactions of 2-chloro-2-(4-pyridyl)propane (**2**) with various nucleophiles.

Treatment of **2** with lithium 2-propanenitronate in hexamethylphosphoric triamide (HMPA) under a "light source" (2) in an argon atmosphere afforded a mixture of products. After 48 hours at 30° the reaction was only 35% complete. Four products were obtained which were identified by comparison of their nmr spectra and gc retention times with those of authentic samples, as 2-nitro-3-(4-pyridyl)-2,3-dimethylbutane (**3**), 2-nitro-2-methyl-4-(4-pyridyl)pentane (**4**), 4-isopropenylpyridine (**5**), and 2-(4-pyridyl)-2-propanol (**6**) in yields of ca. 13%, 2%, 17%, and 3%, respectively (Equation 1). The amount of unreacted **2** was 65%.

In contrast to these results, the reaction of compound **1**



with lithium 2-propanenitronate gave only the C-alkylate **3** in 86% yield (1).

When the reaction, shown in Equation 1, was performed in the presence of radical inhibitors such as *m*-dinitrobenzene (*m*-DNB) or di-*t*-butylnitroxide (DTNB), only the

formation of C-alkylate **3** was inhibited. As shown by the data in Table I, the formation of the Michael adduct **4**, the olefin **5**, and the tertiary alcohol **6** was not influenced by the presence of inhibitors.

Evidence was obtained that olefin **5** was involved in the formation of **4**. When **5** was treated with lithium 2-propanenitronate in HMPA at ambient temperature, the reaction was complete in 115 hours and **4** was obtained in 70% yield (Equation 2).

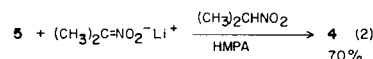


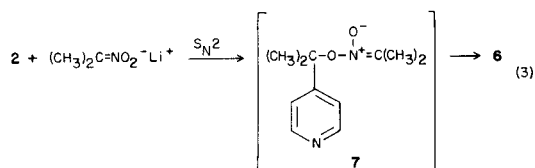
Table I

Effect of Inhibitors on the Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Lithium 2-Propanenitronate (a)

Inhibitor	Recovery, %		Yield, %		
	2	3 (b)	4 (c)	5 (d)	6 (e)
	65	13	2	17	3
<i>m</i> -DNB (11 mole %)	75	0	5	15	5
DTNB (13 mole %)	70	0	5	21	4

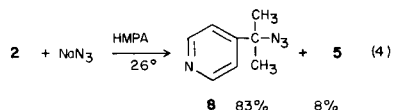
(a) Reactions were carried out in HMPA with FPT in the light for 48 hours. The molar ratio of **2** to the lithium salt was 1:10. The yield of products was determined by nmr and gc by comparison of the spectra and retention times with those of authentic samples. (b) 2-Nitro-3-(4-pyridyl)-2,3-dimethylbutane. (c) 2-Nitro-2-methyl-4-(4-pyridyl)pentane. (d) 4-Isopropenylpyridine. (e) 2-(4-pyridyl)-2-propanol.

The formation of the tertiary alcohol **6** is very likely due to the hydrolysis of the nitronic ester **7** which is presumed to arise from a S_N2-type displacement by 2-propanenitronate on compound **2** (Equation 3).



The reaction of Equation 1 is an example of competition between radical anion chain type and ionic type processes. Similar competitive events have been reported in the reaction of 3,5-bis(trifluoromethyl)cumyl chloride with lithium 2-propanenitronate (3).

The reaction of **2** with sodium azide under the lights for 168 hours gave 2-azido-2-(4-pyridyl)propane (**8**) in 83% yield. The only other product formed was the olefin **5** in 8% yield (Equation 4). The formation of **8** did not show the characteristics of an electron transfer process. The reaction proceeded equally well in the dark and in the presence of radical inhibitors such as *m*-DNB, DTBN, and oxygen.



Under all of these reaction conditions, the rate of tertiary azide formation was found to follow second order kinetics (4), first order in sodium azide and first order in compound **2**. A threefold increase in the concentration of sodium azide increased the rate approximately by a factor of 2.7 (Table II). The increase was not due to a positive salt effect, for addition of sodium perchlorate had little effect on the rate of the reaction.

Table II

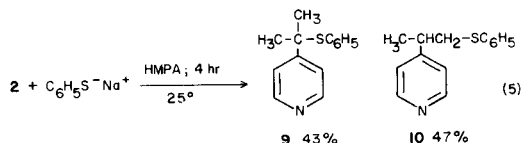
Pseudo First Order Rate Constants for the Reaction of **2** with Sodium Azide in HMPA (a)

Reaction Conditions	[NaN ₃] [M]	10 ⁶ k, sec ⁻¹
under the lights	0.05	6.55 ± 0.11
under the lights (b)	0.05	6.69 ± 0.10
under the lights (c)	0.05	6.26 ± 0.10
under the lights	0.15	17.52 ± 0.27
in the dark	0.05	6.57 ± 0.46
in the dark	0.15	18.00 ± 0.30

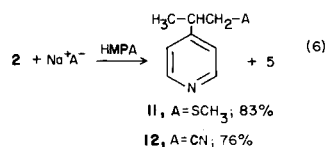
(a) The concentration of **2** was 0.01M. The rate constants and standard deviations were obtained from a computer analysis by the method of least squares. (b) In the presence of 0.01M *m*-DNB. (c) In the presence of 0.10M NaClO₄.

Also unaffected by light or radical inhibitors were the reactions of **2** with sodium benzenethiolate, sodium methanethiolate, and sodium cyanide.

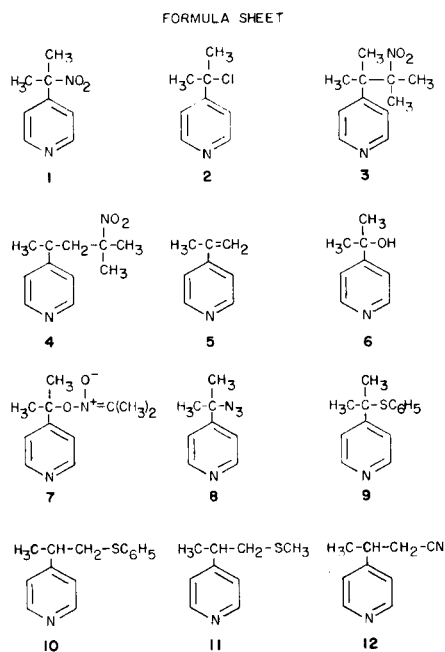
The reaction of **2** with sodium benzenethiolate in HMPA was complete in less than 4 hours at 25° and gave the two isomeric thioethers, 2-mercaptophenyl-2-(4-pyridyl)propane (**9**) and 1-mercaptophenyl-2-(4-pyridyl)propane (**10**) in yields of 43% and 47%, respectively (Equation 5). When the reaction was interrupted after 90 minutes, in addition to **9** and **10**, olefin **5** was also present.



The presence of **5** was also noted in reactions of **2** with sodium methanethiolate and sodium cyanide. The products of these reactions were the Michael adducts 1-mercaptomethyl-2-(4-pyridyl)propane (**11**) and 3-(4-pyridyl)butanenitrile (**12**) in yields of 83% and 76%, respectively (Equation 6).



Olefin **5** was obtained as the only product when **2** was treated in HMPA with sodium phenoxide or sodium methoxide. The yields were 83% and 90%, respectively.



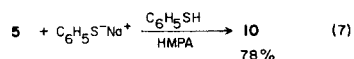
Discussion.

This investigation has shown that in contrast to 2-nitro-2-(4-pyridyl)propane (**1**), the reactions of 2-chloro-2-(4-pyridyl)propane (**2**) with nucleophiles proceed by ionic rather than electron transfer pathways. Except for the formation of 2-nitro-3-(4-pyridyl)-2,3-dimethylbutane (**3**) from **2** and sodium 2-propanenitronate, the formation of all products was found to proceed readily in the absence of light and was not influenced by the presence of radical inhibitors.

The difference in the course of reactions of compounds **1** and **2** with sodium azide is rather remarkable. While **1** was converted to 2,3-bis-(4-pyridyl)-2,3-dimethylbutane in a radical anion-free radical chain process (1), compound **2** gave the tertiary azide **8** in a S_N2 type displacement reaction. This was clearly indicated when the rate of the reaction was determined (Table II). Several examples of bimolecular reactions at a tertiary carbon atom have been substantiated in the literature (4).

With the chloride **2** the S_N2 displacement process competes with electron transfer substitution more effectively than in the case of *p*-nitro cumyl chloride. This is clearly a consequence of the greater ease with which *p*-nitro cumyl chloride undergoes electron transfer chain substitution.

The formation of primary adducts **4**, **10**, **11**, and **12** in the reaction of **2** with nucleophiles arises from a Michael-type addition of the nucleophile to 4-isopropenylpyridine (**5**) which was formed in all reactions studies. Evidence for this was obtained in control experiments illustrated by Equation 2, and by the reaction of sodium benzenethiolate with **5** in the presence of benzenethiol, which afforded **10** in 78% yield (Equation 7).



EXPERIMENTAL

Equipment.

All infrared spectra were taken with a Perkin Elmer recording spectrophotometer, Models 21 and 421. Nuclear magnetic resonance spectra were taken on a Model A-60 analytical nmr spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on either an Aerograph A-350B or A-700 using either 10% QF-1, Sf-96, or FFAP on acid washed Chromosorb W 10 ft columns. Solvents were evaporated on a Buchler flash evaporator.

Materials.

2-Nitropropane (IMC Chemical Group Inc.) 99.9% was distilled prior to use. Sodium azide (Baker Analyzed) was used as received. *m*-Dinitrobenzene (Matheson, Coleman and Bell) was recrystallized from 95% ethanol prior to use. Di-*t*-butylnitroxide (6) sodium benzenethiolate (1), sodium phenoxide (7) and lithium 2-propanenitronate (8) were prepared by methods described in the literature. HMPA (DuPont Chem. Corp.) was distilled from calcium hydride *in vacuo* (9). Argon and nitrogen were Airco high purity.

Sodium Methanethiolate.

To 350 ml of 2-propanol was added 9.2 g (0.40 g-atom) of sodium under a nitrogen atmosphere and the mixture refluxed for 3 hours. After all of the sodium had reacted, 25.0 g (0.52 mol) of methanethiol was condensed into the alcoholic solution by means of a Dry-Ice condenser. After 25 minutes, the solution was concentrated *in vacuo* and 100 ml of cyclohexane was added. The isopropanol-cyclohexane azeotrope was removed *in vacuo*. This procedure was repeated seven times and the solution evaporated to dryness. The resulting white solid was dried at 55° (0.8 mm) for 5 hours. Potentiometric titration with 0.1009*N* hydrochloric acid of a sample dissolved in water gave an equivalent weight of 72.0; theoretical 70.0.

The Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium Azide.

The following is representative of the general procedure for the reactions of compound **2** with nucleophiles.

A. In the Light Source.

Into a 3-necked round-bottom flask were placed 3.28 g (50 mmoles) of sodium azide and 100 ml of HMPA. In the side arm test tube was placed 1.55 g (10 mmoles) of **2** (**10**). The reaction mixture was subjected to F.P.T. three times under argon (**11**). Then the test tube was inverted and the reaction placed in the light source (**2**) at 26°.

After 168 hours, the reaction mixture was poured into 200 ml of water layered with 100 ml of ether. The aqueous phase was extracted with 3 x 100 ml portions of ether. The extracts were washed with 4 x 100 ml portions of water, dried (calcium chloride) and concentrated *in vacuo* to yield 1.70 g of material. Nmr analysis indicated the presence of 90% 2-azido-2-(4-pyridyl)propane (**8**) and 8% 4-isopropenylpyridine (**5**).

Distillation of this material afforded 1.40 g (86%) of compound **8**: bp 58-60° (0.15 mm); n_D^{25} 1.5251; ir (neat) 2083 (N_3) and 1595 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.60 (s, 6, CH_3), 7.30 (m, 2, pyr C_3H , C_5H) and 8.60 (m, 2, pyr C_4H , C_6H).

The analytical sample was obtained by preparative glpc using a A-350B with a 10 ft FFAP (10%) on Chromosorb W column at 150°.

Anal. Calcd. for $C_8H_{10}N_4$: C, 59.25; H, 6.18; N, 34.57. Found: C, 59.51; H, 6.30; N, 34.49.

B. In the Absence of Light.

Experiment A was repeated except that the reaction flask was wrapped with three layers of aluminum foil to exclude light, and the reaction allowed to proceed on the benchtop at 26° for 168 hours. Nmr analysis of the crude material (1.67 g) indicated the presence of azide **8** (92%) and olefin **5** (6%). Distillation afforded 1.50 g (88%) of pure **8**.

C. In the Presence of *m*-Dinitrobenzene (*m*-DNB).

Experiment A was repeated in the presence of 1.68 g (10 mmoles) of *m*-DNB. After 168 hours, the organic phase was extracted with 3 x 50 ml portions of 3*N* hydrochloric acid, dried (magnesium sulfate) and concentrated *in vacuo* to give 1.60 g (95%) of recovered *m*-DNB, mp 88° [lit. (12) mp 90°]. The acidic extracts were basified with solid sodium carbonate, extracted with 4 x 50 ml portions of ether, dried (calcium chloride) and concentrated *in vacuo* to yield 1.62 g of material. Nmr analysis indicated the presence of azide **8** (89%) and olefin **5** (4%). Distillation afforded 1.48 g (85%) of pure **8**.

D. In the Presence of Di-*t*-butylnitroxide (DTBN).

Experiment A was repeated in the presence of 1.44 g (10 mmoles) of DTBN. After 168 hours, the reaction mixture was worked up and the material was evacuated at 25° (0.5 mm) for 4 hours. From the dry-ice trap was obtained 1.20 g (83%) of recovered DTBN. Distillation of the evacuated material afforded 1.41 g (82%) of pure **8**.

E. In the Presence of Oxygen.

Experiment A was repeated again except that the F.P.T. procedure was omitted and oxygen was passed through the solution *via* a syringe needle for the entire reaction time. Distillation of the crude material afforded 1.50 g (88%) of pure **8**.

Procedure for the Determination of Rate Constants for the Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium Azide.

On each side of a 2 l beaker filled with water and provided with a stirrer, was placed the light source (**2**). The temperature was maintained at $25 \pm 1^\circ$ by circulating water from a constant temperature bath through a copper coil placed in the bottom of the beaker.

In the absence of light, the rate constants were determined in a standard constant temperature bath.

Standard solutions of 0.25M sodium azide, 0.1M sodium perchlorate, and 0.1M tertiary chloride **2** were prepared in HMPA. Into a 100 ml volumetric flask were pipetted appropriate volumes of the standard solutions, and the mixture was diluted to 100 ml with HMPA. Then the flask was placed in the constant temperature bath at 25° . Samples of the reaction mixture (1 ml) were periodically removed *via* pipette and added to a mixture consisting of 1.5 ml water and 3 ml benzene. The mixture was stirred *ca.* 30 seconds and the benzene layer, which contained any unreacted **2**, was separated. After a second washing with benzene, 4 ml of standard electrolyte (prepared from 100 ml of acetic acid and 7 ml of nitric acid and diluted to 1 l with deionized water) was added to the aqueous sample followed by a small amount (*ca.* 10 mg) of sodium nitrite (to destroy azide ion). The solution was stirred for 5 minutes and excess sodium nitrite destroyed by adding two drops of concentrated nitric acid and urea (*ca.* 0.5 g). After stirring for 5 minutes, the amount of chloride ion was determined as silver chloride by silver electrolysis using a Buchler-Cotlove Chloridometer. Samples of the standard electrolyte were titrated in a similar manner to determine whether any contaminant was introduced into the chloride ion solution. The accuracy of the procedure was determined to be about 0.5% by titrating samples of a standard sodium chloride solution.

The pseudo first order rate constants were calculated by the method of least squares, and were then corrected for azide ion concentration.

The Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Lithium 2-Propanenitronate.

A. In the Light Source.

The general procedure was employed except that 2.38 g (25.0 mmoles) of lithium 2-propanenitronate, 0.39 g (2.5 mmoles) of **2** and 50 ml of HMPA were used. After 48 hours, the reaction mixture was poured into water and extracted with 4 x 50 ml portions of ether-benzene (50:50 v/v). The combined extracts were washed with water, dried (calcium chloride) and concentrated *in vacuo* to give 0.38 g of a mixture. Nmr and gc analyses of this mixture indicated that 35% of **2** had reacted and that four compounds were present namely 13% 2-nitro-3-(4-pyridyl)-2,3-dimethylbutane (**3**), 2% 2-nitro-2-methyl-4-(4-pyridyl)pentane (**4**), 17% 4-isopropenylpyridine (**5**), and 3% 2-(4-pyridyl)-2-propanol (**6**). Their gc retention times and nmr spectra were identical to these of authentic samples (**1**). Unreacted **2** was present to the extent of 65%.

B. Inhibition Studies.

Experiment A was repeated in the presence of 0.048 g (0.29 mmole) of *m*-dinitrobenzene. After 48 hours, the reaction mixture was worked up to give 0.43 g of product. Nmr and gc analyses showed that 25% of **2** had reacted and that compounds **4**, **5** and **6** had formed in yields of 5%, 15%, and 5%, respectively, and that none of compound **3** was present.

Experiment A was repeated except this time in the presence of 0.046 g (0.32 mmole) of di-*t*-butylnitroxide. Compounds **4**, **5**, and **6** were formed in yields of 5%, 21%, and 4%, respectively and, *again*, compound **3** could not be detected by nmr or gc.

2-Methyl-2-nitro-4-(4-pyridyl)pentane (**4**).

Under a nitrogen atmosphere, 12 g (0.1 mole) of 4-isopropenylpyridine was added to 9.5 g (0.1 mole) of lithium 2-propanenitronate and 20 g (0.22 mole) of 2-nitropropane dissolved in 150 ml of HMPA. The reaction was allowed to proceed in the dark at ambient temperature for 115 hours. Then the mixture was poured into 250 ml of ice-water and extracted with 4 x 150 ml portions of ether. The extract was dried (magnesium sulfate)

concentrated *in vacuo* and distilled to yield 14.5 g (69.7%) of compound **4**, bp 94° (0.03 mm); n_D^{20} 1.5090; ir (neat): 1630 (C=N), 1538 and 1351 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.23 (d, 3, CH_3), 1.48 (d, 6, CH_3), 2.25 (d, 2, CH_2), 2.70 (m, 1, CH), 7.10 (m, 2, pyr C_3H , C_5H) and 8.20 (m, 2, pyr C_2H and C_6H).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$: C, 63.45; H, 7.71; N, 13.45. Found: C, 63.36; H, 7.79; N, 13.24.

1-Mercaptophenyl-2-(4-pyridyl)propane (**10**).

A mixture consisting of 0.132 g (1.0 mmole) of sodium benzenethiolate, 1.10 g (10 mmoles) of benzenethiol, 0.8 g (6.60 mmoles) of 4-isopropenylpyridine (**5**) and 75 ml of HMPA was stirred under nitrogen for 18 hours at ambient temperature. The aqueous phase was extracted with 4 x 100 ml portions of benzene-ether (50:50, v/v). The combined extracts were washed with 3 x 50 ml portions of 5% aqueous sodium hydroxide and extracted with 3 x 50 ml portions of 1M hydrochloric acid. The extracts were basified with 30% sodium hydroxide and extracted with 3 x 50 ml portions of ether. The combined organic extracts were washed with 3 x 50 ml portions of water, dried (magnesium sulfate) and concentrated *in vacuo* to yield 1.116 g (74%) of pure **10** n_D^{20} 1.6027; ir (neat): 1597 (C=N) and 735 cm^{-1} (C-S); nmr (deuteriochloroform): δ 1.31-1.38 (d, 3, CH_3), 2.70-3.20 (m, 3, CHCH_2), 7.2 (m, 7, C_6H_5 and pyr C_3H , C_5H) and 8.5 (m, 2, pyr C_2H , C_6H).

The analytical sample was prepared by gc using an Aerograph A600 with a 4 feet DC-200 on Chromosorb W column at 160° .

Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{NS}$: C, 73.45; H, 6.54; N, 6.11; S, 13.90. Found: C, 73.68; H, 6.60; N, 6.28; S, 13.71.

Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium Benzenethiolate.

A. In the Light Source (**2**).

The general procedure was followed except that 7.0 g (53 mmoles) of sodium benzenethiolate, 1.55 g (10 mmoles) of compound **2** and 100 ml of HMPA were used.

After 4 hours, the reaction mixture was poured into water and extracted with 4 x 50 ml portions of ether-benzene (50:50, v/v). The organic phase was extracted with 2 x 50 ml portions of 1.0M hydrochloric acid, the acid extract basified with sodium carbonate and extracted with 4 x 50 ml portions of ether. The combined ethereal extracts were washed with water, dried (calcium chloride) and concentrated *in vacuo* to yield 2.10 g (92%) of a mixture consisting of 43% 2-mercaptophenyl-2-(4-pyridyl)propane (**9**) (**1**); nmr (deuteriochloroform): δ 1.65 (s, 6, CH_3), 7.20 (m, 7, C_6H_5 and pyr C_3H , C_5H) and 8.50 (m, 2, pyr C_2H , C_6H); and 47% 1-mercaptophenyl-2-(4-pyridyl)propane (**10**); nmr (deuteriochloroform): δ 1.31-1.38 (d, 3, CH_3), 2.70-3.20 (m, 3, CH-CH_2), 7.20 (m, 7, C_6H_5 and pyr C_3H , C_5H) and 8.50 (m, 2, pyr C_2H , C_6H). The nmr spectral data and gc retention times of **9** and **10** were identical to those of authentic samples. No attempt was made to separate this mixture.

B. In the light source without F.P.T.

Experiment A was repeated except that 1.65 g (12.5 mmoles) of sodium benzenethiolate, 0.39 g (2.5 mmoles) of compound **2**, and 25 ml of HMPA were used. The reaction was carried out under nitrogen for 90 minutes at ambient temperature. Nmr and gc analyses of the crude product (0.45 g) indicated the presence of chloride **2** (10%), olefin **5** (10%), thioether **9** (42%), and thioether **10** (38%).

C. In the Absence of Light.

Experiment B was repeated except that the reaction was carried out in the dark for 90 minutes at ambient temperature. Nmr and gc analyses of the crude product (0.48 g) indicated the presence of chloride **2** (17%), olefin **5** (9%), thioether **9** (40%) and thioether **10** (34%).

D. In the Presence of Nitrobenzene.

Experiment B was repeated again in the presence of 0.63 g (5 mmoles) nitrobenzene. Nmr and gc analyses of the crude reaction mixture (1.05 g) indicated the presence of chloride **2** (10%), olefin **5** (12%), thioether **9** (39%), thioether **10** (36%), and nitrobenzene (95%).

The Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium methanethiolate.

A. In the Light Source.

The general procedure was employed except that 2.1 g (30 mmoles) of sodium methanethiolate, 1.55 g (10 mmoles) of compound **2** and 100 ml of HMPA were used. The reaction was allowed to proceed for 4 hours at ambient temperature. The mixture was poured into 200 ml of water and extracted with 4 x 40 ml portions of ether. The extract was washed with water, dried (calcium chloride) and distilled to give 1.35 g (81%) of 1-mercaptomethyl-2-(4-pyridyl)propane (**11**), bp 72° (0.2 mm); n_D^{20} 1.5473; ir (neat): 1597 (C=N) and 735 cm^{-1} (C-S); nmr (deuteriochloroform): δ 1.37 (d, 3, CH_3), 2.01 (s, 3, CH_3S), 2.50-3.20 (m, 3, CHCH_2), 7.10 (m, 2, pyr C_3H , C_5H) and 8.51 (m, 2, pyr C_2H , C_6H).

Anal. Calcd. for $\text{C}_9\text{H}_{13}\text{NS}$: C, 64.67; H, 7.79; N, 8.38; S, 19.16. Found: C, 64.82; H, 7.64; N, 8.40; S, 18.90.

B. In the Absence of Light.

Experiment A was repeated and the reaction was allowed to proceed for 4 hours at ambient temperature. Work up gave 1.33 g (80%) of thioether **11**.

The reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium Cyanide.

A. In the Light Source.

The general procedure was followed except that 2.45 g (50 mmoles) of sodium cyanide, 1.55 (10 mmoles) of **2** and 100 ml of HMPA were used. The reaction was 85% complete after 10 days.

The reaction mixture was poured into 100 ml of water, extracted with 4 x 50 ml portions of ether, the extract washed with water and dried (calcium chloride). Concentrating the solution *in vacuo* gave 0.51 g (34%) of 3-(4-pyridyl)butanenitrile (**12**), mp 69-70° (hexane); ir (potassium bromide): 2252 (CN) and 1610 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.42 (d, 3 CH_3), 2.60 (d, 2, CH_2), 3.72 (m, 1, CH), 7.72 m, 2, pyr C_3H , C_5H) and 8.60 (m, 2, pyr C_2H , C_6H).

The analytical sample was obtained by distillation at 70° (0.1 mm).

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_2$: C, 73.99; H, 6.84; N, 19.17. Found: C, 74.25; H, 7.01; N, 18.90.

B. With No Additional Light Source at 75°.

The experimental procedure described in A was followed except that the reaction was carried out under nitrogen at 75° on the benchtop without F.P.T. and without the aid of any additional light source for 7 hours. The reaction mixture was worked up and the residue recrystallized from hexane to yield 1.10 g (76%) of **12**.

The Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium Methoxide.

The general procedure was employed except that 1.25 g (23.1 mmoles) of sodium methoxide, 0.775 g (5 mmoles) of compound **2** and 25 ml of HMPA were used. The reaction was carried out under nitrogen at 10° for 2 hours without F.P.T. and without the aid of any additional light source. The reaction mixture was poured into 100 ml of water and extracted with ether, the extracts washed with water and dried (calcium chloride). Concentrating the solution *in vacuo* gave 0.54 g (90%) of 4-isopropenyl-

pyridine (**5**); n_D^{20} 1.5421 [lit. (13) mp 1.5422].

The Reaction of 2-Chloro-2-(4-pyridyl)propane (**2**) with Sodium Phenoxide.

The general procedure was employed except that 5.60 g (50 mmoles) of sodium phenoxide, 1.55 g (10 mmoles) of compound **2** and 100 ml of HMPA were used. The reaction was carried out at 0° under nitrogen without F.P.T. and without the aid of any additional light source.

After 16 hours the reaction mixture was poured into 200 ml of water and extracted with 4 x 50 ml portions ether. The combined extracts were treated with 25 ml of 0.75M hydrochloric acid. The acid extract was basified with sodium carbonate, extracted with 4 x 50 ml portions of ether, dried (magnesium sulfate) and concentrated *in vacuo* to yield 1.00 g (84%) of 4-isopropenylpyridine (**5**).

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REFERENCES AND NOTES

- (1) H. Feuer, J. K. Doty and N. Kornblum, *J. Heterocyclic Chem.*, **15**, 1419 (1978).
- (2) The light source employed in all experiments consisted of two 20-watt General Electric F20T12 daylight fluorescent lights.
- (3) B. N. Newton, Ph.D. Thesis, Purdue University, January 1972, cited by N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).
- (4) A. Miotti and A. Fava, *J. Am. Chem. Soc.*, **88**, 4274 (1966); F. G. Bordwell and T. Mecca, *ibid.*, **94**, 2119 (1972); R. A. Sneen and P. S. Kay, *ibid.*, **94**, 6983 (1972); R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973); C. A. Grob, K. Seckinger, S. W. Tam and R. Traber, *Tetrahedron Letters*, 3051 (1973).
- (5) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser and d. H. Snow, *J. Am. Chem. Soc.*, **89**, 725 (1967); N. Kornblum, *Proc. Int. Cong. Pure Appl. Chem.*, 23rd, **4**, 81 (1971).
- (6) A. K. Hoffman, A. M. Feldman, E. Gelblum and A. Henderson, *Org. Synth.*, Coll. Vol. **5**, 355 (1973).
- (7) M. F. Berny and R. Perrin, *Bull. Soc. Chim. France*, 1013 (1967).
- (8) N. Kornblum, S. D. Boyd and N. Ono, *J. Am. Chem. Soc.*, **96**, 2580 (1974).
- (9) **CAUTION**. HMPA should be handled with care since it has been reported to cause nasal tumors in rats; *Chem. Eng. News*, **54** (5), 3 (1976).
- (10) H. Feuer and J. K. Doty, *J. Heterocyclic Chem.*, **15**, 1517 (1978).
- (11) A. detailed description of the freeze-pump-thaw procedure is given in reference 1.
- (12) R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds", 5th Ed., John Wiley and Sons, New York, NY, 1967, p. 371.
- (13) H. Feuer, J. Doty and J. P. Lawrence, *J. Org. Chem.*, **38**, 417 (1973).