46–48°. The infrared spectrum of a Nujol mull of the hemiacetal is reproduced in Fig. 1.

***n*-Dodecanal Trimer.**—Four grams of *n*-dodecanal was placed in a stoppered test tube under nitrogen. The test tube contained a side arm in which 1 drop of concentrated hydrochloric acid was placed to promote the polymerization. The aldehyde was frozen and kept in the refrigerator at 4–5° for 1 month. The product was then transferred to an erlenmeyer flask and 25 ml. of alcohol, 3.1 ml. of 0.5 *N* sodium hydroxide solution, and 40 ml. of 3.0 *N* hydroxylamine hydrochloride reagent were added. The mixture was stored at room temperature for 2 weeks to convert all unchanged aldehyde to the oxime, and the insoluble polymer was then filtered, washed with water, and air-dried; yield, 3.5 g. Recrystallization from alcohol afforded pure *n*-dodecanal trimer, m.p. 55–57° (lit.[8] m.p. 57°). Molecular weight determinations in benzene by the freezing point technique gave values of 526 and 529, calcd. 553. The infrared spectrum of a Nujol mull is reproduced in Fig. 1.

The Addition of Aromatic Nitroso Compounds to Conjugated Dienes

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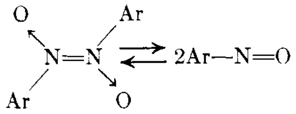
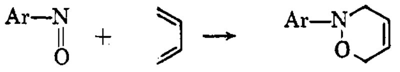
The addition of aromatic nitroso compounds to 2,3-dimethyl-1,3-butadiene was found to be a first-order reaction in respect to the nitroso compound and to the diene. The energies of activation of the reaction betweeen the conjugated diene and nitrosobenzene or *p*-bromonitrosobenzene were found to be, respectively, 14.23 and 12.46 kcal./mole. Nitrosobenzene failed to react with anthracene, but yielded an adduct with 1,3-cyclooctadiene.

Reactions involving the aromatic nitroso group lend themselves well to kinetic studies, since the nitroso group exhibits specific absorption bands in the visible, ultraviolet, and infrared spectra. Complications may arise from the fact that for many aromatic nitroso compounds in solution an equilibrium exists between the monomeric and dimeric forms. This complication may be avoided by the selection of aromatic nitroso compounds known to be monomeric in solution, *e.g.*, nitrosobenzene, *p*-halonitrosobenzenes, and *p*-nitroso-N,N-dimethylaniline.[1]



The addition of aromatic nitroso compounds to conjugated dienes is commonly considered a Diels–Alder reaction of heteroatomic compounds.[2] The reaction generally proceeds smoothly at moderate temperatures. With few exceptions the sole reaction product has been found to be a substituted 3,6-dihydro-1,2-oxazine.[2–4] Kinetic studies of the addition of aromatic nitroso compounds to conjugated dienes have not been reported thus far.



The dissociation of a 3,6-dihydro-1,2-oxazine into conjugated diene and nitroso compound normally requires considerably higher temperatures than the addition. The formation of an aromatic nitroso compound by the dissociation of the Diels–Alder adduct of various aromatic nitroso compounds and 2,3-dimethyl-1,3-butadiene could not be detected at temperatures below 35°. The rate of this reverse reaction at temperatures below 35° is, therefore, negligible, facilitating the determination of the rate of the addition of aromatic nitroso compounds to 2,3-dimethyl-1,3-butadiene.

Nitrosobenzene when treated with 2,3-dimethyl-1,3-butadiene has been reported to yield small quantities of a side product of unknown structure in addition to the expected N-phenyl-3,6-dihydro-4,5-dimethyl-1,2-oxazine.[5] When a large excess of diene was employed the sole product of the reaction was the oxazine. The side product is believed to be derived from the reaction of nitrosobenzene and the oxazine derivative.[6] For *p*-bromonitrosobenzene, on the other hand, only one product, the expected oxazine, was observed in the addition reaction, employing various concentrations of 2,3-dimethyl-1,3-butadiene.

Results

In order to suppress the formation of a side product, the reaction of nitrosobenzene and 2,3-dimethyl-1,3-butadiene was studied in dichloromethane with a fiftyfold excess of diene. Several Guggenheim plots were constructed at 2° and 25°. The reaction was found to be a first-order reaction in respect to nitrosobenzene, with a specific rate constant at 2° and 25° of 2.84×10^{-4} and 2.10×10^{-3} l. moles^{-1} sec.$^{-1}$. The energy of activation was found to be 14.23 kcal./mole, and the frequency factor, 6.2×10^{6} l. moles^{-1} sec.$^{-1}$.

Nitrosobenzene did not form an adduct with anthracene, even after prolonged reflux in chloroform. An adduct between nitrosobenzene and 1,3-cyclooctadiene was obtained, but the yield was less than 5%, and the reaction was too slow to permit observation.

The reaction between *p*-bromonitrosobenzene and a fiftyfold excess of 2,3-dimethyl-1,3-butadiene also was found to be a first-order reaction (see Fig. 1). It was found to be first order in respect to *p*-bromonitrosobenzene and first order in respect to 2,3-dimethyl-1,3-butadiene when the concentrations of the reactants were of the same magnitude. The specific rate constants were found to be 1.10×10^{-3}, 3.84×10^{-3}, 7.60×10^{-3}, and 8.29×10^{-3} l. moles^{-1} sec.$^{-1}$ at 2,

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(1) B. O. Gowenlock and W. Luettke, *Quart. Rev.* (London), **12**, 385 (1958); W. J. Mijs, "Structure and Properties of Some Monomeric and Dimeric Aromatic Nitroso Compounds," dissertation, University of Leyden, 1959.

(2) S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, **62**, 407 (1962).

(3) J. Hamer and R. E. Bernard, *Rec. trav. chim.*, **81**, 734 (1962).

(4) J. Hamer and R. E. Bernard, *J. Org. Chem.*, **28**, 1405 (1963).

(5) Yu A. Arbuzov, N. L. Fedyukina, U. V. Shavyrina, and R. I. Shepeleva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 539 (1952); *Chem. Abstr.*, **47**, 4341 (1953).

(6) J. Hamer and A. Macaluso, *Tetrahedron Letters*, No. **6**, 381 (1963).

18, 25, and 30°, respectively. The energy of activation was found to be 12.46 kcal./mole, and the frequency factor, 9.3×10^6 l. moles^{-1} sec.$^{-1}$ (see Fig. 2).

The rate of the reaction between *p*-nitroso-N,N-dimethylaniline and 2,3-dimethyl-1,3-butadiene was too slow to permit observation.

Discussion

The positive value of Hammett's σ-constant for the bromo substituent, together with the higher rate constant and the lower energy of activation for the reaction of *p*-bromonitrosobenzene with 2,3-dimethyl-1,3-butadiene than for the corresponding reaction of nitrosobenzene, indicated that the reaction was accelerated by electron-withdrawing substituents on the phenyl ring.

A tentative ρ-constant may be found from the rate constants at 2 and 25° for the reactions of nitrosobenzene or *p*-bromonitrosobenzene and 2,3-dimethyl-1,3-butadiene. Employing +0.23 as the value of the σ-constant of the *para* bromo substituent, ρ was calculated to be 2.51 ± 0.04.

The sluggishness of the reaction between *p*-nitroso-N,N-dimethylaniline and 2,3-dimethyl-1,3-butadiene is then due to the electron donating effect of the dimethylamino group. The half-time of this reaction should be *ca.* forty-two hours at 25° if 0.1 *M* concentrations of nitroso compound and diene are used, assuming −0.60 as the value of the σ-constant of the *para* dimethylamino group.

It has been reported that *o*- or *p*-substituted nitrosobenzenes react considerably slower with dienes than nitrosobenzene, while the reverse was reported for *m*-substituted nitrosobenzenes.[7] Among the reported substituents were the nitro, methyl, and bromo groups.

Recently, however, we reported that the presence of a nitro group in either the *ortho*, *meta*, or *para* position in nitrosobenzene seemed to accelerate the reaction with dienes considerably.[3,4] It also is known that aliphatic nitroso compounds will undergo a Diels–Alder reaction only if a strong electron-withdrawing substituent is present on the carbon carrying the nitroso group.[2] Our results also indicate clearly that the electronic character of the substituent determines the acceleration or retardation of the addition reaction, and not, as reported by Kojima, the position of the substituent.

Our results fall in the general pattern of Diels–Alder reactions. The more electron-poor dienophiles commonly exhibit higher reactivities in these reactions. The frequency factor and energies of activation reported here are of the same order of magnitude as those reported for some conventional Diels–Alder reactions.[8] In view of this the failure of nitrosobenzene to add to anthracene is rather surprising. Maleic anhydride and other dienophiles add easily to anthracene.[9] The reason for the failure does not seem to lie with an excessively high energy of activation, the instability of the formed adduct, or the frequency factor. An attempted reaction of anthracene with *p*-nitronitrosobenzene also failed.

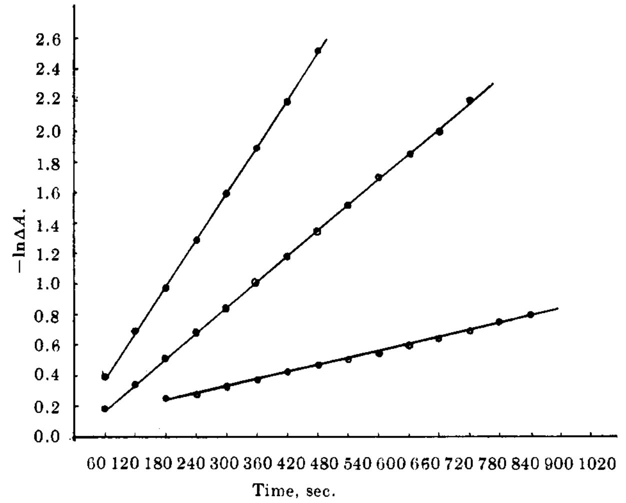

Fig. 1.—Guggenheim plot of the addition of nitrosobenzene or *p*-bromonitrosobenzene to 2,3-dimethyl-1,3-butadiene (fiftyfold excess), in dichloromethane: middle, *p*-bromonitrosobenzene at 2°; lower, nitrosobenzene at 2°; upper, nitrosobenzene at 25°.

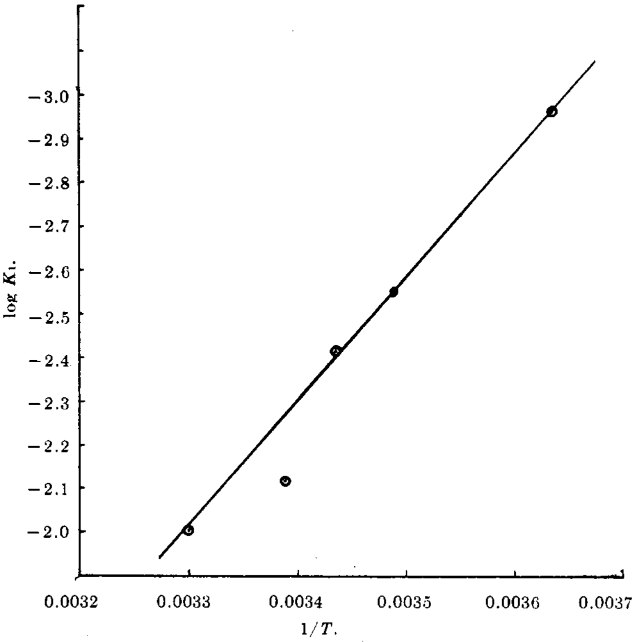

Fig. 2.—Log *k* *vs.* 1/*T* for the reaction between *p*-bromonitrosobenzene and 2,3-dimethyl-1,3-butadiene.

The Diels–Alder reaction fails with dienes having rings of eight to eleven members.[10] Nitrosobenzene, however, when treated with 1,3-cyclooctadiene at 5° for nearly one month yielded less than 5% of an adduct. The same adduct was obtained in approximately the same yield when nitrosobenzene was treated at room temperature for about five days with 1,3-cyclooctadiene. Attempts in this laboratory to effect a reaction between maleic anhydride and 1,3-cyclooctadiene failed.

Elemental analysis of the adduct of nitrosobenzene and 1,3-cyclooctadiene indicated a compound of the formula $C_{14}H_{17}NO$. The infrared spectrum of the adduct, determined in a potassium bromide pellet, showed the presence of a phenyl ring, and the absence

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(7) S. Kojima, *Kogyo Kagak u Zasshi*, **58**, 540 (1958); **59**, 951 (1959) (cited from ref. 2).

(8) A. Wasserman, *J. Chem. Soc.*, 1028 (1936); G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.*, **58**, 123 (1936).

(9) L. J. Andrews and R. M. Keefer, *ibid.* 6294 (1955).

(10) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 542 (1961).

of an NH or OH bond, excluding the possibility of an allylic addition such as that found with azodicarboxylate esters.[11] A weak band was found at 6.10 μ, indicating the presence of an isolated double bond, while the typical —N=O band had disappeared.

Experimental

Reagents.—Nitrosobenzene,[12] m.p. 68°, p-bromonitrosobenzene,[13] m.p. 94°, and p-nitroso-N,N-dimethylaniline,[14] m.p. 85°, were prepared by known procedures. Anthracene, 2,3-dimethyl-1,3-butadiene, and 1,3-cyclooctadiene were obtained from Columbia Organic Chemicals.

Kinetic Measurements.—The change of concentrations of the nitroso compounds were followed in the visible region (720–730 mμ) with a Beckman DB. Spectrograde dichloromethane was employed as the solvent. Solvent, dienes, and products did not absorb in the visible region. Solutions of the nitroso compounds were found to follow the Lambert–Beer law when the concentrations were between 0.025 and 0.002 mole/l.

In a typical run to obtain Guggenheim plots, the following concentrations were employed: diene, 2.5000 moles/l., and nitroso compound, 0.050 mole/l. Several Guggenheim plots were obtained for the reaction between nitrosobenzene and 2,3-dimethyl-1,3-butadiene at 2° and 25°, and for p-bromonitrosobenzene and the same diene at 2° (see Fig. 1).

p-Bromonitrosobenzene was treated with the same diene at 18°, 25°, and 30°, employing the following approximate concentrations: nitroso compound, 0.025 mole/l., and 2,3-dimethylbutadiene, 0.100 mole/l. A graph of time *vs.* log $b/a\ (a - x/b - x)$ yielded a straight line from which k was calculated.

Anthracene.—0.53 g. (3 mmoles) was treated with nitrosobenzene, 0.53 g. (5 mmoles) in chloroform, 75 ml., at room temperature. The optical density of the solution at 730 mμ remained unchanged after several hours standing, indicating that nitrosobenzene had not reacted. The solution was then refluxed under nitrogen for 2 hr. The optical density at 730 mμ was again unchanged.

Nitrosobenzene.—5.5 g. (51 mmoles) was mixed with 1,3-cyclooctadiene, 7.8 g. (72 mmoles) in ether, 50 ml. The optical density at 730 mμ was slightly reduced after 1 week of standing at 5°. After about 25 days of standing at 5°, the solution was concentrated to approximately 5 ml. by evaporation under reduced pressure. Ethyl alcohol, 5 ml., was added, and crystals precipitated after standing for 2 hr. at 5°. The yield of the isolated crude product was 0.5 g. (4.53%, based on nitrosobenzene), m.p. 80–83°. The crude product was purified by washing with ethanol, yielding 30 mg. of a white solid, m.p. 83.5–84.5°.

Anal.[15] Calcd. for $C_{14}H_{17}NO$: C, 77.73; H, 8.28; N, 6.48. Found: C, 77.78; H, 8.13; N, 6.40.

Infrared bands (determined in a potassium bromide pellet): 3.4 (m), 3.45 (s), 3.52 (s), 6.1 (w), 6.3 (s), 6.74 (s), 6.95 (s), 8.1 (s), 8.52 (s), 9.75 (s), 9.9 (m), 11.26 (m), 12.7 (s), 12.96 (m), 13.3 (s), 13.6 (m), and 14.48 (s) μ.

Acknowledgment.—Financial support of the Petroleum Research Fund enabled us to carry on this investigation.

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[11] B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **27**, 1947 (1962); B. Franzus and J. H. Surridge, *ibid.*, **27**, 1951 (1962).

[12] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 668.

[13] E. Bamberger, *Ber.*, **28**, 1222 (1895).

[14] A. I. Vogel, "Practical Organic Chemistry," Longmans Green and Co., New York, N. Y., 1957, p. 573.

[15] Microanalysis by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Free Radical Addition of Cyclic Ethers to Maleic Anhydride

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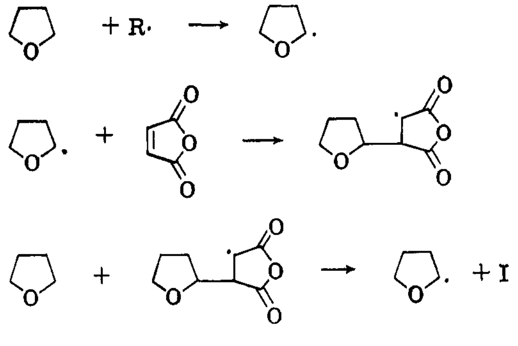
It has been found that free radicals initiate a reaction between tetrahydrofuran and maleic anhydride to form (tetrahydro-2-furyl)succinic anhydride in 70% yield. An analogous reaction using tetrahydro-2-methylfuran formed (tetrahydro-2-methyl-2-furyl)succinic anhydride in 70% yield. This reaction appears to be specific with respect to five-membered cyclic ethers since efforts to utilize other ethers either failed to yield a 1:1 adduct with maleic anhydride or gave only low conversions.

The free radical-promoted reactions of olefins with acetals and ortho esters have been studied extensively[2]; however, little is known relative to the behavior of simple ethers in this type of reaction. The formation of (α-alkoxybenzyl)succinic anhydrides by the addition of benzyl alkyl ethers to maleic anhydride in the presence of free radical initiators has been described.[3] More recently, the peroxide-induced reaction of various cyclic ethers with 1-octene was reported.[4] Ketonic products were obtained, and a chain mechanism involving α-hydrogen abstraction followed by decyclization of the ether was postulated.

The latter study prompts us to report the results of a similar investigation involving free radical-initiated reactions between cyclic ethers and maleic anhydride. Our results differ significantly from those reported by Wallace and Gritter[4] in that addition without ring opening has been observed as the major course of reaction. The reaction of tetrahydrofuran with maleic anhydride in the presence of free radical initiators was found to give a 70% yield of (tetrahydro-2-furyl)-succinic anhydride (I). The reaction probably proceeds by the following chain process.



The difference in the course of reaction of tetrahydrofuran with maleic anhydride and with 1-octene may arise from the double bond of maleic anhydride being more reactive than that of 1-octene. With the more reactive olefin, capture of the furyl radical might occur

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[1] Maumee Chemical Co., Toledo, Ohio.

[2] For references see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 287.

[3] T. Patrick, Jr., U. S. Patent 2,841,592 (1958).

[4] T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962).