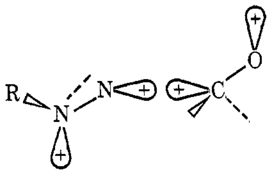
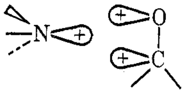
noted that we are proposing cyclic transition states for formally noncyclic reactions. The extra stability of these transition states over the corresponding acyclic transition states (*e.g.*, IV) is, of course, due to the



IV

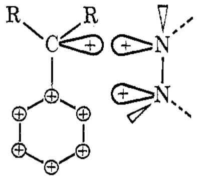
aromatic character of this 6-electron cyclic array. Although a cyclic transition state clearly is entropically disfavored, we may estimate the magnitude of the entropy change on ring formation by a comparison of the model compounds butane and cyclobutane. For these compounds at 300°K, the entropy difference of these molecules is only 10.73 eu or 3.2 kcal/mol.[22] It is reasonable to suppose that the extra stability of an aromatic transition state more than compensates for this entropic loss.[23]

Non-$\alpha$-effect nucleophiles, on the other hand, cannot react through aromatic transition states similar to I–III and must react through acyclic transition states such as IV. Any interaction of a single orbital from the nucleophile with both orbitals of the $\pi$ bond would produce a transition state such as V which is antiaromatic as it has only 4 electrons.



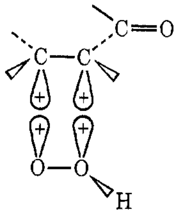
V

The occurrence of an $\alpha$ effect on the addition of nucleophiles to Malachite Green may be explained similarly. Treating Malachite Green as a substituted benzyl cation, an orbital arrangement such as VI may

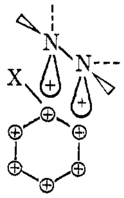


VI

be drawn which has 10-$\pi$ electrons and is therefore aromatic. Michael addition of peroxides and aromatic nucleophilic substitutions may be treated by drawing structures analogous to I and VI, respectively, such as VII and VIII.



VII



VIII

Other reactions for which $\alpha$ effects have been observed are subject to related analysis. Although this treatment is apparently successful in explaining the enhanced nucleophilicities of certain species, a definitive experimental proof remains to be produced.

**Acknowledgment.**—Both J. F. L. and R. M. P. wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Received May 22, 1973

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[22] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

[23] The nearly ubiquitous success of the Woodward–Hoffman rules indicates that the extra stability of these transition states is quite large.[24] For the pyrolysis of *cis*-3,4-dimethylcyclobutene, the extra stability is ≥15 kcal/mol.[25] Similar conclusions have been reached by Hsu, *et al*,[26] who performed *ab initio* SCF and CI calculations on the potential surfaces of cyclobutene, butadiene, and the corresponding electrocyclic transition states.

[24] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[25] J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972).

[26] K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **93**, 2117 (1971); **93**, 5005 (1971); **94**, 5639 (1972).

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## The Reaction of Aryl Nitrones with Thionyl Chloride or Phosgene

*Summary:* Aryl nitrones react with thionyl chloride or phosgene to yield the corresponding *o*-chloroaniline hydrochlorides.

*Sir:* In the course of our investigations of aryl nitrones the immediate formation of a copious yellow precipitate was observed upon addition of a molar equivalent of thionyl chloride or phosgene to $\alpha$,*N*-diphenylnitrone (Ia) dissolved in a minimum amount of benzene at room temperature. The precipitate was purified by sublimation [150° (760 Torr)] yielding a white crystalline substance, the mass spectrum of which exhibited a base peak at *m/e* 215. Elemental analysis indicated a composition of $C_{13}H_{11}Cl_2N$. The ir spectrum, measured as both Nujol and Fluorolube mulls, exhibited strong absorptions at 3.55 and 3.85 $\mu$ and medium absorptions at 4.28 and 5.03 $\mu$, all of which have been shown to be characteristic of protonated nitrogen compounds.[1]

The reaction product was thus indicated to be the hydrochloride of benzylidene-*o*-chloroaniline (IIa), a fact confirmed by comparison with an authentic sample prepared according to a method described in the literature.[2] Similar analysis of the residue left after sublimation of the reaction mixture indicated the presence of a small amount of benzylidene-*p*-chloroaniline hydrochloride (IIa′).

This represents a new and interesting reaction route for nitrones. Previous investigations of the reaction of nitrones with acid chlorides (*e.g.*, $POCl_3$, $PCl_3$) have shown only rearrangement of the nitrone to the corresponding amide.[3]

The closest analogy to the presently reported system is that of aromatic amine oxides with acid chlorides; Meisenheimer reported[4] that quinoline *N*-oxide reacted with acid chlorides to yield 2- and 4-chloroquinoline.

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[1] K. Nakanishi, "Infrared Absorption Spectroscopy—Practical," Holden-Day, San Francisco, Calif., 1964, pp 39–45.

[2] O. Fischer and P. Neber, *Ber.*, **45**, 1094 (1912).

[3] J. Hamer and A. Macaluso, *Chem. Rev.*, **64**, 489 (1964).

[4] J. Meisenheimer, *Ber.*, **59**, 1848 (1926).

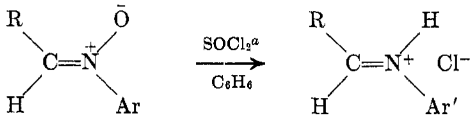
Later work has expanded upon this observation.[5] Indeed, the present work indicates a significant similarity in the chemistry of these two classes of compounds (aromatic amine oxides and aromatic nitrones) which has previously been neglected.[6]

To test the generality of this reaction, a number of other nitrones were synthesized[7] and allowed to react with thionyl chloride or phosgene. These include α-styryl-*N*-phenylnitrone (Ib), α-4-nitrophenyl-*N*-phenylnitrone (Ic), α-styryl-*N*-4-methylphenylnitrone (Id), and α-phenyl-*N*-4-chlorophenylnitrone (Ie). The results are listed in Table I.

The applicability of this reaction as a general, regioselective method for the synthesis of *o*-chloro aromatic imines (and by hydrolysis, the corresponding amines) promises to be quite exceptional. Three steps are involved: (1) reduction of the appropriate nitro compound to the hydroxylamine using $Zn/NH_4Cl$ in aqueous ethanol; (2) condensation of the hydroxylamine with the aldehyde yielding the nitrone; (3) treatment of the nitrone with thionyl chloride or phosgene. In the examples cited each of these steps proceeds rapidly and in high yield. Typically the overall time for the three steps is 2–3 hr, the latter requiring only about 15 min.

Studies are currently in progress to obtain evidence for the mechanism of the above reactions of aryl nitrones and to investigate analogous reactions of compounds containing the –X=N—O grouping (*e.g.*, where X = N).

TABLE I



| Reactants | | | Products[b] | | |
|---|---|---|---|---|---|
| Compd | R | Ar | Compd | Ar′ | Isolated yield, % |
| Ia | $C_6H_5$ | $C_6H_5$ | IIa | $2\text{-}ClC_6H_4$ | 81 |
| | | | IIa′ | $4\text{-}ClC_6H_4$ | 6 |
| Ib | $C_6H_5CHCH$ | $C_6H_5$ | IIb | $2\text{-}ClC_6H_4$ | 71 |
| | | | IIb′ | $4\text{-}ClC_6H_4$ | 3 |
| Ic | $4\text{-}NO_2C_6H_4$ | $C_6H_5$ | IIc | $2\text{-}ClC_6H_4$ | 82 |
| | | | IIc′ | $4\text{-}ClC_6H_4$ | *c* |
| Id | $C_6H_5$ | $4\text{-}CH_3C_6H_4$ | IId | $2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3$ | 91 |
| Ie | $C_6H_5$ | $4\text{-}ClC_6H_4$ | IIe | $2,4\text{-}Cl_2C_6H_3$ | 92 |

[a] No significant differences in yield were observed when phosgene was used instead of thionyl chloride. [b] The structure of each product was determined by comparison of its spectral and physical properties with those of an authentic sample prepared from the known imine. [c] Trace amounts of this material were noted in the crude product but were not isolated. Slight heating was also required for the initiation of this reaction.

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RECEIVED JULY 20, 1973

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(5) T. Ochiai, "Aromatic Amine Oxides," Elsevier, Amsterdam, The Netherlands, 1967, pp 247–339.

(6) In a comparison of aromatic amine oxides with nitrones, reactions involving the carbon–nitrogen double bond should be substantially different, as in aromatic amine oxides the carbon–nitrogen double bond is intimately involved in the aromatic sextet of electrons. However, reactions involving both classes of compounds where they behave as nucleophiles should proceed in similar fashion.

(7) O. H. Wheeler and P. H. Gore, *J. Amer. Chem. Soc.*, **78**, 3363 (1956).