trichloroacetonitrile.) These chlorinations may be interpreted on an ionic basis as follows:

$$HCl + CH_2{=}CHCN \longrightarrow CH_2ClCH_2CN \qquad (7)$$

$$CH_2ClCH_2CN + H^+ \longrightarrow CH_2ClCH_2\overset{+}{C}{=}NH \overset{-H^+}{\rightleftharpoons} CH_2ClCH{=}C{=}NH \xrightarrow{Cl_2} CH_2ClCHClCN + HCl \qquad (8)$$

$$CH_2ClCHClCN + H^+ \longrightarrow CH_2ClCHCl\overset{+}{C}{=}NH \overset{-H^+}{\rightleftharpoons} CH_2ClCCl{=}C{=}NH \xrightarrow{Cl_2} CH_2ClCCl_2CN + HCl \qquad (9)$$

Step (7) is known to take place in the absence of light.[11] The rate of step (9) should be greater than step (8) because the carbonium ion of step (9) should eject a proton more readily than the corresponding carbonium ion of step (8). This is in agreement with the observation that the 2,3-dichloropropionitrile is chlorinated at a higher rate than 3-chloropropionitrile.

Acknowledgment. The author wishes to thank J. H. Brown, Jr., Professor Lewis Hatch, and Professor Harry Walborsky for their advice and help.

FREEPORT, TEX.

---

[11] R. Stewart and R. H. Clark, *J. Am. Chem. Soc.*, **69**, 713 (1947).

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., RESEARCH AND ENGINEERING DIVISION]

Ozonation of Azo and Azomethine Double Bonds

ROBERT E. MILLER

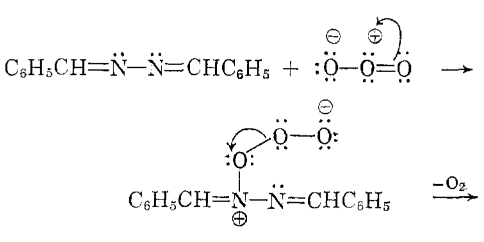
Received October 5, 1960

The ozonolysis of the azomethine double bond with ozone-oxygen mixtures has been investigated. Cleavage was the principal reaction with azines and Schiff bases. Carbonyl compounds were isolated in reasonably good conversions. These reactions were also accompanied by a variety of other products, which are best accounted for by an ozone-initiated autoxidation as a secondary reaction. Oxanilide, formanilide, and s-diphenylurea were isolated from the ozonolysis of *N*-cinnamylideneaniline. Azobenzene was unexpectedly resistant to ozonolysis.

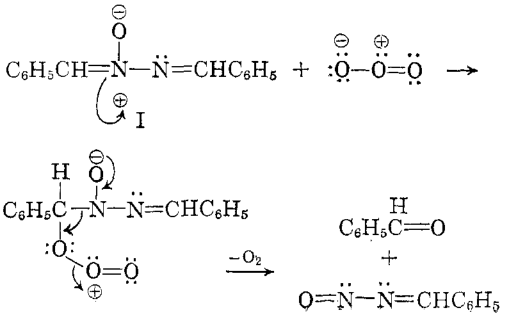
The literature[1] indicates significant differences in the ease of ozonolysis of azo and azomethine linkages. An unsuccessful attempt in these laboratories to ozonize azobenzene prompted a further investigation of the reaction of azo and azomethine compounds with ozone-oxygen mixtures. Azobenzene was recovered nearly quantitatively on treatment with one, four and eight molar equivalents of ozone in oxygen mixtures at −40 to 34°. Trace amounts of glyoxal and a compound (isolated as the 2,4-dinitrophenylhydrazone, m.p. 252–255° dec.), possibly salicylaldehyde, were the only products isolated from the water-soluble oils obtained from these reactions (see table). Azoxybenzene formation was not detected. The ozonation reaction is in contrast to the peracetic acid oxidation of azobenzenes which yields azoxybenzenes.[2] However, it has been stated[3] that the ozonation of hydrazobenzene yielded azobenzene without "noteworthy" formation of other products.

The ozonation of benzalazine, on the other hand, resulted in a facile cleavage of the carbon-nitrogen double bond. An excellent conversion of benzaldehyde was obtained (see table). This reaction was characterized by the rapid development of a blue color, attributed to the formation of dinitrogen trioxide, which persisted throughout the oxonation. It has recently been observed that a blue to green color also resulted during the ozonation of nitrones, which was shown to be due to the formation of nitroso compounds.[1b]

Since this coloration does not result during ozonation of Schiff bases, the initial reaction of ozone with benzalazine must involve an electrophilic attack on the nitrogen atom of the carbon-nitrogen double bond followed by the loss of oxygen



I (1)



(2)

---

[1] The literature is reviewed by (a) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958); (b) A. H. Riebel, R. E. Erickson, C. J. Ashire, and P. S. Bailey, *J. Am. Chem. Soc.*, **82**, 1801 (1960).

[2] (a) A. Angeli, *Atti. accad. Lincei*, **19**, 794 (1910); (b) P. Gagnon and B. T. Newbold, *Can. J. Chem.*, **37**, 366 (1958).

[3] W. Strecker and M. Baltes, *Ber.*, **54B**, 2693 (1921).

TABLE I

Ozonation of Azo and Azomethine Compounds

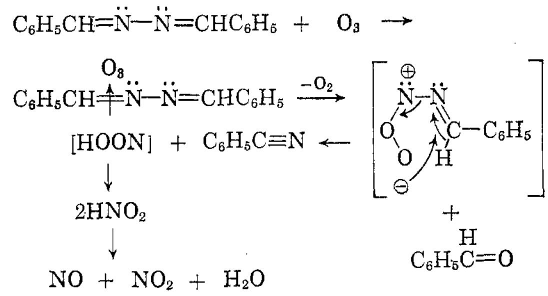
Compound	Moles	Solvent[a]	Ozone, Moles	Temp.	Products[b]		
					Carbonyl	% Conv.	Other (% Conv.)
Azobenzene	0.05	B	0.06	22–26	—	—	[c,d]
	0.05	B	0.19	30–34	—	—	[d]
	0.02	C	0.17	−40	OCH—CHO[e]	—	—
Benzalazine	0.1	D	0.1	8–12	C_6H_5CHO[f]	61.4	N_2O_3[g]
Cyclohexanone ketazine	0.02	D	0.03	−45	$C_6H_{11}O$	60	N_2O_3[g]
	0.05	A	0.11	−40	$C_6H_{11}O$[h] $OCH(CH_2)_4CHO$[j]	36 18.4	Dimethyl adipate (17.2)[i]
Cinnamalazine	0.05	C	0.1	25	C_6H_5CHO $C_6H_5CH{=}CHCHO$	61 —	"Cinnamal *N*-formylhydrazone"[k]; unknown, m.p. 196.5–197°[l]
	0.59	D	xx	15	C_6H_5CHO OHC—CHO[e]	60.4 —	Benzoic acid (22.5)[m]
N-Benzylideneaniline	0.1	A	0.11	−35	C_6H_5CHO	43	[n]
	0.05	A	0.05	2–6	C_6H_5CHO	60	
N-Benzylidene-*p*-chloroaniline	0.09	D	0.3	−18	C_6H_5CHO	36	*p*-Chloronitrobenzene (10)[o]; "4,4′-dichlorooxanilide"[p]
N-Benzylidene-*p*-nitroaniline	0.1	D	0.3	−18	C_6H_5CHO	41	1,4-Dinitrobenzene (14)[q]; "4,4′-dinitrooxanilide"[r]
N-Cinnamylideneaniline	0.12	D	0.12	18–21	C_6H_5CHO $C_6H_5CH{=}CHCHO$[s]	60.6 —	Benzoic acid; nitrobenzene[t]; oxanilide (7.6)[u]; s-diphenylurea (28)[v]
	0.13	D	0.24	14–17	C_6H_5CHO $C_6H_5CH{=}CHCHO$ OHC—CHO[y]	55.1 — —	Benzoic acid (26.7); oxanilide (5.7); oxalic acid (16.8)[w]; formanilide (22.3)[x]
p-Nitroaniline	0.1	D	0.3	9	—	—	1,4-Dinitrobenzene (17.9); 4,4′-dinitroazobenzene (21.2)[z]

[a] A = methanol; B = acetic acid; C = chloroform; D = ethyl acetate. [b] Where conversion is not indicated only trace amounts of product were isolated. Identification of compounds enclosed in quotations is tentative. [c] Recovery of azobenzene was 78–95% in all three experiments. [d] A 2,4-dinitrophenylhydrazone was obtained from the water-soluble oil, m.p. 252–255° dec. *Anal.* Calcd. for $C_{13}H_{11}N_4O_5$: C, 52.71; H, 4.31; N, 17.62. Found: C, 52.55; H, 4.33; N, 18.31. Salicylaldehyde 2,4-dinitrophenylhydrazone has a reported melting point of 254–255° dec. N. R. Campbell, *Analyst*, **61**, 392 (1936). [e] Dioxime melted at 169–171°. E. C. Barany, E. A. Braude, and M. Pianka, *J. Chem. Soc.*, 1902 (1949), give m.p. 179°. *Anal.* Calcd. for $C_2H_4N_2O_2$: N, 31.85. Found: N, 30.81. [f] Distilled at 44–48° (4 mm.); 2,4-dinitrophenylhydrazone, m.p. 235–237°. [g] The solution developed a blue-green color, which is characteristic of solutions of N_2O_3 in nonpolar solvents. [h] Distilled at 36–40° (10 mm.); 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 162–163°. [i] Distilled at 96–99° (4 mm.). P. E. Verkade, J. Coops, and H. Hartman, *Rec. trav. chim.*, **45**, 590 (1926) give b.p. 107° (11 mm.). Infrared spectrum is identical with authentic sample. [j] Recovered from aqueous extracts; 2,4-dinitrophenylhydrazone, m.p. 238–240°. R. Pappo, B. S. Allen, R. V. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956), give m.p. 241.2–241.6°. [k] Melted at 150–153° dec. *Anal.* Calcd. for $C_{10}H_{10}N_2O$: N, 16.09. Found: N, 15.98, 15.83. K. v. Auwers and P. Heimke, *Ann.*, **408**, 208 (1927), report m.p. of cinnamyl *N*-formylhydrazone as 155–156°. [l] Yellow crystals, insoluble in hot methanol, water, dioxane, ethyl acetate, benzene, and acetone. *Anal.* Calcd. for $(C_5H_7N_3O)_x$: C, 48.00; H, 5.60; N, 33.60. Found: C, 48.54; H, 5.27; N, 32.13, 32.74. [m] M.p. 121–122°. [n] The solid residue after removal of benzaldehyde was separated into two fractions: (A) soluble in benzene, m.p. 105–110° dec. *Anal.* C, 68.5; H, 5.6; N, 6.6. (B) benzene insoluble, m.p. 248–253° dec. *Anal.* C, 67.0; H, 5.7; N, 7.6. (See Ref. 1b, p. 1806.) [o] Melted at 81–83°. Infrared spectrum was identical with authentic specimen. [p] Melted at 289–291°. Infrared spectrum is consistent with this structure. F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, **89**, 158 (1906), report m.p. 288°. [q] M.p. and mixed m.p., 174–175°. [r] Melting point, 357–359°. M. J. Bornwater, *Rec. trav. chim.*, **31**, 117 (1912), gives 358–359°. Infrared spectrum is consistent with this structure. [s] Distilled at 105° (4 mm.); 2,4-dinitrophenylhydrazone, m.p. and mixed m.p., 254–255° dec. (Ref. d.) [t] Indicated in benzaldehyde distillate by I.R. bands at 1530 and 1340 cm.$^{-1}$ [u] Melted at 246.5–248.5°. A. D. Macallum, *J. Soc. Chem. Ind.*, **42**, 469T (1923), gives 247–248°. *Anal.* Calcd. for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00; N, 11.68. Found: C, 69.44; H, 4.62; N, 11.25, 11.40. Infrared spectrum identical with reference standard (Sadtler No. 5856). [v] M.p. and mixed m.p., 238–241°. *Anal.* Calcd. for $C_{13}H_{12}N_2O_2$: C, 73.59; H, 5.66; N, 13.21. Found: C, 73.65; H, 5.53; N, 13.60. [w] M.p. 188–189°. [x] M.p. and mixed m.p., 47–48.5°. Distilled at 126–131° (3.5 mm.). O. Schmidt, *Ber.*, **36**, 2476 (1903), gives b.p., 166° (13 mm.); m.p., 47°. Infrared spectrum was identical with reference standard (Sadtler No. 1031B). [y] 2,4-Dinitrophenylhydrazone melted at 320–323° dec. H. J. Lucas and W. T. Stewart, *J. Am. Chem. Soc.*, **62**, 1794 (1940), report m.p. 323° dec. [z] Melted at 219–220.5°. Mixed m.p. with authentic sample was not depressed. O. N. Witt and E. Kopetschini, *Ber.*, **45**, 1134 (1912), report m.p. 222–223°.

to give a nitrone-like structure (I). The formation of the observed products is explained by a second, nucleophilic ozone attack[1b] on the carbon atom of the double bond followed by loss of oxygen (Equation 3).

Repeating the reaction described by Equation 3 on the remaining carbon-nitrogen double bond would yield oxides of nitrogen. Formation of the trioxide, N_2O_3, could occur by two alternate routes. It may be formed directly by oxidation of lower nitrogen oxides (analogous to the formation of nitro compounds from their nitroso precursors[1b,4]), or indirectly through the decomposition of dinitrogen pentoxide,[5] which can arise by the action of ozone on dinitrogen tetroxide.[6]

The alternate possibility of ozone addition to the carbon-nitrogen double bond, similar to that which occurs on reaction with carbon-carbon double bonds, has been examined. In this event, phenyl cyanide should be formed, according to the sequence:

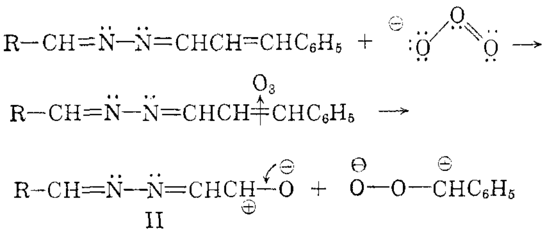


(3)

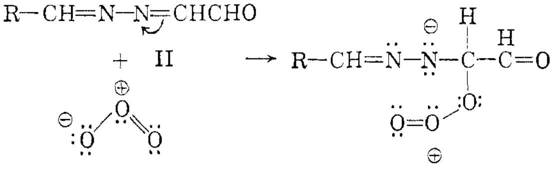
Phenyl cyanide, however, was not found among the products of this reaction. This result is in accord with the evidence presented by Bailey,[1b] *i.e.*, only one atom of the ozone molecule is utilized during the ozonolysis of Schiff bases and nitrones.

The ozonation of cyclohexanone ketazine in ethyl acetate also produced a blue solution; cyclohexanone was the only isolable product. However, when the ozonation was conducted in methanol, no color developed. This result is consistent with the behavior of dinitrogen trioxide in polar solvents. The isolation of adipaldehyde and dimethyl adipate together with cyclohexanone, indicated a further ozone-initiated radical oxidation of the cyclohexanone by oxygen. The ability of ozone to function as a radical initiator in autoxidations, and especially with ketones, has been reported.[7]

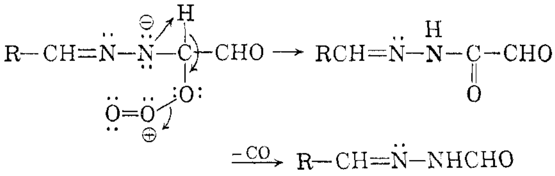
In contrast, the ozonation of cinnamalazine did *not* develop a distinctive blue coloration. Presumably, the initial ozone reaction involved addition to the carbon-carbon double bond. Benzaldehyde and benzoic acid resulted from this reaction (Equation 4). A subsequent nucleophilic attack by ozone at the carbon atom of the carbon-nitrogen double bond of the intermediate (II) is then postulated. This intermediate might undergo (1) loss of oxygen and shift of a proton to yield cinnamal *N*-formylhydrazone (Equation 6), or (2) loss of oxygen and cleavage of the double bond to give glyoxal and cinnamaldehyde (Equation 7). Actually, trace amounts of all three products were isolated.



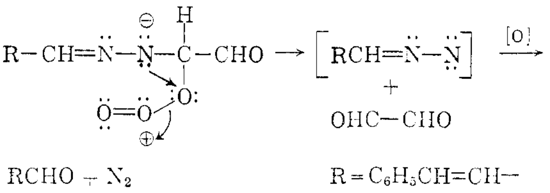
(4)



(5)

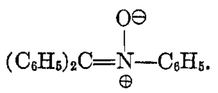


(6)



(7)

Ozonation of *N*-cinnamylideneaniline was investigated in a further attempt to evaluate the differences in the reactivities of exocyclic carbon-nitrogen and carbon-carbon double bonds towards ozone-oxygen mixtures. Ozonolysis of the carbon-carbon double bond was the major reaction, as evidenced by the excellent conversions (55–60%) of benzaldehyde obtained. The formation of small amounts of cinnamaldehyde and nitrobenzene indicated that cleavage of the carbon-nitrogen double bond had also taken place. Nitrobenzene has previously been isolated from the ozonation of benzal nitrone[1b] and from benzophenone nitrone,[8]



$$(C_6H_5)_2C{=}\underset{\oplus}{\overset{O^{\ominus}}{N}}{-}C_6H_5.$$

Formanilide (III) was isolated in significant amounts from this reaction. The formation of this compound must arise from the nucleophilic attack of ozone on the carbon atom of the carbon-nitrogen double bond of the fragment produced by ozonolysis of the carbon-carbon double bond. Shift of a proton, followed by loss of oxygen, and subsequently, of carbon monoxide, yields formanilide (Equation 9).

An ozone-initiated autoxidation of formanilide (Equation 10) is postulated to account for the

---

(4) J. S. Belew and J. T. Person, *Chemistry and Industry*, **40**, 1246 (1959).

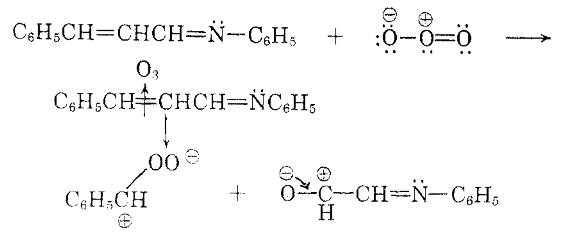
(5) M. Bodenstein, *Z. Phys. Chem.*, **104**, 51 (1923).

(6) (a) T. M. Lowry and J. T. Lemon, *J. Chem. Soc.*, 695; (1935) (b) O. R. Wulf, F. Daniels, and S. Karrer, *J. Am. Chem. Soc.*, **44**, 2398 (1922); (c) F. Foerester and M. Koch, *Angew. Chem.*, **21**, 2216 (1908).

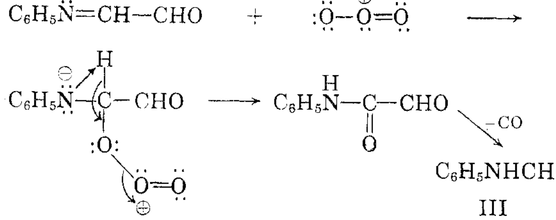
(7) (a) C. C. Schubert and R. N. Pease, *J. Am. Chem. Soc.*, **78**, 2044, 5553 (1956); (b) E. Briner, *Advances in Chem. Ser.*, **21**, 184 (1959).

(8) H. Staudinger and K. Mischer, *Helv. Chim. Acta*, **2**, 554 (1919).

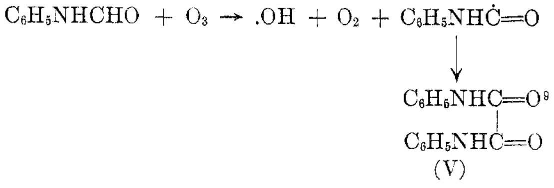
derivation of oxanilide (V) from this ozonation reaction.



(8)



(9)



$$C_6H_5NHCHO + O_3 \rightarrow .OH + O_2 + C_6H_5NH\dot{C}{=}O \quad (10)$$

$$\downarrow$$

$$\begin{array}{c} C_6H_5NHC{=}O^{9} \\ | \\ C_6H_5NHC{=}O \\ \text{(V)} \end{array}$$

s-Diphenylurea was obtained from a single experiment during the ozonation of *N*-cinnamylideneaniline. The formation of this product was not confirmed in subsequent experiments, however.

Ozonolysis of the azomethine bond was also observed with *N*-benzylidene-*p*-chloroaniline and *N*-benzylidene-*p*-nitroaniline. *p*-Chloronitrobenzene and 1,4-dinitrobenzene, respectively, were obtained (10–14%), together with larger amounts (36–56%) of benzaldehyde. Products presumably derived from an ozone-initiated cleavage of the carbon-nitrogen single bond, *i.e.*, 4,4′-dichlorooxanilide and 4,4′-dinitrooxanilide, were isolated in trace amounts. In agreement with previous investigators,[1b,10] 2-phenyloxaziranes were not isolated.

The reaction of *p*-nitroaniline with an ozone-oxygen mixture gave 1,4-dinitrobenzene and *trans*-4,4′-dinitroazobenzene, possibly formed by the reaction:

$$O_2NC_6H_4NH_2 + O{=}NC_6H_4NO_2 \longrightarrow O_2NC_6H_4N{=}NC_6H_4NO_2 \quad (11)$$

Isolation of analytical samples from the tarry reaction product produced by the reaction of ozone-oxygen mixtures with *N*-benzylaniline failed. Previous investigators[4,11] have noted the decomposition of primary and secondary amines by the action of ozone.

EXPERIMENTAL

Materials. Azobenzene, benzalazine (m.p. 92–93°), and cyclohexanone ketazine (m.p. 36–37°) were purchased and recrystallized before use. *N*-Cinnamylideneaniline (m.p. 109°), cinnamalazine (m.p. 175–176°), *N*-benzylideneaniline (m.p. 53–54°), *N*-benzylidene-*p*-chloroaniline (m.p. 64–66°),[12] and *N*-benzylidene-*p*-nitroaniline (m.p. 117–118°)[13] were synthesized by known methods.

Apparatus. The reactor was a cylindrical flask of 300 ml. capacity with a T/S 45/50 joint at the top. Connections for a stirrer, thermometer, and Dry Ice condenser were built into a T/S joint which fitted the top of the reactor flask. A fritted gas inlet tube entered the reactor at the bottom. The ozone source was a Welsbach Model T-3 ozonator. Oxygen pressure to the ozonator was controlled at 8 p.s.i.g. by a Matheson 70A regulator. Oxygen-ozone flow rates from the ozonator were usually 0.25–0.35 cfm. Ozone concentrations were measured by a Welsbach ozone meter, which had previously been standardized by the potassium iodide–sodium thiosulfate procedure for determining ozone concentrations.

General procedure. The reactor was charged with 27 g. (0.13 mole) of *N*-cinnamylideneaniline dissolved in 150 ml. of dry ethyl acetate. The ozonolysis was conducted at 14–17° since the anil crystallized from the solution at lower temperatures. An oxygen-ozone mixture, containing 33–34 mg. ozone/l. of oxygen, was passed through the solution until 0.24 mole of ozone had been absorbed. The yellow solution gradually turned orange; a slight precipitate formed. The reaction mixture was flushed with dry nitrogen and evaporated at room temperature under reduced pressure to about one-third its volume. Ether was added (precipitation occurred) and the solution extracted with 100 ml. of 20% sodium hydroxide solution. In other experiments a 20% sodium sulfite solution was also used. Acidification of the aqueous alkaline solution caused precipitation of benzoic acid (4.2 g.). Oxalic acid (2.0 g.) was recovered by ether extraction of the aqueous acid solution. The residual aqueous solution was treated with 2,4-dinitrophenylhydrazine reagent. A trace of glyoxal bis-2,4-dinitrophenylhydrazone was isolated (see Table I).

The original ether-ethyl acetate extracts were dried over magnesium sulfate. During evaporation of the solvents under reduced pressure, oxanilide (0.8 g.) precipitated. This material was filtered from the liquid residues and recrystallized from benzene. The filtrate was distilled. Benzaldehyde (7.6 g.), cinnamaldehyde (1.0 g.) and a fraction distilling at 126–131° (3.5 mm.) were obtained. A portion of the latter fraction crystallized. This material (2.7 g.) was recrystallized from benzene, and subsequently identified as formanilide.

DAYTON 7, OHIO

---

[9] The author is indebted to the referee for indicating this possibility. A mechanism analogous to that proposed by Schubert and Pease[7a] might also pertain.

[10] W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

[11] W. Strecker and H. Thieneman, *Ber.*, **53**, 2096 (1920).

[12] H. D. Law, *J. Chem. Soc.*, **101**, 160 (1912).

[13] W. v. Miller, J. Plöchl, and G. Rohde, *Ber.*, **25**, 2053 (1895).