dichromate and sulfuric acid for 30 min at −5 to −10°. The crude *p*-chloronitrosobenzene was steam distilled twice. It was then purified chromatographically by absorption on alumina and elution with diethyl ether. Finally the compound was recrystallized, from ethanol, mp 88°, yield 29% (lit.[6] mp 88°).

p-Bromonitrosobenzene was prepared by the oxidation of N-(4-bromophenyl)hydroxylamine with sodium dichromate and sulfuric acid at −5 to −10° during a period of 25 min. The crude *p*-bromonitrosobenzene was purified by repeated recrystallization from ethanol, mp 95°, yield 35% (lit.[13] mp 95°).

p-Iodonitrosobenzene was prepared by reducing *p*-iodonitrobenzene with zinc and ethanol to *p*-iodophenylhydroxylamine. This was added to ferric chloride solution in water and ice. The crude product, *p*-iodonitrosobenzene was filtered and steam distilled twice. The final purification was accomplished by repeated recrystallizations from ethanol at low temperatures (−25 to −45°), mp 104°, yield 20% (lit.[14] 104°).

p-Methylnitrosobenzene was prepared by the oxidation of N-(4-methylphenyl)hydroxylamine with sodium dichromate and sulfuric acid at −5 to −10° during a period of 25 min. The crude *p*-methylnitrosobenzene was purified by steam distillation and chromatographically by absorption on alumina. It was eluted with diethyl ether. The final purification was accomplished by recrystallization from ethanol at low temperatures (−25 to −45°), mp 48°, yield 30% (lit.[15] 48–49°).

m-Chloro- and *m*-bromonitrosobenzenes were prepared from their corresponding nitro compounds by the method described by Lutz and Lytton.[14] These compounds were steam distilled twice and further purified by repeated recrystallizations: *m*-chloronitrosobenzene, mp 72° (lit.[16] mp 72°), yield 25%; *m*-bromonitrosobenzene, mp 78° (lit.[16] mp 78°), yield 30%.

Kinetic Measurements. 1. Mechanics of Measurements.—A Beckman Model DB spectrophotometer was used for these studies. Solutions were measured in a 1.00-cm silica cell (3-ml capacity) fitted with a ground-glass stopper. The spectrophotometer cell compartment was thermostated by means of circulating water jacket. Within the cell-compartment temperature measurements were made with a caliberated thermometer. Observations of the closed compartment over prolonged periods showed that temperature variation was less than ±0.1° at the temperatures employed, 2, 10, 18, 25, and 30°. A Mettler analytical balance was used for weighings and hypodermic syringes were employed to measure the small volumes of liquids.

2. Determination of Rates.—Samples of 2,3-dimethyl-1,3-butadiene, and arylnitroso compounds were accurately weighed into volumetric flasks and solutions were made up with spectrograde quality solvents, acetonitrile, benzene, carbon tetrachloride, chloroform, cyclohexane, dichloromethane, and nitromethane. Plots of absorbances versus concentrations were constructed for the aromatic nitroso compounds at about 720 mμ in appropriate solvents. The concentrations of arylnitroso compounds employed were such that they obeyed Lambert-Beer's Law. The reactant solutions were placed in a water bath thermostated at the reaction temperature 1.5 hr prior to each run. At time zero, a 5.0-ml portion of the arylnitroso compound solution was transferred by means of a syringe into 5.0 ml of conjugated diene solution and the stop watch was started. Mixing was carried out in a flask (25-ml capacity) maintained at the reaction temperature. A portion (3 ml) of the reaction mixture was transferred by means of hypodermic syringe into the cell, placed in the themostated cell compartment and the absorbance was measured at appropriate time intervals. The reactions were followed more than 80% completion. A typical run lasted for more than 90 min.

Plots of log $a(b - x)/b(a - x)$ *vs.* t were constructed, the specific rate constants were obtained from the slope and the initial concentrations. Rate constants presented in Table I are average of two or more determinations, using different initial concentrations of conjugated dienes and arylnitroso compounds for each run. The average deviation (0.5–3%) showed the method to be satisfactorily precise.

As a check on the accuracy of the initial rate method, the rate constant of the reaction between *p*-bromonitrosobenzene and 2,3-dimethyl-1,3-butadiene at 2° was also determined by pseudo-first-order technique (Guggenheim method).[3] Using a large initial 2,3-dimethyl-1,3-butadiene concentration (1.25 M) and a low initial *p*-bromonitrosobenzene concentration (0.025 M), the reaction was followed at 720 mμ to more than 80% completion.

---

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

[14] R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 68 (1937).

[15] H. Zimmer, Ph.D. Dissertation, Technische Universitaet, Berlin, 1962.

[16] R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **119**, 773 (1921).

The Addition of Aromatic Nitroso Compounds to Conjugated Dienes. III. Effect of Solvent on Reaction Rates and Equilibrium Constant

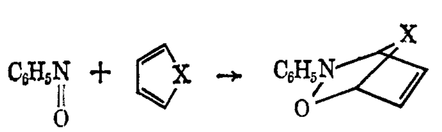
MUSHTAQ AHMAD[1] AND JAN HAMER

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received April 26, 1966

The influence of solvent on reaction rate and equilibrium constant for the 1,4 cycloaddition of nitrosobenzene to cyclic conjugated dienes has been studied. The reaction is essentially insensitive to solvent. Thermodynamic parameters for the equilibrium reaction between 1,3-cyclopentadiene and nitrosobenzene have been determined.

The 1,4 cycloaddition of nitrosobenzene to 1,3-cyclohexadiene or 1,3-cyclopentadiene exhibits a notable difference. With the former diene a cycloadduct is obtained which does not dissociate into its components at or around room temperature, while the cycloadduct obtained from the latter diene dissociates quite appreciably under these conditions.[2]



X = CH_2 or $(CH_2)_2$

The difference in the thermal stability of the cycloadducts may be rationalized by assuming that the cycloadduct of 1,3-cyclohexadiene is the more stable one, and that the activation energy for its formation is larger, so that the activation energy for the reverse reaction will be far larger for the 1,3-cyclohexadiene adduct than for the 1,3-cyclopentadiene adduct.

These assumptions are not unreasonable, since in the 1,3-cyclopentadiene cycloadduct the methylene bridge will cause a larger ring strain than the ethylene bridge in the 1,3-cyclohexadiene cycloadduct. That the transition state leading to the 1,3-cyclohexadiene cyclo-

---

(1) Abstracted from the Ph.D. dissertation of M. Ahmad presented to Tulane University, June 1965.

(2) For an extensive review on the addition of nitroso compounds to conjugated dienes, see J. Hamer and M. Ahmad, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1966, Chapter 12.

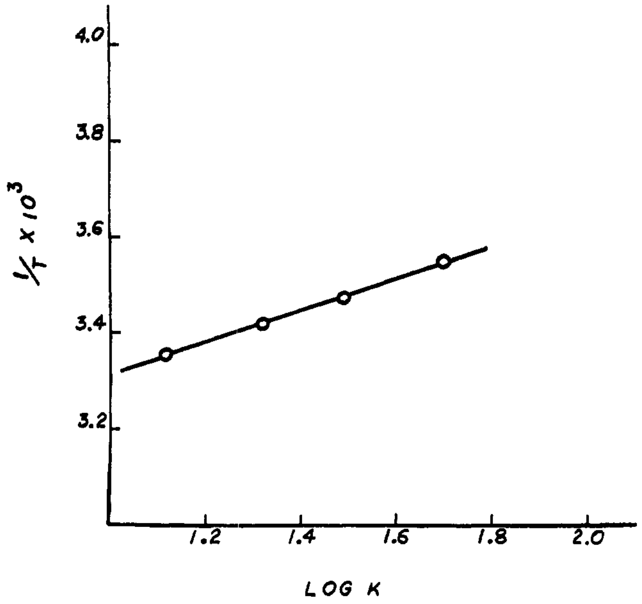
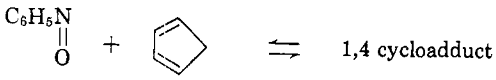


Figure 1.—Log *K* vs. 1/*T* for the following reaction.



adduct is the higher energy may be inferred from a study of the similar addition of maleic anhydride to 1,3-cyclopentadiene or 1,3-cyclohexadiene. In this study[3] it was shown that the energy of activation of the reaction with 1,3-cyclohexadiene was 3.7 kcal/mole higher than for the reaction with 1,3-cyclopentadiene. This observation in turn was rationalized by assuming that the distortion energy needed to build up the 1,3-cyclohexadiene–maleic anhydride transition state should be larger, since the distance between atoms 1 and 4 in 1,3-cyclopentadiene is about 20% smaller than between atoms 1 and 4 in 1,3-cyclohexadiene.

The influence of solvent on activation parameters is generally small for cycloaddition reactions. Polar groups in the reactants however may cause a considerable variation. Thus for the reaction between 1,3-cyclopentadiene and *p*-benzoquinone the activation energy varies between 8.0 and 12.7 kcal/mole depending upon the solvent.[3] This indicates that on passing from initial to transition state a change of polarity occurs.

The nitroso group is a highly polar group. This polar group itself is participating directly in the transition state of the cycloaddition reactions, since it is forming new bonds. Consequently, one would expect an even larger solvent effect here than for the system cited above, since with *p*-benzoquinone the carbonyl groups do not form new bonds, and therefore are not directly involved in the transition state.

The addition of nitrosobenzene to 1,3-cyclohexadiene has been studied in 95% ethanol.[4] The reaction has the normal[5] second-order kinetic dependence, with an enthalpy of activation of 10.6 kcal/mole and an entropy of activation of −37 eu. By a spectrophotometric method described previously[5-7] in detail, the rate of this reaction was determined at 25° in various solvents. The results are summarized in Table I. Although sizable variations occur in both dielectric constant and dipole moment of the solvent employed, the reaction rates are essentially constant. Because of this no further attempt was made to determine the activation parameters.

TABLE I

REACTION RATES OF THE 1,4 CYCLOADDITION REACTION BETWEEN NITROSOBENZENE AND 1,3-CYCLOHEXADIENE IN VARIOUS SOLVENTS AT 25 ± 0.1°

Solvent[a]	Dielectric constant	Dipole moment	$k \times 10$, l./mole × min[b]
Ethanol (95%)	36.3	1.80	6.98[c]
Dichloromethane	9.1	1.96	6.44
Chloroform	4.8	1.55	6.64
Carbon tetrachloride	2.2	0.00	6.25
Benzene	2.3	0.00	6.02
Cyclohexane	2.0	0.00	6.29

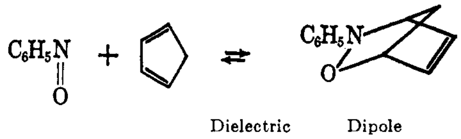
[a] Turbid solutions of 1,3-cyclohexadiene precluded rate measurements in methanol, nitromethane, or acetonitrile. [b] Average value for three to four determinations. Variations between 0.5–3%. [c] Calculated at 25° from data provided by G. Kresze, J. Firl, H. Zimmer, and V. Wollnik, *Tetrahedron*, **20**, 1605 (1964).

This surprising insensitivity of the reaction rate to the solvent finds a parallel in the 1,3 cycloaddition of phenyl azide to norbornene.[8] For the 1,3 cycloaddition of aryl azides to norbornene, however, the azide group is much less sensitive to electronic effects ($\rho = +0.85$) than the nitroso group in the corresponding addition to conjugated dienes ($\rho = +2.51$). Nevertheless, a 50% difference in the rate of addition has been observed for aryl azides depending upon the solvent, a far higher percentage than reported in Table I for the nitroso group.

The lack of solvent sensitivity on the reaction rate makes a lack of solvent sensitivity on the equilibrium constant not unlikely. The equilibrium constant for the reaction between nitrosobenzene and 1,3-cyclopentadiene was determined in various solvents at 25°, and the results are summarized in Table II. The variations in the value of the equilibrium constant again are

TABLE II

EQUILIBRIUM CONSTANT DETERMINATION IN VARIOUS SOLVENTS AT 25 ± 0.1°



Solvent	Dielectric constant	Dipole moment	*K*[a]
Nitromethane	35.8	4.39	12.7
Methanol	32.6	2.97	16.6
Dichloromethane	9.1	1.96	13.2
Chloroform	4.8	1.55	13.8
Carbon tetrachloride	2.2	0.00	12.5
Cyclohexane	2.0	0.00	12.6

[a] Average value of *K* for three determinations each. Maximum deviation from average value 1.8%.

---

(3) A. Wassermann, "Diels-Alder Reactions," Elsevier Publishing Co., Inc., New York, N. Y., 1965.

(4) G. Kresze, J. Firl, H. Zimmer, and V. Wollnick, *Tetrahedron*, **20**, 1605 (1964).

(5) J. Hamer, M. Ahmad, and R. O. Holliday, *J. Org. Chem.*, **28**, 3034 (1963).

(6) M. Ahmad and J. Hamer, *J. Chem. Ed.*, **41**, 249 (1964).

(7) M. Ahmad and J. Hamer, *J. Org. Chem.*, **31**, 2829 (1966).

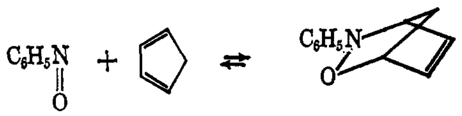
(8) P. Scheiner, J. P. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).

small, except for methanol where the equilibrium is shifted somewhat to the 1,3 cycloadduct. Although methanol could not be employed as a solvent in the determination of the reaction rate in Table I, the reported[4] value for ethanol falls in the same range. The interpretation of the influence of methanol on the equilibrium constant is not immediately apparent.

In order to determine the thermodynamic parameters the equilibrium constant was measured at several temperatures in dichloromethane, as summarized in Table III. A plot (Figure 1) of log K *vs.* $1/T$ provided the standard heat of reaction from the slope of the straight line, using the Gibbs-Helmholtz equation. The standard heat of reaction was found to be −14.8 kcal/mole, the standard entropy change −44.6 eu, and the standard free energy change −1.5 kcal at 25°.

TABLE III

EQUILIBRIUM CONSTANT DETERMINATION IN DICHLOROMETHANE AT VARIOUS TEMPERATURES



Temp, ±0.1°	K^a (av)	No. of detn
25	13.23	4
20	21.04	3
15	31.37	4
10	49.20	3

[a] Maximum deviation from average value 1.1%.

The standard entropy change is of the order of magnitude reported for "conventional" Diels-Alder reactions,[3] although a bit on the low side. On the other hand, the standard heat of reaction is somewhat on the high side.

Since at low temperature (about −70°) the 1,4-cycloadduct of 1,3-cyclopentadiene and nitrosobenzene can be isolated,[9,10] an opportunity was provided to study a retrograde 1,4 cycloaddition reaction at convenient temperatures. The rate of the dissociations was found to follow the sample first-order rate equation at the initial intervals of time, since the rate of dissociation of the cycloadduct was fast compared with the rate of formation of the cycloadduct or around room temperature. However, the difficulties encountered in the purification of the cycloadduct, because of its tendency to revert to its components, precluded measurement of the rate constant with the accuracy necessary to obtain meaningful data.

Experimental Section

The technique of the spectrophotometric kinetic measurements have been described in detail in previous papers.[5-7]

1,3-Cyclopentadiene (bp 39–40°, n^{22}_{D} 1.4446) was prepared by pyrolytic depolymerization and distillation of the commercially available dicyclopentadiene at atmospheric pressure.[11] The purity of the monomer was ascertained by gas–liquid partition chromatography. The Perkin-Elmer Model 154 gas chromatograph was also used for this analysis with 20% QF-1 on Chromosorb P 30–60 mesh column packing. The gas–liquid partition chromatographic analyses of the cyclopentadiene was carried out at two different column temperatures (~100 and ~180°) to ascertain the absence of impurities such as cyclopentane or polymerized cyclopentadiene. In each case a single peak was obtained.

3-Phenyl-2-ox-3-azabicyclo[2.2.1]hept-5-ene was prepared by the reaction between nitrosobenzene (5.35 g, 0.05 mole), and 1,3-cyclopentadiene (29.7 g, 0.45 mole), in diethyl ether (50 ml). The reaction mixture was allowed to stand for 12 hr at about −5° in an ice–salt bath. The solvent was then evaporated under vacuum at ice-bath temperature and the residue was extracted with five 50-ml portions of cold pentane. The pentane extracts were cooled to −70° in a Dry Ice–acetone bath until crystallization was complete, then filtered through a jacketed sintered-glass funnel which was cooled with powdered Dry Ice. The funnel was immediately closed with a tight-fitted one-hole stopper through which nitrogen gas was admitted. Drying of the product was achieved by passing cold dry nitrogen through the colorless crystals. The product was further purified by repeating the same sequence. The samples used for kinetic studies were recrystallized twice, mp 32° (lit.[9,10] 32–34°), yield 72–75%.

---

(9) N. L. Hepfinger, Ph.D. Dissertation, University of Pittsburgh, 1963.

(10) G. Kresze and G. Schulz, *Tetrahedron*, **17**, 7 (1961).

(11) G. Wilkinson, *Org. Syn.*, **36**, 31 (1956).

Reactions of α-Keto p-Toluenesulfonates with Trialkyl Phosphites[1]

DONALD B. DENNEY, NANCY GERSHMAN, AND JACK GIACIN

The School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey

Received March 16, 1966

The α-keto p-toluenesulfonates, $RCOCH_2OSO_2C_6H_4CH_3$, R = C_6H_5, CH_3, $(CH_3)_3C$, have been allowed to react with trimethyl and/or triethyl phosphite. In all cases vinyl phosphates, the Perkow reaction product, were formed. Reactions of two of these p-toluenesulfonates, R = C_6H_5, $(CH_3)_3C$, with triphenylphosphine and tributylphosphine, respectively, yielded the C-phosphonium salts. No enol phosphonium salts were detected. These results are discussed from a mechanistic point of view and are related to the mechanisms of the Perkow reaction and similar displacement processes.

The reactions of α-halocarbonyl compound with various phosphorus containing nucleophiles have been the subject of extensive study.[2] The products formed from these reactions are of several general structural types. It has become increasingly clear that the product(s) obtained from any given reaction depend on the nature of the nucleophile, the structure of the α-halocarbonyl compound and the reaction conditions. Typical products from the reaction of a trialkyl phosphite and an α-halo ketone are the vinyl phosphate, II, the Perkow reaction product, and an α-keto phosphonate, III, the Arbusov reaction product; when alcohols or acetic acid is present, α-hydroxy phosphonates, V, are

---

(1) This research has been supported by the National Science Foundation under NSF GP202 and GP4997.

(2) For general reviews, see (a) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961); (b) B. Miller, "Topics in Phosphorus Chemistry," Vol., 2, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons Inc., New York, N. Y., 1965, pp 178–187.