TABLE II

1-STYRYLDIHYDROISOQUINOLINE METHIODIDES[a]

Compd	Mp, °C[b]	Yield, %[c]
5a	168–170	78
5b	202–204	92
5c	236–238	97
5d	194–197	86
5e	232–235	54
5f	195–198	43
5g	205–208	58
5h	205–207	58

[a] Satisfactory analytical values (C, H, N) were reported for all compounds (Ed.). [b] All the compounds melted with decomposition. [c] Yields are based on the starting amides.

Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.52; H, 7.06; N, 4.46.

Registry No.—**5a**, 22796-30-1; **5b**, 22796-31-2; **5c**, 22796-32-3; **5d**, 22796-33-4; **5e**, 22796-34-5; **5f**, 22796-35-6; **5g**, 22796-36-7; **5h**, 22796-37-8; **7**, 22796-38-9.

Acknowledgment.—This work was supported by Grant CA-06140 from the National Cancer Institute.

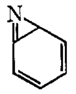
Structural Rearrangements of Arylnitrenes and Related Intermediates[1]

RICHARD J. SUNDBERG AND STUART R. SUTER

Department of Chemistry, University of Virginia,
Charlottesville, Virginia 22901

Received July 11, 1969

A number of skeletal rearrangements are believed to involve the conversion of arylnitrenes into isomeric reactive intermediates. These include the formation of derivatives of 2-amino-3H-azepine when phenylnitrene is formed in the presence of amines by thermal or photolytic decomposition of phenyl azide[2a,b] or photolysis of N-phenyloxaziridines.[2c,d] It has been proposed that the skeletal rearrangement involves conversion of singlet phenylnitrene[2c] into the azirine intermediate **1**, which subsequently reacts with amines to give azepines.[2a] Azepine formation is also observed during thermal deoxygenation of nitrosobenzene[3] or nitrobenzene[4] by trivalent phosphorus compounds and in photochemical deoxygenations[5] of aromatic nitro compounds in triethyl phosphite. Phenylnitrene is considered to be an intermediate in the pyrolytic conversion of phenyl azide into cyanocyclopentadiene.[6] We have also attributed the formation of pyridine derivatives during photochemical deoxygenation of *o*-alkylnitrobenzenes[5] or thermal deoxygenation of *o*-alkylnitrosobenzenes[7] to skeletal rearrangements of aryl nitrenes. The formation of azobenzene by pyrolysis of triazolo[1,5-*a*]pyridine is considered to involve the rearrangement of 2-pyridylcarbene to phenylnitrene.[8] As a step toward providing insight into the nature of the intermediates in these rearrangements, we have investigated further the structural relationships between the starting material and product in the conversion of *o*-nitrotoluene into N-(*o*-tolyl)-2-acetimidylpyridine (**4**).



1

o-Nitrotoluene labeled with ^{14}C at C-1 was prepared and subjected to photochemical deoxygenation in triethyl phosphite.[5] 2-Acetylpyridine was isolated by hydrolysis of **4** and subjected to the degradation shown in Scheme I. The data in Table I prove that C-1 in *o*-nitrotoluene becomes the exocyclic carbon atom in **5**.

SCHEME I

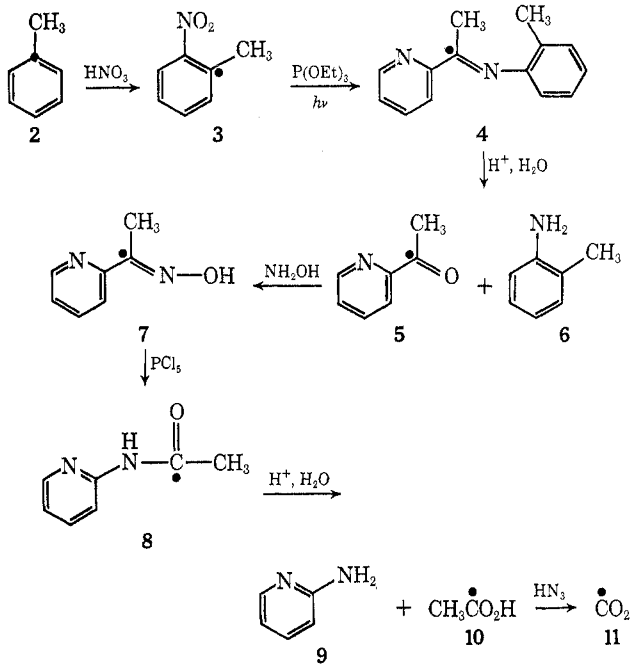


TABLE I

SPECIFIC ACTIVITY DATA

Compd	Specific activity, dpm/mmol	Dilution factor
2	1.07×10^6	1
3	0.51×10^6	2
7	0.51×10^6	2
8	0.26×10^6	4
9	0.64×10^4 [a]	4
11[b]	0.17×10^6	4

[a] Activity prior to the final recrystallization was 1.1×10^4. Further purification by preparative tlc led to no reduction in activity. [b] As $BaCO_3$.

---

(1) Supported by National Institutes of Health, Grant GM-14344-02.

(2) (a) R. Huisgen and M. Appl, *Chem. Ber.*, **91**, 12 (1958); (b) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966); (c) J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1445 (1968); (d) E. Meyer and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, **6**, 634 (1967).

(3) R. A. Odum and M. Brenner, *J. Amer. Chem. Soc.*, **88**, 2074 (1966).

(4) J. I. G. Cadogan and M. J. Todd, *Chem. Commun.*, 178 (1967).

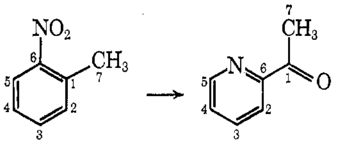
(5) R. J. Sundberg, B. P. Das, and R. H. Smith, Jr., *J. Amer. Chem. Soc.*, **91**, 658 (1969).

(6) (a) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967); (b) E. Hedaya, M. E. Kent, D. W. McNeil, R. P. Lossing, and T. McAllister, *ibid.*, 3415 (1968); (c) W. D. Crow and C. Wentrup, *ibid.*, 5569 (1968).

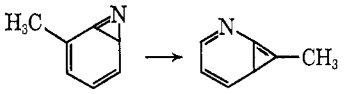
(7) R. J. Sundberg, *J. Amer. Chem. Soc.*, **88**, 3781 (1966).

(8) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968).

Taken in connection with earlier data on nitroxylenes,[5] these results define the structural relationship between *o*-nitrotoluene and 2-acetylpyridine, as shown



above. These data rule out our most recent mechanistic proposal.[5] Other proposals[9,10] are in accord with these results, although the nature of the rearranged intermediate and its relationship to the azirine **12** remain incompletely defined. The azirine **12** may be formed and undergo further skeletal rearrangement to **13**.[10] However, an intermediate containing the rearranged skeleton and a molecule of triethyl phosphite cannot be ruled out at this point.



12 **13**

Experimental Section

o-**Nitroluene-1-^{14}C.**—Toluene-1-^{14}C (9.2 g, 0.1 mol, 50 μCi, New England Nuclear) was nitrated using the procedure of Hurd and Jenkins.[11] Vacuum distillation of the product using a 290-mm spinning-band still gave *o*-nitrotoluene (4.48 g) containing 11% *para* isomer. A second fraction (1.38 g, 79% pure) was also colected.

Photolysis of *o*-Nitrotoluene-1-^{14}C in Triethyl Phosphite.—*o*-Nitrotoluene (6.85 g, 0.0500 mol, 0.51 × 10^6 dpm/mmol, 5.5% *p*-nitrotoluene impurity) was dissolved in freshly distilled triethyl phosphite (*ca.* 190 ml) and the solution was flushed with nitrogen for 30 min and then photolyzed for 24 hr using a type S 200-W Hanovia mercury lamp and Pyrex filter. A nitrogen flow was maintained through the solution during the photolysis. The unreacted triethyl phosphite was distilled from the reaction mixture, bp 25–30° (0.3 mm), followed by a fraction, bp 30–62° (0.25 mm), containing triethyl phosphate and *o*-nitrotoluene. The residue was mixed with 10% hydrochloric acid (100 ml) and continuously extracted with ether for 24 hr. The aqueous layer was separated and made alkaline with 30% sodium hydroxide. The solution was extracted with ether. The extract was dried, concentrated, and distilled, giving a mixture containing 2-acetylpyridine (0.44 g, 0.0036 mol, 14%) and *o*-toluidine (1.26 g, 0.0118 mol, 24%) as indicated by nmr analysis.

2-(Acetyl-1-^{14}C)pyridine Oxime (7).—The mixture of **5** and **6** described above was added to a solution of hydroxylamine hydrochloride (1.4 g) and sodium hydroxide (0.8 g) in water (10 ml). The resulting mixture was stirred at room temperature for 20 hr. The pH was adjusted to 7 with acetic acid and the solution was extracted with ether. The ether was dried (potassium carbonate) and evaporated, leaving an oil from which the oxime crystallized. The solid was washed with petroleum ether, giving **7** (0.247 g), mp 117–118° (lit.[12] mp 121°), having an ir spectrum identical with that of an authentic sample.

N-(2-Pyridyl)acetamide-1-^{14}C (8).—2-Acetylpyridine oxime (0.236 g, 0.00173 mol) was dissolved in anhydrous ether (5 ml) and the solution was cooled in ice. Phosphorus pentachloride (0.530 g, 0.00255 mol) was added with stirring to the cooled solution. The solution was stirred for 30 min at 0° and then refluxed gently for 1.25 hr. The reaction mixture was poured onto ice. The resulting aqueous solution was made alkaline with 30% sodium hydroxide and extracted with ether. The crude product obtained by evaporation of the ether was triturated with hexane and filtered, giving **8** (0.145 g, 61%), mp 61–65° (lit.[13] mp 71°), having an ir spectrum identical with that of an authentic sample.

Hydrolysis of N-(2-Pyridyl)acetamide-1-^{14}C.—A solution of **8** (0.218 g, 0.00160 mol) in 6 *N* hydrochloric acid (5 ml) was refluxed for 3 hr. The solution was cooled, made alkaline with 30% sodium hydroxide, extracted with ether, dried over potassium carbonate, and evaporated to give 2-aminopyridine (0.128 g, 0.00136 mol, 85%), mp 53–55°, 55–57° after recrystallization from hexane (lit.[14] mp 56°).

Evaporation of the aqueous alkaline solution gave residual salts (1.88 g) which were used in the Schmidt degradation described below.

Schmidt Reaction on Sodium Acetate.[15]—The residual salts were mixed with concentrated sulfuric acid (6 ml) and cooled to 0°, and sodium azide (0.31 g) was added. The reaction was swept with carbon dioxide free nitrogen which was then passed through 5% potassium permanganate in 5% sulfuric acid into barium hydroxide solution. The reaction flask was heated at 80–85° for 2.5 hr and 64 mg of barium carbonate was collected.

Counting Procedures.—Samples of compounds **2**, **3**, **7**, **8**, and **9** were counted in toluene solution (10 ml) containing 4.0 g/l. of POP and 50.0 mg/l. of POPOP on a Nuclear-Chicago Model 723 counter. Counting efficiencies, as determined from a standard channels-ratio quenching curve, ranged from 69 to 81%. The barium carbonate was counted on a planchet using a Nuclear-Chicago 2-π gas-flow low-background counter. Dilutions with inactive materials were made during the degradative scheme, as noted in Table I.

Registry No.—**2**, 22794-71-4; **3**, 22794-72-5; **7**, 22866-46-2; **8**, 22794-73-6; **9**, 504-29-0.

Acknowledgment.—We thank Professor Oscar R. Rodig for advice on technique and counting procedures.

---

[9] R. J. Sundberg, W. G. Adams, R. H. Smith, Jr., and D. E. Blackburn, *Tetrahedron Lett.*, 777 (1968).

[10] J. I. G. Cadogan, *Quart. Rev.* (London), **22**, 222 (1968).

[11] C. D. Hurd and W. W. Jenkins, *J. Org. Chem.*, **22**, 1418 (1957).

[12] T. Nakashima, *Yakugaku Zasshi*, **77**, 1298 (1957); *Chem. Abstr.*, **52**, 6345 (1958).

[13] R. Camp, *Arch. Pharm.* (Weinheim), **240**, 345 (1902).

[14] W. Marckwald, *Ber.*, **26**, 2187 (1893).

[15] A. R. Friedman and E. Leete, *J. Amer. Chem. Soc.*, **85**, 2141 (1963).

Studies of Nitriles. II.[1a] Synthesis of β,β-Dichloroacrylonitrile and Its Reactions with Some Nucleophilic Reagents[1b]

NAOTO HASHIMOTO, YASUHIKO KAWANO, AND KATSURA MORITA

Chemical Research Laboratories, Research and Development Division, Takeda Chemical Industries, Ltd., Juso, Osaka, Japan

Received March 6, 1969

β,β-Dichloroacrylonitrile (I) was first prepared by Miller and Kalnins[2] in 1967 by reducing α-acetoxy-β,-β,β-trichloropropionitrile with zinc dust in boiling THF. The previous paper[1a] dealt with a novel pyrolytic coupling reaction of chloroacetonitrile. Now the proposed mechanism of the reaction led us to an idea that, when carbon tetrachloride or chloroform is pyrolyzed with acetonitrile, β,β-dichloroacrylonitrile would probably be obtained as depicted by the following reactions.

$$CCl_4 \longrightarrow \cdot CCl_3 + \cdot Cl \qquad (1)$$

$$Cl\cdot + CH_3CN \longrightarrow \cdot CH_2CN + HCl \qquad (2)$$

$$\cdot CCl_3 + \cdot CH_2CN \longrightarrow Cl_3CCH_2CN \qquad (3)$$

$$Cl_3CCH_2CN \longrightarrow Cl_2C{=}CHCN + HCl \qquad (4)$$

---

[1] (a) Paper I: N. Hashimoto, K. Matsumura, and K. Morita, *J. Org. Chem.*, **34**, 3410 (1969); (b) presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1968.

[2] B. Miller and M. V. Kalnins, *Tetrahedron*, **23**, 1145 (1967).