Proton exchange processes, which also occur in our systems, will be the subject of future publications. We are also involved in experiments to determine the effect of other phosphonium halides as well as ammonium halides on hydrogen bonding in nonpolar media. Acids, other than phenols, are also being investigated.

Registry No.—*p*-**1**, 150-76-5; *m*-**1**, 150-19-6; *o*-**1**, 90-05-1; *p*-**2**, 98-54-4; *m*-**2**, 585-34-2; *o*-**2**, 88-18-6; *p*-**3**, 106-44-5; *m*-**3**, 108-39-4; *o*-**3**, 95-48-7; *p*-**4**, 101-53-1; *o*-**4**, 534-83-8; *p*-**5**, 1073-72-9; *p*-**6**, 831-82-3; *m*-**6**, 713-68-8; *o*-**6**, 2417-10-9; **7**, 108-95-2; *p*-**8**, 371-41-5; *m*-**8**, 372-20-3; *o*-**8**, 367-12-4; *p*-**9**, 106-48-9; *m*-**9**, 108-43-0; *o*-**9**, 95-57-8; *p*-**10**, 106-41-2; *m*-**10**, 591-20-8; *o*-**10**, 95-56-7; *p*-**11**, 540-38-5; *m*-**11**, 626-02-8; *o*-**11**, 533-58-4; *p*-**12**, 99-76-3; *o*-**12**, 119-36-8; *p*-**13**, 99-93-4; *m*-**13**, 121-71-1; *o*-**13**, 118-93-4; *p*-**14**, 767-00-0; *m*-**14**, 873-62-1; *o*-**14**, 611-20-1; *p*-**15**, 123-08-0; *m*-**15**, 100-83-4; *o*-**15**, 90-02-8; *p*-**16**, 100-02-7; *m*-**16**, 554-84-7; *o*-**16**, 88-75-5; *p*-**17**, 92-69-3; *m*-**17**, 580-51-8; *o*-**17**, 90-43-7; *p*-**18**, 1137-42-4; *o*-**18**, 117-99-7; *p*-**19**, 6554-98-7; *p*-**20**, 599-64-4; *p*-**21**, 1689-82-3; *m*-**22**, 99-07-0; chloride ion, 16887-00-6.

Acknowledgment.—The very generous donation, by Hans-Dieter Becker, of several phenols used in this work is gratefully acknowledged.

Nitrones. IV.[1a] A Facile Cope-Type Reaction

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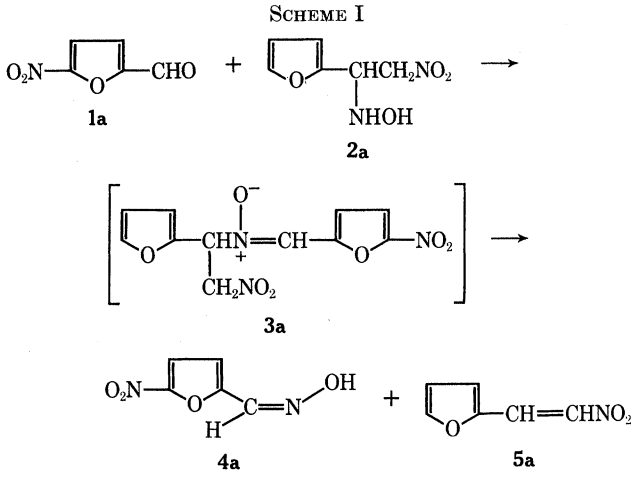
Received April 17, 1970

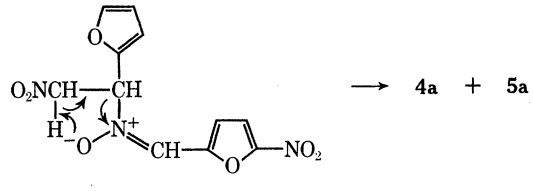
As part of a study of nitrofurylnitrones,[1a] we wanted a compound containing a nitro group in the *N*-alkyl portion of α-(5-nitro-2-furyl)-*N*-alkylnitrone. Attempts to synthesize α-(5-nitro-2-furyl)-*N*-(1-furyl-2-nitroethyl)nitrone (**3a**) by the reaction of 5-nitrofurfural (**1a**) and *N*-(1-furyl-2-nitroethyl)hydroxylamine (**2a**)[2] at room temperature gave unexpected results. Thin layer chromatography (tlc) of the reaction mixture revealed two components which were readily separated by column chromatography to give 2-(2-nitrovinyl)furan (**5a**)[3] and 5-nitro-2-furaldehyde *anti*-oxime (**4a**).[4] Their identity was proven by comparison with authentic samples (Scheme I).

While we were unable to isolate any reaction intermediates, we believe nitrone **3a** is formed as an intermediate and rearranges spontaneously to the observed products. This reaction is analogous to the pyrolysis of tertiary amine oxides[5] (the Cope reaction), of aldazine

SCHEME I



monoxides,[6] and of the methoxazonyl group.[7] The presence of a strong electron-withdrawing group on the α carbon of the nitrone must be essential for spontaneous rearrangement since Hurd and Patterson[2] were able to isolate α-phenyl-*N*-(1-phenyl-2-nitroethyl)nitrone. We propose a mechanism involving a five-membered transition state[8,9] as shown below.



To study the scope of this rearrangement, we successfully extended the reaction to other aromatic carboxaldehydes: 5-nitro-2-thiophenecarboxaldehyde (**1e**), 5-nitro-2-pyrrolecarboxaldehyde (**1f**), *p*-nitrobenzaldehyde (**1g**), 5-nitro-2-furanacrolein (**1h**), and *o*-nitrocinnamaldehyde (**1i**), and to other *N*-(1-aryl-2-nitroethyl)hydroxylamines, **2b**, **2c**, and **2d**.

Yields of aldoximes and nitro olefins isolated by silica gel column chromatography were 46–83 and 35–97%, respectively (see Table I). Assignments to *anti*-aldoximes were based on comparisons of nmr spectra[10] (DMSO-d_6) and melting points with authentic samples.

Although authentic samples of anti and syn isomers of **4e** are not reported, the assignment was made on the basis that rearrangement would produce an anti isomer. The nmr spectrum of **4f** showed the presence of two nitrone methine protons at 8.21 (syn) and 7.65 (anti) in a 1:1 ratio. Nmr analysis could not be applied to the vinyl oximes **4h** and **4i**. The spectra of the anti isomers **4h** and **4i** were different from those of the syn isomers; however, signals due to the nitrone methine proton were

(1) (a) For paper III, see H. K. Kim, R. E. Bambury, and H. K. Yaktin, *J. Med. Chem.*, submitted for publication. (b) Research Division, Bristol Laboratories, Division of Bristol-Meyers Company, Syracuse, N. Y. 13201. (c) Wm. S. Merrell, Division of Richardson-Merrell, Inc., Cincinnati, Ohio 45215.

(2) C. D. Hurd and J. Patterson, *J. Amer. Chem. Soc.*, **75**, 285 (1953). All the *N*-(1-aryl-2-nitroethyl)hydroxylamines showed a single spot on tlc in 2-propanol and also gave a positive Tollens test.

(3) J. Thiele and H. Landers, *Justus Liebigs Ann. Chem.*, **369**, 303 (1909).

(4) (a) H. Gilman and G. F Wright, *J. Amer. Chem. Soc.*, **52**, 2550 (1930); (b) R. F. Raffauf, *ibid.*, **68**, 1765 (1946).

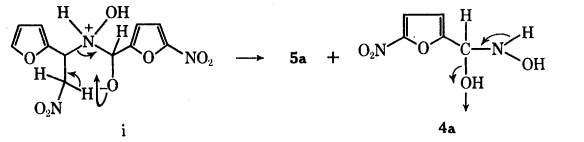
(5) A. C. Cope, T. T. Foster, and P. H. Towle, *ibid.*, **71**, 3929 (1949).

(6) W. M. Williams and W. R. Dolbier, Jr., *J. Org. Chem.*, **34**, 155 (1969).

(7) R. B. Woodward and C. Winter, *Tetrahedron Lett.*, 2689 (1969).

(8) A. C. Cope and A. C. Haven [*J. Amer. Chem. Soc.*, **72**, 4896 (1950)], proposed this mechanism to explain an in-acid rearrangement. We do not believe the mechanism is operative in that example.

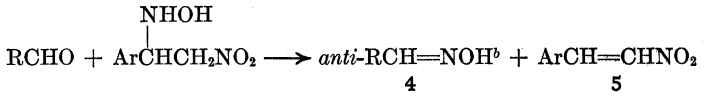
(9) One of the referees suggested that the initial intermediate i of **1a** and **2a** might collapse directly to products without nitrone formation.



(10) I. Pejkovic-Tadic, M. Hranisvljevic-Jakovljevic, S. Nesic, C. Pascual, and W. Simon, *Helv. Chim. Acta*, **48**, 1157 (1965).

TABLE I

ISOLATION OF THE ALDOXIMES AND NITRO OLEFINS[a]



Run	Compd 4 R	Mp, °C	Lit. mp, °C	Yield, %	Compd 5 Ar	Mp, °C	Lit. mp, °C	Yield, %
a	5-Nitro-2-furyl	158–160[c]	159–161[g]	65	2-Furyl	74–75	74–75[m]	45
b	5-Nitro-2-furyl	155–156[c]		54	2-Thienyl	79–80	79–80[n]	35
c	5-Nitro-2-furyl	158–160[c]		46	Phenyl	56–57	57–58[o]	73
d	5-Nitro-2-furyl	155–158[c]		47	3,4-Methylenedioxyphenyl	159–160	158[p]	50
e	5-Nitro-2-thienyl	157–158	156.5–157.5[h]	47	2-Furyl	74		58
f	5-Nitro-2-pyrryl	179–180 dec	168[i]	55	2-Furyl	74		35
g	4-Nitrophenyl	176[d]	176[j]	72	2-Furyl	74–75		44
h	(5-Nitro-2-furyl)vinyl	167–168[e]	163[k]	64	2-Furyl	74–75		97
i	(2-Nitrophenyl)vinyl	148[f]	138[l]	83	2-Furyl	73–75		83

[a] The products were isolated by column chromatography on silica gel. Materials from runs a–d were eluted with benzene–chloroform (4:1) while runs e–i were eluted with benzene–acetonitrile (9:1). Purities were determined by tlc (Eastman chromagram sheet, 6060 silica gel) using the same solvent system as the columns. [b] Syn is the isomer having the hydroxyl cis to the hydrogen: S. W. Tinsley, *J. Org. Chem.*, **26**, 4723 (1961). [c] Syn oxime, mp 119–120, (reported[14] mp 121). [d] Syn oxime, mp 129–131 (reported[16] mp 129). [e] Syn oxime, mp 160 (reported[20] mp 156). [f] Syn oxime, mp 131–133 (reported[15a] mp 134). [g] See ref 4b. [h] Reference 18. [i] Reference 25. [j] Reference 17. [k] Reference 14. [l] Reference 15b. [m] Reference 3. [n] Reference 11. [o] Reference 12. [p] Reference 13.

hopelessly mixed with the vinyl protons. As a result, assignments were made by melting points.

Experimental Section

Melting points were taken in open capillary tubes using a Thomas–Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained with a Beckman IR-5 infrared spectrophotometer (KBr). Nmr spectra were obtained with a Varian A-60 spectrometer, using Me_4Si as an internal standard. Evaporation of solvents was done under reduced pressure using a rotary evaporator.

Starting Materials.—The nitro olefins 2-(2-nitrovinyl)furan,[3] 3-(nitrovinyl)thiophene,[11] ω-nitrostyrene,[12] and 3,4-(methylenedioxy)-β-nitrostyrene[13] were prepared according to the literature.

***N*-(1-Thienyl-2-nitroethyl)hydroxylamine (2b).**—**2b** was prepared by a procedure of Hurd and Patterson[2] from 2-(2-nitrovinyl)thiophene (62.07 g, 0.40 mol). Recrystallization of the crude product from 2-propanol gave a white solid (31.60 g, 42%): mp 61–62°; ν_{max} 3311, 3125 (–NHOH), 1550, and 1370 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 7.48 (q, 1 H, thienyl H_5), 7.16 (t, 2 H, thienyl H_4 and H_3), 6.28, 5.83 (2 s, 2 H, exchangeable with D_2O, –NHOH), and 4.49 (m, 3 H, $-CHCH_2NO_2$).

Anal. Calcd for $C_6H_8N_2O_3S$: C, 38.29; H, 4.28; N, 14.89; S, 17.04. Found: C, 38.18; H, 4.16; N, 14.95; S, 17.18.

***N*-(1-Piperonyl-2-nitroethyl)hydroxylamine (2d).**—This compound was obtained from 3,4-(methylenedioxy)-β-nitrostyrene (19.32 g, 0.10 mol) in a manner similar to that described for **2b**. Recrystallization of the product from absolute EtOH gave a white solid (14.34 g, 63%): mp 95–96°; ν_{max} 3425, 3226 (–NHOH), 1553, 1381 (NO_2), and 1247 cm^{-1} (–CO–); nmr ($CDCl_3$) δ 7.37 (s, 1 H, H_2), 6.92 (s, 2 H, H_5 and H_6), 6.07 (s, 2 H, $-CH_2-$), 5.45 (b, –NHOH), and 4.78 (m, $-CHCH_2NO_2$) (total area = 5 H).

Anal. Calcd for $C_9H_{10}N_2O_5$: C, 47.79; H, 4.46; N, 12.39. Found: C, 47.89; H, 4.53; N, 12.31.

Nitroaromatic Carboxaldehyde Oximes.—Syn[14] and anti isomers of 5-nitrofuranacrolein oxime, *o*-nitrocinnam-*syn*-aldoxime[15a] and *anti*-aldoxime,[15b] syn[16] and anti[17] isomers of *p*-nitrobenzaldoxime, syn and anti isomers of 5-nitrofuraldoxime,[4] 5-nitro-2-thiophene carboxaldehyde oxime,[18] and 5-nitro-2-pyrrolecarboxaldehyde oxime[19] were prepared according to the literature.

Rearrangement to *anti*-Aldoximes and Nitro Olefins. General Procedure.—A solution of nitroaromatic carboxaldehyde (**1**, 25 mmol) and *N*-(1-aryl-2-nitroethyl)hydroxylamine (**2**, 25 mmol) in absolute EtOH was stirred at 0°. The reaction temperature was gradually brought to room temperature and the solution was stirred overnight. Tlc of the reaction mixture showed two spots corresponding to nitro olefin and aldoxime. The crude product was chromatographed on a silica gel column[20] (100 g, 4.3 × 18 cm) with eluents described in Table I. The nitro olefin was always eluted first. Recrystallization of the products from appropriate solvents gave pure material. Results are shown in Table I.

Registry No.—**2b**, 26153-96-8; **2d**, 26153-97-9; **5e**, 699-18-3.

(11) W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 405 (1949).

(12) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1941, p 413.

(13) W. Wiegrebe, *Arch. Pharm.*, **297**, 362 (1964); *Chem. Abstr.*, **61**, 6988 (1964).

(14) M. Ikeda, *Ann. Rep. Fac. Pharm. Kanazawa Univ.*, **3**, 25 (1953); *Chem. Abstr.*, **50**, 10701 (1956).

(15) (a) O. L. Brady and C. D. Thomas, *J. Chem. Soc.*, **121**, 2098 (1922); (b) O. L. Brady and H. J. Grayson, *ibid.*, **125**, 1418 (1924).

(16) O. L. Brady and F. P. Dunn, *ibid.*, **103**, 1619 (1913).

(17) (a) A. Raoult and M. Vilkas, *Bull. Soc. Chim. Fr.*, 3315 (1968); (b) M. O. Forster and F. P. Dunn, *J. Chem. Soc.*, **95**, 425 (1909).

(18) E. C. Hermann, U. S. Patent 2,649,461 (1953); *Chem. Abstr.*, **48**, 8264 (1954).

(19) P. Fournari and J. Tirouflet, *Bull. Soc. Chim. Fr.*, 484 (1963); *Chem. Abstr.*, **59**, 1570 (1963).

(20) Silica gel was purchased from Gebr. Hermann, D 5000 Köln-Ehrenfeld, Grüner Weg 8–10, West Germany, under the name kieselegel.

Formation of Cyclopentadienone Oxime[1]

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Received May 15, 1970

Considerable interest has been focused in recent years on the highly elusive cyclopentadienone molecule **1**. The extreme reactivity of this dienone as predicted by molecular orbital calculations[2] has been borne out experimentally by several unsuccessful attempts to isolate

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(1) Presented in part at the Southeastern Regional meeting of the American Chemical Society, Richmond, Va., Nov 5, 1969.

(2) W. C. Herndon and L. H. Hall, *Theor. Chim. Acta*, **7**, 4 (1967), and references cited therein.