crystals that precipitated were recrystallized from water to yield 1.1 g (68.0%), mp 205–206°.

*Anal.* Calcd for $C_6H_{11}O_4N$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.43; H, 7.01; N, 8.90.

**5-(4-Aminobutylidene)-2-thiohydantoin (7).**—A solution of **3** (4.5 g, 0.025 mol) in tetrahydrofuran (200 ml) was treated with 3 g of lithium aluminum hydride in the usual manner. After the reaction was completed, 150 ml of 10% hydrochloric acid was added. Picric acid was then added to the aqueous layer. Picrate of **7** was obtained and recrystallized from water to yield 4.3 g (41.2%), mp 250° dec.

*Anal.* Calcd for $C_{13}H_{14}O_8N_6S$: C, 37.68; H, 3.41; N, 20.28. Found: C, 37.46; H, 3.57; N, 20.44.

**Lysine (8) from 7.**—By Rice's method, the picrate of **7** (4.1 g, 0.01 mol) was converted into about 10 ml of an aqueous solution of the hydrochloride of **7**. Phosphorus (1.5 g), 57% hydroiodic acid (15 ml), and iodine (3 g) were added to this solution, and the mixture was refluxed for 5 hr. After phosphorus was filtered off, the filtrate was passed through an anion exchange resin (Amberlite IRA-400) and concentrated to about 10 ml. By the addition of picric acid, 2.5 g of lysine monopicrate was obtained to yield 66.7%, mp 208°.

*Anal.* Calcd for $C_{12}H_{17}O_9N_5$: C, 38.40; H, 4.57; N, 18.66. Found: C, 38.62; H, 4.77; N, 18.81.

The product was also identified as dihydrochloride by the agreement of $R_f$ value on paper chromatography.

**Registry No.**—2, 17190-64-6; **3**, 17190-65-7; **4**, 17190-66-8; **5**, 13593-99-2; **6**, 542-32-5; **7** picrate, 17190-69-1; **8** monopicrate, 6150-71-6.

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# The Addition of Oxime Anions to Dienophiles

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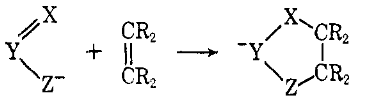
The concerted thermal cycloaddition of allylic anions to double bonds is predicted to be a facile process[1] (eq 1), but no unambiguous examples of it appear to have been reported. There are, however, many examples of a formally analogous process in which the central atom of the allylic system is a positively charged nitrogen (eq 1, Y = RN+). These reactions have been formulated as 1,3-dipolar additions.[2] Alternatively, these reactions may be regarded as examples of 4 + 2 electrocyclization.[3] In the former view, the positive charge plays an essential role in the reaction process, while in the latter view the positive charge is incidental and plays no role in the electronic process leading to new bond formation.



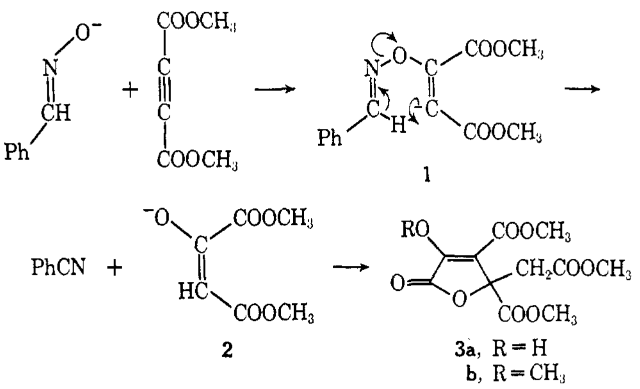
(1)

We sought to gain more information about the effect of the positive charge in this process by examining the reaction of oxime anions with dienophiles (eq 1, X = $CR_2$; Y = N; Z = O). The analogous 1,3-dipolar addition reaction, the addition of nitrones to dienophiles (eq 1, X = $CR_2$; Y = $RN^+$; Z = O) occurs readily to form isoxazolidines.[4]

It was found that the dry sodium salt of *syn*-benzaldoxime reacted exothermically with dimethyl acetylenedicarboxylate at room temperature in the absence of solvent. The major products of the reaction were benzonitrile and an acidic substance which could be isolated as a methyl derivative after treatment of the reaction mixture with diazomethane. This methyl derivative was identified from its spectral characteristics as the previously unreported methyl ether of oxalocitric anhydride trimethyl ester **3b**, and its identity was confirmed by independent preparation from authentic **3a**.

The formation of these products is rationalized in Scheme I. Initial Michael addition of the oxime anion to the dienophile is proposed. The proton abstraction by the resulting anion **1** has analogy in the reactions of anions formed by addition of other nucleophiles to dimethyl acetylenedicarboxylate.[5] The formation of **3a** from the anion of dimethyl oxaloacetate **2** has been reported.[6]

SCHEME I



The same products were formed when the reaction was carried out in aprotic solvents or when dimethyl acetylenedicarboxylate, benzaldehyde *syn*-oxime, and potassium t-butoxide were refluxed in t-butyl alcohol. With sodium methoxide in methanol, unreacted oxime and dimethyl 2,2-dimethoxysuccinate were isolated. In no case was isoxazoline formation or any evidence for concerted cycloaddition observed.

The reaction of dimethyl acetylenedicarboxylate with the sodium salt of acetone oxime, in which nitrile formation by proton abstraction is not possible, yielded a resinous solid from which no low molecular weight products could be isolated.

The reaction of the sodium salt of *syn*-benzaldoxime with maleic anhydride occurred at 115°. The major products were benzonitrile and sodium maleate. Since the reactants were stable separately at 115°, and since no other source of oxygen was present, the transfer of hydroxyl must have occurred by addition of the oxime

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[1] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2048 (1965).

[2] R. Huisgen, R. Graskey, and J. Sauer, in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, pp 806–878.

[3] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); R. Huisgen and H. Gotthardt, *Chem. Ber.*, **101**, 1059 (1968).

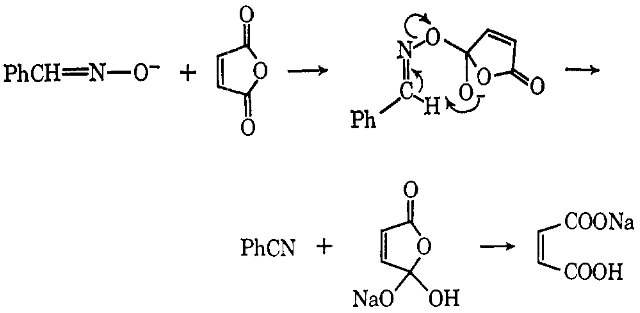
[4] See ref 2, pp 861–867; R. Graskey, R. Huisgen, and H. Leiterman, *Tetrahedron Lett.*, No. 12, 9 (1960).

[5] J. B. Hendrikson, R. Rees, and J. F. Templeton, *J. Amer. Chem. Soc.*, **86**, 107 (1964).

[6] A. Michael and H. D. Smith, *Ann.*, **363**, 36 (1908).

anion to the anhydride. A plausible reaction path involves initial addition to a carbonyl group (Scheme II).

SCHEME II



The contrast between these results and the smooth cycloaddition of C-phenyl-N-methyl nitrone to dienophiles[4] suggests that the positive charge on the central nitrogen atom is indeed essential for concerted cycloaddition. A possible explanation is as follows: in the 4 + 2 electrocyclic reaction between enes and allylic anions, the negative charge of the allylic system becomes localized on a single atom in the product (eq 1) and thus also in the transition state. In the absence of structural features which would stabilize this localized charge, the concerted electrocyclization will be energetically unfavorable compared to nonconcerted nucleophilic attack on the double bond.

## Experimental Section

**Reaction of Sodium Benzaldoximate with Dimethyl Acetylenedicarboxylate. A. Without Solvent.**—Sodium *syn*-benzaldoximate, prepared according to Vogel,[7] was washed with saturated aqueous NaCl until free of hydroxide and was dried *in vacuo* over $P_2O_5$ at 110°. The dry sodium salt (3.87 g, 0.027 mol) was added in small portions to dimethyl acetylenedicarboxylate (3.87 g, 0.027 mol), the exothermic reaction being moderated by ice-bath cooling. The reaction mixture was dissolved in water, acidified (pH 1) with hydrochloric acid, and extracted with ether. The ethereal extract was treated with ethereal diazomethane. Chromatography on alumina yielded benzonitrile (eluted with hexane, 1.92 g, 70%, identified by ir spectra and vpc retention time), benzaldoxime-O-methyl ether (eluted with 6:1 hexane–ether, 0.48 g, 14%, identified by ir comparison with an authentic sample[8]), and **3b** (eluted with ether, 2.44 g, 65%): mp 89.5–90° (prisms from hexane–benzene); uv $\lambda_{max}$ (95% ethanol) 258 m$\mu$ ($\epsilon$ 11,700); ir (Nujol mull), 5.60, 5.69, 5.73, 5.80 (ester and lactone C=O), 6.03 (C=C), 13.2 $\mu$; nmr ($CDCl_3$), $\delta$ 4.28, 3.80, 3.77, 3.63 (all sharp s, 3 each, $OCH_3$), 3.28 (broad s, 2, $CH_2$); mass spectrum (70 eV) *m/e* (relative intensity) 302 (0.6), 258 (21), 243 (44), 215 (12), 211 (100), 201 (49), 199 (18), 173 (16), 141 (13), 115 (13).

*Anal.* Calcd for $C_{12}H_{14}O_9$: C, 47.7; H, 4.64. Found: C, 47.5; H, 4.79.

Authentic **3b** was prepared by reaction of ethereal diazomethane with **3a** (made by the procedure of Michael and Smith[6]). The two samples had identical ir spectra and showed no mixture melting point depression.

**B. In Methanol.**—Benzaldehyde *syn*-oxime[7] (0.80 g, 0.0066 mol) was added to a solution of 0.15 g (0.0066 mol) of sodium in 25 ml of methanol, followed by 0.94 g (0.0066 mol) of dimethyl acetylenedicarboxylate in 25 ml of methanol. The mixture was refluxed for 24 hr, then was poured into water and extracted with ether. The ether-soluble material was separated by chromatography on alumina into benzonitrile (0.31 g, 46%, eluted with hexane), benzaldehyde *syn*-oxime (0.46 g, 57%, eluted with 30:1 hexane–ether), and dimethyl 2,2-dimethoxysuccinate[9] (0.86 g, 63%, eluted with 3:1 hexane–ether): ir (thin film), 5.80 $\mu$; nmr ($CCl_4$), $\delta$ 3.73 (s, 3, $CO_2CH_3$), 3.62 (s, 3, $CO_2CH_3$), 3.23 (s, 6, $OCH_3$), 2.86 (s, 2, $CH_2$). A comparison sample was prepared by reaction of sodium methoxide in methanol with dimethyl acetylenedicarboxylate.[10]

**Reaction of Sodium Benzaldoximate with Maleic Anhydride.**—A mixture of the dry sodium salt of benzaldehyde *syn*-oxime (0.75 g, 0.0052 mol) and maleic anhydride (0.51 g, 0.0052 mol) was heated in an oil bath at 115° for 10 min. The reaction mixture was dissolved in hot ethanol–water; on cooling 0.38 g (53%) of sodium maleate was obtained. The mother liquor was evaporated and the residue was taken up in hexane. Passage through a column of alumina yielded benzonitrile (0.31 g, 58%).

**Registry No.**—**3b,** 17061-09-5.

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[8] O. L. Brady, F. P. Dunn, and R. F. Goldstein, *J. Chem. Soc.*, 2386 (1926).

[9] W. J. Croxall and H. J. Schneider, *J. Amer. Chem. Soc.*, **71**, 1257 (1949).

[10] The analogous reaction of diethyl acetylenedicarboxylate with sodium ethoxide in ethanol has been described: A. Michael and J. E. Bucher, *Chem. Ber.*, **29**, 1792 (1896).

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# Reactions of Peroxides. I. Preparation of Aryl and Alkyl Iodides by Decomposition of Aroyl and Acyl Peroxides in the Presence of Iodine

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The preparative value of decomposition of benzoyl peroxide in boiling carbon tetrachloride solutions of iodine was reported by Hammond and Soffer who obtained an 85% yield of iodobenzene in 36–48 hr.[3] Low yields (15–20%) were observed in benzene and chlorobenzene.[4] *o*-Iodotoluene was similarly obtained in about 49% yield from *o*-toluoyl peroxide in boiling carbon tetrachloride in 17 hr.[5] The reaction of peroxide with iodine may be more usefully applied by reducing the reaction times at higher temperatures. Accordingly, benzoyl and pelargonyl peroxide, representing aromatic and aliphatic classes, were each decomposed in iodine solutions of higher boiling aromatic and aliphatic solvents to determine the appropriate solvent, optimum conditions, and some of the accompanying side products of the reaction.

Benzoyl peroxide is converted into iodobenzene to the extent of 80–90% in 2–4 hr at 100–110° in several

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[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] G. S. Hammond and L. M. Soffer, *J. Amer. Chem. Soc.*, **72**, 4711 (1950).

[4] G. S. Hammond, *ibid.*, **72**, 3737 (1950).

[5] F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, **25**, 1790 (1960).