***cis*-Dimethyl Pentacyclo[4.4.0.0^{2,5}.0^{3,10}.0^{4,7}]decane-1,9-dicarboxylate (7).** A solution of 4.52 g (22.3 mmol) of **5** in 40 ml of methanol was heated at reflux for 6 hr. Evaporation of the solvent gave **6** as a viscous oil. This material was directly dissolved in ether and treated with diazomethane. Evaporation gave a semisolid mixture which was recrystallized three times from hexane to afford 2.12 g (38%) of **7** as white crystals, mp 78–82°. Two more recrystallizations from hexane gave crystals melting at 80–82° (lit.[11] mp 81–82°).

***cis*-Dimethyl Pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]decane-9,10-dicarboxylate (8).** A solution of 2.08 g of **7** and 150 mg of silver fluoroborate in 10 ml of acetone was heated at reflux for 2 hr. The cooled solution was passed through a short column of alumina to remove the silver salt; elution with acetone yielded 2.03 g (97%) of **8** as white needles, mp 95–101°. Recrystallization of this solid from hexane gave crystals melting at 101–103° (lit.[14] mp 102°).

Pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene. Snoutene (3). Diester **8** (2.00 g, 8.06 mmol) and sodium hydroxide (1.2 g, 30 mmol) were heated at reflux in 50 ml of water until the solid dissolved (*ca.* 2 hr). The solution was cooled and acidified with sulfuric acid. The resulting precipitate was filtered, washed with water, and dried to give 1.37 g (77%) of crude diacid (mixture of cis and trans isomers), mp 210–224°.

This diacid (1.36 g) and 1.4 ml of triethylamine were dissolved in 10 ml of water and added to 90 ml of pyridine in a water-jacketed electrolysis cell equipped with platinum electrodes. The electrolysis was allowed to proceed for 10 hr at 10–23°; initial current 0.5 A, final current 0.1 A. The dark solution was diluted with 250 ml of water and extracted with five 7-ml portions of pentane. The combined pentane extracts were washed with dilute hydrochloric acid, dried, and evaporated through a Vigreux column. The residue was sublimed at room temperature and 20 mm (Dry Ice condenser) to give 133 mg (16.5%) of white crystals, mp 61–62° (lit.[14] mp 61–62°).

9,10-Dideuteriosnoutene (9). Diester **8** was hydrolyzed as above, except that NaOD in D_2O was employed. Electrolysis in the previously described fashion gave **9** with 63% deuteration at the vinyl positions (consult Chart I).

Thermal Rearrangement of Snoutene (3). The hydrocarbon (25 mg) was slowly sublimed into a quartz tube (28 cm × 16 mm) packed with quartz chips maintained at the desired temperature. The pressure in the system was maintained at 20 mm as a slow stream of dry nitrogen was passed through the system. The pyrolysis product (24 mg) was collected in a trap cooled in a Dry Ice-acetone bath. The mixture was analyzed by vpc (SF-96 at 110°) and separated by this technique.

At 530°, there was obtained in addition to recovered snoutene (51%), *cis*-9,10-dihydronaphthalene (32%),[22] 1,2-dihydronaphthalene (4%),[23] 1,4-dihydronaphthalene (8%),[24] and naphthalene (5%). At 580°, the ratio of these products was found to be 8:5:32:36:18.

Degenerate Thermal Rearrangement of 9,10-Dideuteriosnoutene (9). The hydrocarbon (82 mg, 63% d_2 at the vinyl positons) was pyrolyzed as above at 530° to afford 80 mg of a pale yellow liquid. Vpc analysis indicated the presence of snoutene (58%) in addition to the other products found earlier. The snoutene was collected and analyzed by nmr (see Table I). Repetition of the procedure at 500° gave 86% of recovered starting material with the deuterium label specifically scrambled (Chart I).

Acknowledgment. The authors wish to express their indebtedness to the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this work.

(22) Authentic *cis*-9,10-dihydronaphthalene was prepared by pyrolysis of bicyclo[4.2.2]decatetraene.[18]

(23) H. Hock and S. Lang, *Chem. Ber.*, **75**, 313 (1942).

(24) We thank Dr. John F. Hansen for a sample of this hydrocarbon which was prepared according to the procedure of E. S. Cook and A. J. Hill, *J. Amer. Chem. Soc.*, **62**, 1995 (1940).

Photochemical Synthesis. The Addition of Aromatic Nitro Compounds to Alkenes[1,2]

J. L. Charlton, C. C. Liao, and P. de Mayo*

Contribution from the Department of Chemistry,
University of Western Ontario, London, Canada.
Received August 18, 1970

Abstract: It is shown that the photochemical addition of aromatic nitro compounds to alkenes gives 1,3,2-dioxazolidines. Certain members of this group of substances have been obtained in pure crystalline form at low temperature, but decompose readily at room temperature. Evidence is provided that the addition proceeds through an n,π* triplet in a two-step electrophilic process. The mode of decomposition of the dioxazolidine derived from *m*-chloronitrobenzene and cyclohexene has been examined. It seems very probable that an intermediate nitrenium ion is involved. In the presence of diethylamine, however, hydrogen abstraction followed by cyclization occurs in preference.

The photocycloaddition of the carbonyl group to alkenes has been extensively studied,[3] but, in contrast, the parallel property of the aromatic nitro group has received little attention.[4] In 1956 Büchi and Ayer reported on the irradiation of nitrobenzene in cyclohexene and in 2-methyl-2-butene.[5] They recorded the formation of carbonyl products, azobenzene, and other substances, and rationalized this transformation on the basis of the formation of an intermediate 1,3,2-dioxazolidine (see Scheme I). Both previously and since, such dioxazolidine formation has been postulated, but in most cases the evidence, in comparison with the experiments reported by Büchi and Ayer, has been tenuous,[6] tentative, or has been questioned.[7] The intermediary addition of the nitro group to a Schiff[8] base and

---

(1) Part XXXV in this series. A preliminary account of a part of the work here described has been reported: J. L. Charlton and P. de Mayo, *Can. J. Chem.*, **46**, 1041 (1968).

(2) Publication No. 17 from the Photochemistry Unit, Department of Chemistry, University of Western Ontario.

(3) See, for example, an excellent review by D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

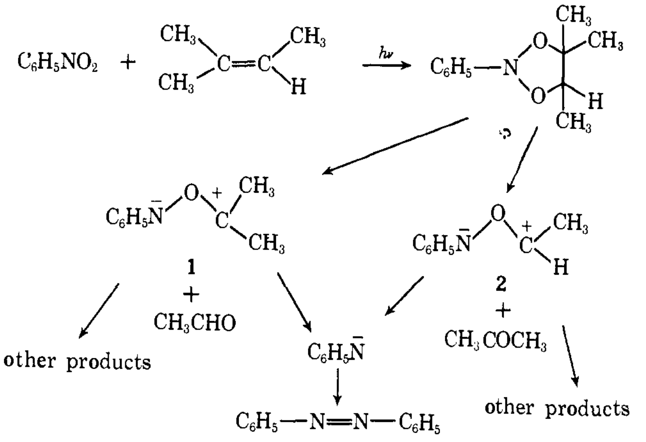
(4) For a review see H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part 1, H. Feuer, Ed., Interscience, New York, N. Y., 1969, p 193.

(5) G. Büchi and D. E. Ayer, *J. Amer. Chem. Soc.*, **78**, 689 (1956).

(6) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

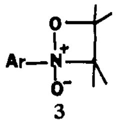
(7) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

Scheme I[a]



[a] The zwitterions 1 and 2 postulated were further transformed. One transformation product was acetanilide. A second was formulated as a neutral six-membered heterocyclic substance. This has been since shown to be the nitrone. We thank Professor Büchi cordially for telling us this.

to diphenylacetylene[9] has also been reported.[10] However, although the arguments of Büchi and Ayer were persuasive (and, in the event, were correct) it was possible to conceive of an alternative pathway to the various products isolated through a four-membered intermediate such as 3. It was to resolve this question that the reaction was reinvestigated.



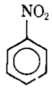
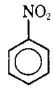
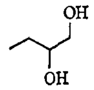
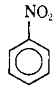
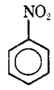
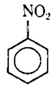
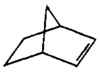
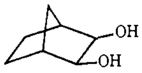
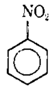
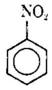
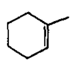
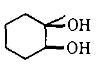
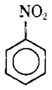
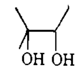
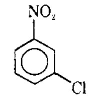
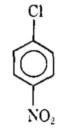
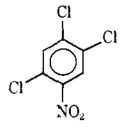
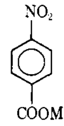
3

Results and Discussion

The Products. Büchi and Ayer irradiated nitrobenzene with the alkene at room temperature, and the isolation of products was achieved by a combination of distillation and chromatography. Thin-layer chromatography revealed to us that, under these conditions, even using a Pyrex filter, the solution contained a very complex mixture of products. Irradiation at −78° led to the formation of a pale, clean solution which colored on warming.

The isolation of the unstable photoproducts was achieved by removal of solvent and alkene–cyclohexene in the first instance—at −20° when, fortunately, the residue crystallized, and could be recrystallized at low temperature from an ethyl acetate–*n*-pentane mixture. The nmr spectrum of the adduct is shown in Figure 1 taken in $CDCl_3$ at −25°, and when the solution was allowed to warm, the changes observed are shown (inset). These were the disappearance of the signal at δ 4.38 (methine hydrogens on carbon-bearing oxygen) and the appearance of an aldehydic signal at 9.53. Similarly, the infrared spectrum taken in chloroform at −20° showed no carbonyl absorption. On warming to room temperature such absorption was observed at 1720 cm^{-1}. Such changes are compatible with the overall decomposition process envisaged by Büchi and Ayer,[5] and indicated, for the case of 2-methylbut-2-ene, in Scheme I.

Table I. Hydrogenation Products of Photoadducts

Nitro compd	Alkene	Diol	—Yield, %— Diol	Aniline
	Cyclohexene	*cis*-Cyclohexane-1,2-diol[d]	51[b] 93[a]	53[b] 86[a]
			89[b]	87[b]
		2,3-Butanediol[c]	87[b]	73[b]
		2,3-Butanediol[c]	82[b]	68[b]
			48[b]	47[b]
	Hex-1-ene	Hexane-1,2-diol	38[b]	51[b]
			33[b]	21[b]
			30[b]	34[b]
	Cyclohexene	*cis*-Cyclohexane-1,2-diol	79[b] 93[a]	
	Cyclohexene	*cis*-Cyclohexane-1,2-diol	46[b] 96[a]	
	Cyclohexene	*cis*-Cyclohexane-1,2-diol	19[b]	
	Cyclohexene	*cis*-Cyclohexane-1,2-diol	39[b]	

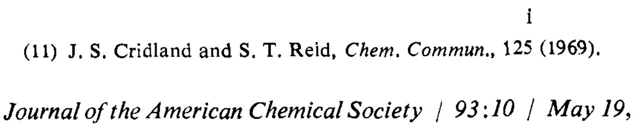
[a] Obtained by vpc analysis of the mixture formed on hydrogenation of the pure photoadduct. [b] Obtained by analysis of the mixture formed on hydrogenation of the crude photoadduct. [c] Mixture of *dl* and meso in the ratio of 65:35. [d] Formed together with ~5% *trans*-diol and a trace of hexane-1,6-diol.

---

(8) E. C. Taylor, B. Furth, and M. Pfan, *J. Amer. Chem. Soc.*, 87, 1400 (1965).

(9) M. L. Scheinbaum, *J. Org. Chem.*, 29, 2200 (1964).

(10) The conversion of the α,β′-unsaturated nitro compound, 3-(2 nitroprop-1-enyl)indole, into i on irradiation may also be formulated in terms of dioxazolidine, but an alternative zwitterionic intermediate was preferred by the authors.[11]



i

(11) J. S. Cridland and S. T. Reid, *Chem. Commun.*, 125 (1969).

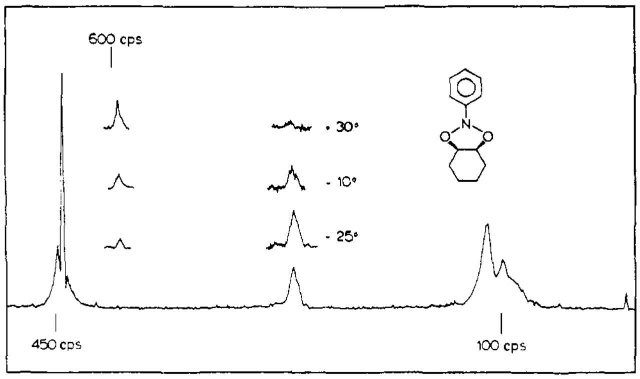
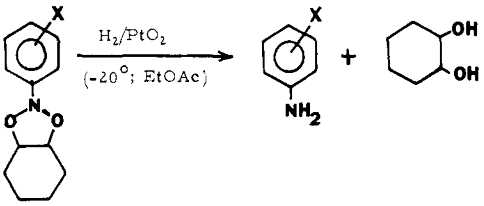


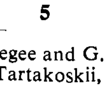
Figure 1. Nmr spectrum of the adduct of nitrobenzene and cyclohexene; inset, changes at the indicated temperature.

More direct proof of the structure **4a** was sought chemically, but in nearly all reactions examined the products were complex. In only one reaction so far studied was the product clean and uncomplicated. It was found that catalytic hydrogenation of the adduct over a prereduced catalyst/platinum oxide at −20° gave, by hydrogenolysis, *cis*-cyclohexane-1,2-diol and aniline. If purified adduct was used the yields were high (see Table I). Similar pure adducts of cyclohexene with *m*-chloronitrobenzene (**4b**,) *p*-chloronitrobenzene (**4c**,) *m*-nitrotoluene, *p*-nitrotoluene, and *m*-nitrobenzonitrile have been prepared (for reasons detailed below) and the first two adducts gave hydrogenation yields as indicated in Table I. In other cases the adducts were formed, but could not be purified successfully. These include those with methyl *p*-nitrobenzoate, dimethyl 4-nitrophthalate, dimethyl 5-nitroisophthalate, and 2,4,5-trichloronitrobenzene.

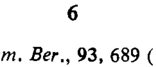


4a, X = H
b, X = *m*-chloro
c, X = *p*-chloro

The evidence, then, establishes these unstable adducts as derivatives, as predicted by Büchi and Ayer,[5] of 1,3,-2-dioxazolidine. (The prior formation of **3** and rearrangement to dioxazolidine, as suggested by a referee, are not excluded.) It will be recoginzed that these substances stand between the very unstable primary ozonides[12] **5**, and the stable ethylene ketals. At the time of the original work no substance was known wherein trivalent nitrogen was attached to two oxygen atoms, whether acyclic, cyclic and distributed between two rings, or in a 1,3,2-dioxazolidine. Recently Russian workers[13,14] have prepared substances such as **6** by chemical routes, and these appear to be stable.



5



6

Bands for N–O stretch are quoted as being near 1045 cm^{-1}; similar bands are present in our infrared spectrum.

Some attempt was made to determine the scope of the reaction. It was at first hoped that the alkene could be used in dilute solution, *i.e.*, that the addition–hydrogenation might serve as an additional method for the hydroxylation of alkenes. This was found not to be possible; dilution led to a rapid decrease in the rate of product formation. The reason for this, as will be seen, is the very rapid, presumably unimolecular, decay of the excited nitrobenzene molecule. This dominates the bimolecular reaction pathway except at high alkene concentration.

Reaction does, however, occur with other alkenes. This was shown by hydrogenation of the crude irradiation products and isolation and estimation of the relevant diols. The results are detailed in Table I. It is interesting that although piperylene and butadiene quench the reactive species involved, nonetheless an adduct was also formed at the exceedingly high concentration used.[15] No adduct was formed in any quantity when *m*-chloronitrobenzene was irradiated in the presence of 3-hexyne, *N*-ethylneopentylimine, and allene. It is not excluded that prolonged irradiation might yield some product, and intensive study was not made.

Mechanism of the Reaction. A number of questions posed themselves. These were those of state, multiplicity, and energy of the reactive species, and its lifetime and rate of reaction. We have made some attempt to answer these, but one major difficulty precluded the possibility of accurate work. In all quantum yield measurements it is desirable to estimate the rate of formation of product rather than the rate of disappearance of starting material. In the present instance the instability of the adduct excluded any possibility of its estimation under conditions suitable for photochemical study. The measurement of the disappearance of starting material is far easier,[18] and this was, in fact, done. But use of this entailed the assumption that no chemical process other than that of concern occurs, and this was, here, unjustified. It was known, for instance, that nitrobenzene in an excited state can abstract hydrogen in much the same way as benzophenone. That we were as successful as we were is due to the fact that the rate constant for addition appears to be significantly larger than the rate constant for hydrogen abstraction.

That the reaction could proceed through a triplet was shown as follows. Equivalent irradiations of *m*-chloronitrobenzene in cyclohexene were performed at

---

(12) R. Criegee and G. Schroeder, *Chem. Ber.*, **93**, 689 (1960).

(13) V. A. Tartakoskii, I. E. Chlenov, S. S. Smagin, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 583 (1964); 552 (1965).

(14) K. V. Altukhov and V. V. Perekalin, *Zh. Org. Khim.*, **2**, 1902 (1966).

(15) The addition of 2,3-dimethyl-1,3-butadiene to benzophenone to give an unstable adduct has been reported by Dauben.[16] This may be a result of energy transfer from excited benzophenone to the diene, followed by back addition of the excited diene, or else perhaps singlet addition by benzophenone. Both possibilities exist in the present case also and chemical reaction has been suggested (see ref 17). It is noteworthy that cyclohexenone and to a lesser extent cyclopentenone give undetermined adducts at very high diene concentration (~5 *M*) (M. F. Tchir, unpublished observations; E. J. Corey, quoted by O. L. Chapman and G. Lenz, *Org. Photochem.*, **1**, 297 (1967)).

(16) J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Amer. Chem. Soc.*, **88**, 2745 (1966).

(17) R. Hurley and A. C. Testa, *ibid.*, **90**, 1949 (1968). An error of a factor of two, for example, does not affect our general conclusions.

(18) Even is this far from reliable. The starting material can only be conveniently estimated in the irradiation mixture directly and only approximately, or by meothds (for instance gas–liquid chromatography) in which the adduct has decomposed to give the plethora of products all of which, it is assumed, do not interfere.

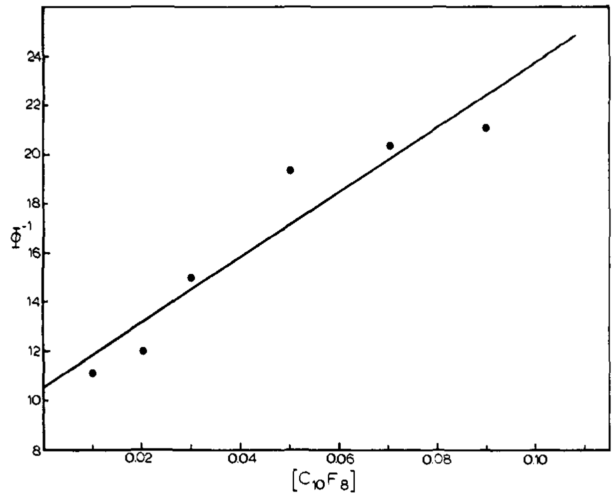


Figure 2. Stern–Volmer plot of the quenching of the addition of *m*-chloronitrobenzene to cyclohexene with octafluoronaphthalene.

−15° using 366-nm light. In one case sufficient benzophenone was added to absorb >90% of the incident light, yet the consumption (5%) of nitro compound was essentially the same as when the ketone was omitted (5.5% conversion). That is, the light absorbed by the benzophenone was as effective in inducing reaction as the light absorbed directly by the nitro compound. Since the photochemical behavior of benzophenone is now reasonably well understood, this was interpreted to mean that the nitrobenzene triplet is here involved. This result was not surprising since it has already been shown[19] that the photoreduction of aromatic nitro compounds in solution proceeds through a triplet. A parallel therefore existed between the nitro and carbonyl groups with respect both to addition to olefins and hydrogen abstraction.[20]

In such a triplet process a concerted addition seemed unlikely although there was possibly sufficient energy for the generation of the triplet adduct.[21] Unless a mechanism existed which permitted decay to the ground state, with spin inversion, when energetic demands were not yet too high, but which were sufficiently advanced in bond formation to ensure stereospecificity, then a biradical (triplet) intermediate was to be expected. In the extreme, with an acyclic olefin, memory of the original geometry could be erased and the same mixture might be obtained irrespective of which geometrical isomer of the olefin was used as starting material.[22] The addition of nitrobenzene to *cis*- and *trans*-2-butene was therefore studied. In both cases after hydrogenation a mixture of 65% *dl*- and 35% *meso*-2,3-butanediol was obtained. Clearly a stepwise reaction was indicated. The formation of the greater than 95% cis adduct in the addition of nitrobenzene to cyclohexene thus required a conformational rationalization. Either ring closure in the axial biradical is faster than cyclohexene ring inversion, or the "equatorial" biradical has a thermodynamic preference for cis ring formation. This contrasts with enone addition which appears to have a preference for the production of trans fusion.

The evidence so far indicated that a stepwise mechanism was involved and that a triplet mechanism was at least possible. To determine whether direct irradiation also implied intervention of the triplet, quenching studies were undertaken. The quantum yield of disappearance of *m*-chloronitrobenzene in 1:1 cyclohexene–ether in the presence of varying quantities of octafluoronaphthalene (E_T = 56.6 kcal/mol) was determined.[18,19,23,24] A solution of cyclopentenone in cyclohexene was used as actinometer.[25] Assuming that the processes involved were decay (k_d) and quenching (k_q) and that addition (k_r) was faster than all other chemical processes the usual steady-state assumption led to the expression

$$\frac{1}{\phi} = \frac{1}{\phi_{ic}}\left(1 + \frac{k_d}{k_r[O]} + \frac{k_q[Q]}{k_r[O]}\right)$$

where ϕ_{ic} is the quantum yield of triplets and [O] and [Q] are the concentration of olefin and quencher, respectively. The results are indicated in Figure 2. While these are clearly unsuitable as an indication of whether the plot is straight or not, results of general interest may be obtained. *On the assumption* that the results indicate a scatter about a straight line (least squares), then the slope is of the order 130 M^{-1} and the intercept approximately 10. With k_q (9.3 × 10^{-9} sec^{-1}) determined from the Debye equation,[26,27] the only value remaining for the obtention of k_r and k_d was ϕ_{ic}, the efficiency of intersystem crossing. This has not been determined for *m*-chloronitrobenzene itself, but for nitrobenzene has been shown in the extensive work of Testa to be 0.67 ± 0.10. Assuming this value[17,28] we obtain the order of magnitude of k_r and k_d as 2 × 10^7 M^{-1} sec^{-1} and 6 × 10^8 sec^{-1}, respectively. These may be contrasted with the more accurate work of Testa who found[17,29] a value of 10^9 sec^{-1} for the radiationless decay constant and 0.8 × 10^6 M^{-1} sec^{-1} for the hydrogen abstraction rate from isopropyl alcohol. Since the abstraction rate from cyclohexene would be expected to be comparable with that from isopropyl alcohol,[30,31] our original assumption may be justified. It is in all event clear how, with such a rapid decay constant, a high concentration of olefin is necessary for effective reaction.

There remains to discuss the energy and state of the triplet involved. This had originally been placed on the

---

(19) J. K. Brown and W. G. Williams, *Chem. Commun.*, 495 (1966); S. Hashimoto, J. Sunamoto, H. Fujii, and K. Kano, *Bull. Chem. Soc. Jap.*, **41**, 1249 (1968); S. Hashimoto, K. Kano, and K. Ueda, *Tetrahedron Lett.*, 2733 (1969); C. Kaneko, S. Yamada, I. Yokoe, N. Hata, and Y. Ubukata, *ibid.*, 4729 (1966).

(20) The fact that the same excited carbonyl species appeared capable of efficient oxetane formation and hydrogen abstraction—the n,π* triplet—was first pointed out by D. R. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964).

(21) Presumably that of the aromatic nucleus, *i.e.*, about 71 kcal/mol if aniline is a suitable model: E. C. Lim and S. K. Chakrabarti, *J. Chem. Phys.*, **47**, 4726 (1967).

(22) This is in contradistinction with the addition of cyclic enones to open-chain alkenes wherein the original approach of the two molecules dictates part of the stereochemical course of the reaction.

(23) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc. C*, 1497 (1968).

(24) R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

(25) R. O. Loutfy, P. de Mayo, and M. F. Tchir, *J. Amer. Chem. Soc.*, **91**, 3984 (1969).

(26) P. J. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(27) The viscosity (6.15 × 10^{-3} P) was taken as the mean value of cyclohexene and ether at −15°.

(28) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **89**, 6917 (1967).

(29) W. Trotter and A. C. Testa, *ibid.*, **90**, 7044 (1968).

(30) Walling [C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965)] has shown that isopropyl alcohol is about four times as reactive as cyclohexane toward the benzophenone triplet. Cyclohexene is four times as reactive as cyclohexane (to phenyl radicals)[31] and both radical species maintain about the same rate ratio between cyclohexane and toluene which may justify the rough extrapolation.

(31) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

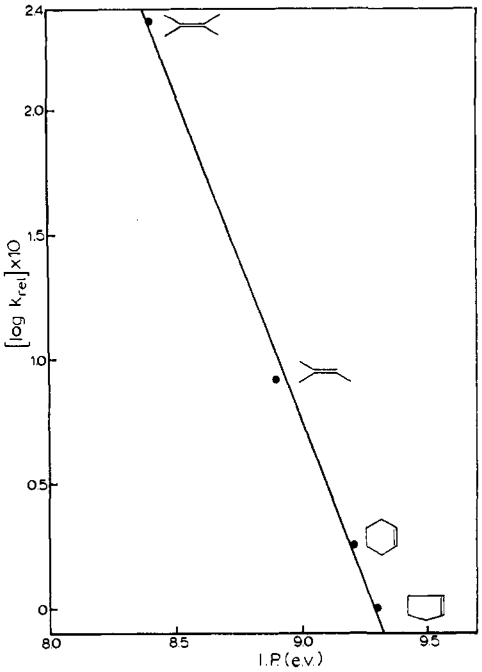


Figure 3. Relative rate of reaction of nitrobenzene with olefins with respect to ionization potential.

basis of phosphorescence emission at 60 kcal/mol.[32] This was apparently confirmed more recently[23] but we have only observed such emission from normal commercial nitrobenzene. Purification by glc destroyed the emission to the limits of our apparatus, and similar observations have been made by Testa.[29] Hence, as regards energy all that can be said is that the effective energy of triplet is below that of benzophenone (probably 3 kcal or more) and above that of octafluoronaphthalene. A figure of 60–66 kcal/mol seems most likely.

Testa[29] has concluded that the lowest triplet state of nitrobenzene is n,π^*. We concur with this view[33] which affirms the parallel between aromatic nitro compounds and carbonyl compounds with n,π^* participation in both addition and hydrogen abstraction. We have found, for instance, that 1-nitronaphthalene which has evidently[29] a lowest π,π^* triplet does not undergo cycloaddition after prolonged irradiation. A similar lack of reactivity was found with 2-nitrobiphenyl.

In order to study the substituent effect on the alkene with regard to cycloaddition, solutions of nitrobenzene in different alkenes were simultaneously irradiated. The relative rates of nitrobenzene disappearance were determined, and the quantum yields measured using a

Table II. Relative Rates of Addition of Nitrobenzene to Alkenes

Alkene	ϕ	$K_r/K_{r(\text{cyclopentene})}$	Ionization potential, eV
Cyclopentene	0.02	1	9.3
Cyclohexene	0.03	1.76	9.2
2-Methyl-2-butene	0.12	8.56	8.9
Tetramethylethylene	0.15	17.2	8.4

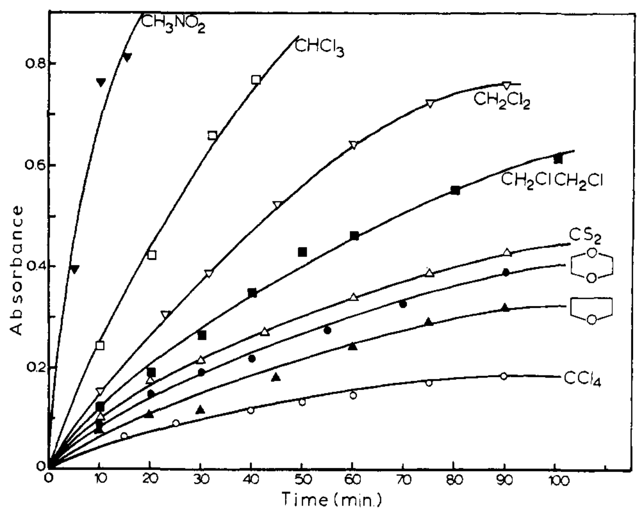


Figure 4. Decomposition curves of the adduct of nitrobenzene and cyclohexene in the indicated solvents.

solution of nitrobenzene in 50% isopropyl alcohol in 6 *N* hydrochloric acid as an actinometer.[28] The relative rates were obtained with respect to cyclopentene as arbitrary standard, and the results are given in Table II.

If the process is, as would be expected, electrophilic then increase of electron availability in the ethylenic linkage should increase the rate of addition. One measure of electron avalability is the ionization potential,[34] and in Figure 3 a plot is shown of log k_{rel} against the ionization potential, where k_{rel} is the rate relative to cyclopentene. Compatible with this interpretation is the observation that *m*-chloronitrobenzene does not react with the ethylenes substituted with electron-withdrawing groups, acrylonitrile and fumaronitrile.[35]

The reaction of aromatic nitro compounds with olefins may be summarized as an electrophilic attack of a short-lived n,π^* triplet on the olefin proceeding through a discrete (biradical) intermediate.

Stability and Mechanism of Decomposition of the Adducts. Since the substances here described appeared to be the first 1,3,2-dioxazolidines we attempted to find both substituents and conditions that could increase stability. With the *m*-chloro adduct as model, the effect of solvent was first examined. The decomposition was followed by the increase in carbonyl absorption at 1720 cm^{-1} at 21 ± 1°. The slopes at zero time were used for the crude relative rates (Figure 4) and were plotted against E_T values[36,37] (see Figure 5). Clearly, although no good correlation was obtained, there was strong indication of charge separation in the process of decomposition. This being the case, appropriate substitution of the aromatic nucleus should be able to oppose this charge accumulation. With substituted nitro compounds a similar crude rate study was performed (Figure 6) and the logarithm of relative rate plotted against σ^+.[37,38] The slope was found to be −0.84 (Figure 7), clearly indicating a positive charge

---

(32) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

(33) The contrary view has been expressed by Barltrop and Bunce.[23]

(34) R. J. Cvetanovic, *J. Chem. Phys.*, **30**, 19 (1959).

(35) It is noteworthy that while *o*-nitrostilbenes are light sensitive, when the olefin is substituted with a cyano group the substances are stable: W. Reid and M. Wilk, *Justus Liebigs Ann. Chem.*, **590**, 91 (1954).

(36) C. Riechardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(37) E. D. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968.

(38) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

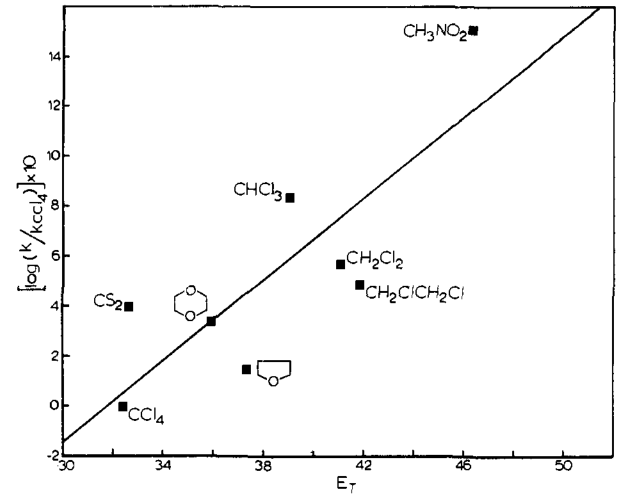


Figure 5. Relation of the initial relative rate of decomposition of the adduct of nitrobenzene and cyclohexene with solvent-change solvation property (E_T).

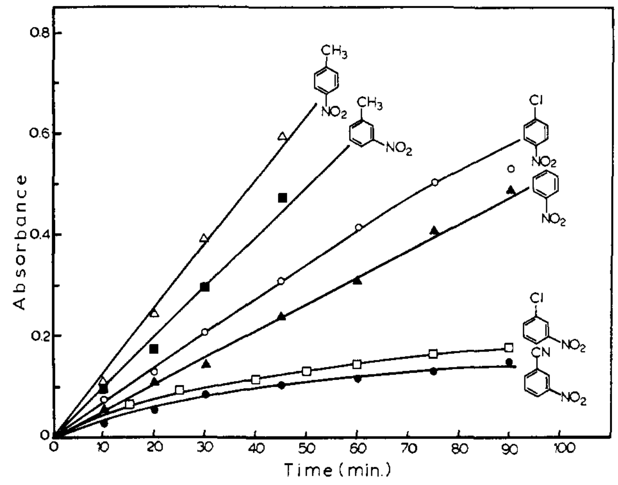


Figure 6. Decomposition curves of the adducts of various nitro compounds with cyclohexene.

proximate to the phenyl group.[39] Electron-withdrawing groups stabilized the adducts, but in no case was a product stable at room temperature obtained. Crystals could be brought to room temperature, but on occasion decomposed abruptly.

We were thus led to suppose that the decomposition of the dioxazolidines proceeded as indicated in Scheme I, but with charges reversed. Evidence for the nitrene, however, first suggested by Büchi and Ayer, was essentially the formation of azobenzene, supposedly by the coupling of two nitrenes. We were led to seek further evidence. It has been reported[40] that ring expansion in-

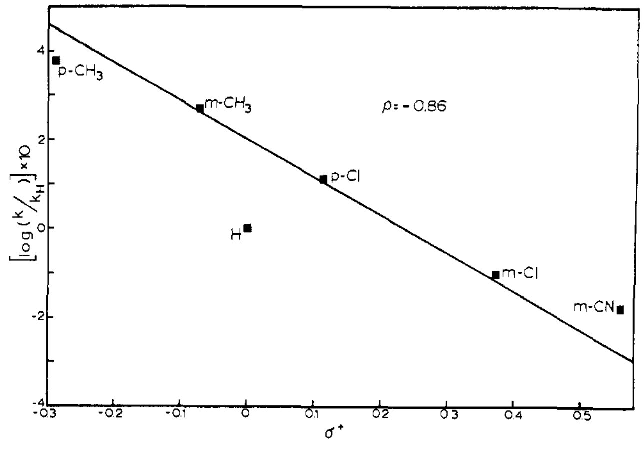
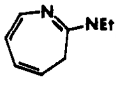
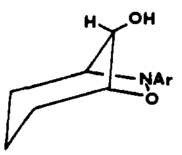


Figure 7. Hammett plot of the relative decomposition rates of aromatic adducts of nitro compounds with cyclohexene in CCl_4.

volving nitrene participation occurred in the deoxygenation of nitro compounds and in the photolysis of phenyl azide in the presence of amines. Thus, the photolysis of phenyl azide in diethylamine has been reported to give **7**, an azepine.[40c] We attempted to generate the same



7



8

nitrene by the decomposition of the adduct by its addition to boiling diethylamine. No 2-diethylamino-3*H*-azepine (**7**) was formed. An alternative reaction—one proceeding at a slower rate than recombination[41]—which could be expected was hydrogen abstraction, but the resultant product, aniline, was not present in detectable quantities. In contrast, however, to the very complex mixture formed on decomposition of the adducts in a neutral solvent, that in diethylamine was not so discouraging. For convenience the decomposition of the *m*-chloro adduct was chosen for study in more detail. It was found that decomposition in refluxing diethylamine gave 3,3′-dichloroazoxybenzene, 3,3′-dichloroazobenzene, cyclopentenaldehyde, and a new substance **8**. There was also a minor product and some polymeric material which were not further examined. In the nmr spectrum of **8**, a signal at δ 3.87 disappeared on equilibration with D_2O, and its chemical shift was solvent dependent. In C_6D_6 (as distinct from $CDCl_3$) it appeared as a doublet (δ 2.44; $J = 4$ Hz) being coupled with the proton at δ 4.84 (δ 5.18 in $CDCl_3$). These signals were those, therefore, of the hydroxyl hydrogen and the methine on carbon-bearing oxygen. The signals at δ 2.95 and 4.25 were complex, but double irradiation (C_6D_6) indicated that these protons were coupled with each other. Although the complexity precluded further detailed analysis of the spectrum, the lack of coupling of the methine proton with the adjacent protons is that to be expected of such a bridged system.[42]

---

(39) Büchi and Ayer suggest in their original paper that decomposition occurs to a zwitterion (shown in Scheme I) which has a negative charge on nitrogen. This zwitterion is mesomeric if allowed the appropriate geometry. To the extent that these authors imply a negative

$$C_6H_5\overset{-}{N}O\overset{+}{C}HR \longleftrightarrow C_6H_5\overset{-}{N}\overset{+}{O}{=}CHR \longleftrightarrow$$

$$C_6H_5N{=}\overset{+}{O}\overset{-}{C}HR \longleftrightarrow C_6H_5\overset{+}{N}O\overset{-}{C}HR$$

charge accumulation on the nitrogen our results contradict their intention.

(40) (a) R. Huisgen and M. Appl, *Chem. Ber.*, **91**, 12 (1958); (b) R. A. Odum and M. Brenner, *J. Amer. Chem. Soc.*, **88**, 2074 (1966); (c) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966); (d) J. I. G. Cadogan and M. J. Todd, *Chem. Commun.*, 178 (1967); (e) J. I. G. Cadogan, *Quart. Rev., Chem. Soc.*, **22**, 222 (1968).

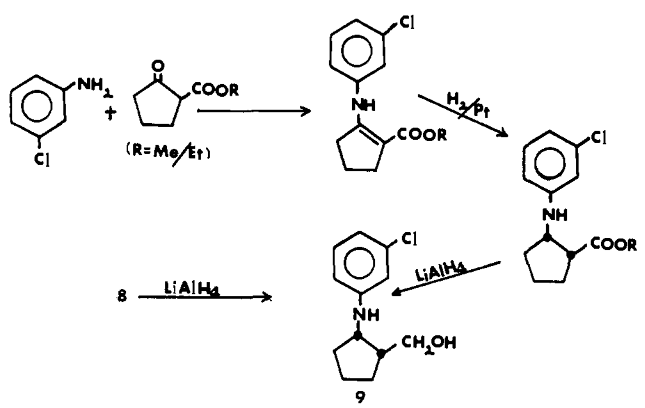
(41) A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, **64**, 3265 (1968).

(42) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 280.

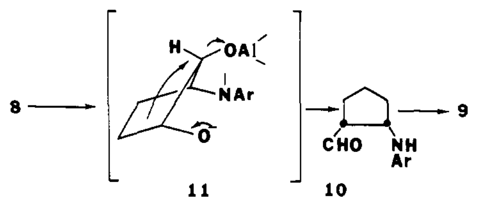
Acetylation gave a monoacetate in which the methine proton had moved to δ 6.0. The infrared showed no NH or OH stretch and had the carbonyl absorption bands for a normal *O*-acetate (1750, 1220 cm^{-1}).

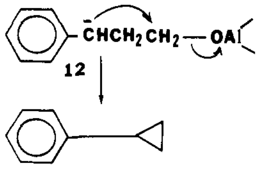
The substance **8** gave a multiplicity of products on hydrogenation in ethyl acetate or methanol over 10% palladium/charcoal or platinum oxide. Reduction with lithium aluminum hydride in ether gave only *cis*-2-(3′-chloroanilino)cyclopentanylcarbinol (**9**) and an unidentified minor product. The alcohol **9** showed absorption at 3580 and 3380 cm^{-1} in the infrared. The nmr revealed the presence of a primary alcohol (δ 3.70, 2 H, d, $J \sim 6$ Hz) and two exchangeable protons. A signal, complex, at δ 2.23 suggested the presence of a methine hydrogen on carbon bearing nitrogen. This evidence that compound **9** was as designated was supported by the results of mild acetylation (acetic anhydride–pyridine at room temperature). A monoacetate was obtained which showed absorption bands at 1735 and 3430 cm^{-1}. The $-CH_2-$ of the primary alcohol moved downfield to δ 4.07 in the acetate, and at δ 3.80 one broad exchangeable proton remained. The signal at δ 2.23 moved, slightly, to 2.46. The structure of compound **9** was finally established by the synthesis summarized in Scheme II. As starting material the keto ester used was a commercially available mixture of methyl and ethyl esters, and this mixture was retained until reduction with lithium aluminum hydride. Details are given in the Experimental Section and no special comment is necessary.

Scheme II



Specific information as to the mode of rearrangement of **8** to **9** is lacking. At the present time we favor preliminary alkoxide formation, reduction of the N–O bond followed by a pinacol-type rearrangement to give the aldehyde **10**. The ejection of an alkoxide as a leaving group appears not to be frequently observed, but at least one instance has been reported. The reduction of β-cinnamyl alcohol by lithium aluminum hydride to give phenylcyclopropane has been interpreted[43] as indicated in **12**.

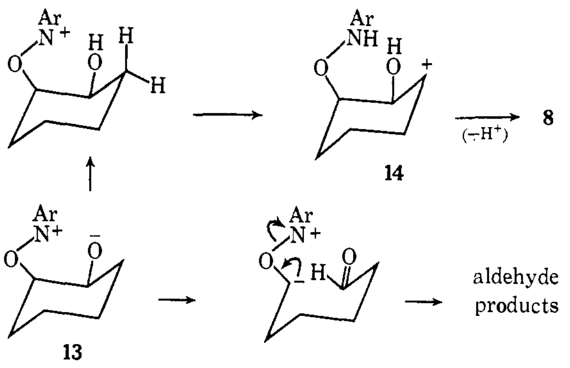




The stereochemistry of **9** would appear to be cis by the fact of its generation in a hydrogenation step from the enamine. With a rearrangement of the type indicated in **11** a cis relationship of the two oxygen functions is likewise indicated.

It was then possible to rationalize the formation of **8**. We had shown that cleavage generated a positive charge on the nitrogen atom. In a neutral nonprotic solvent this zwitterion **13** could decompose further with the ultimate generation of carbonyl compounds. In the presence of a protic solvent (diethylamine) the alkoxy ion was protonated, leaving a nitrenium ion. In principle a nitrenium ion, as has been shown by Gassman, may be a singlet or a triplet.[44] In either event hydrogen abstraction processes would be expected, but in the present instance the presence of an adjacent oxygen atom which can assist in the delocalization of the positive charge by way of an oxonium ion persuaded us that in all probability we were dealing with the singlet. The situation, as far as products are concerned, is similar in the formation of cyclic ethers by the oxidation of alcohols with lead tetraacetate,[45] although here a radical mechanism is usually accepted.

So, in the present case, hydrogen abstraction by the nitrenium ion generates the carbonium ion **14**. Closure leads to the formation of **8**.

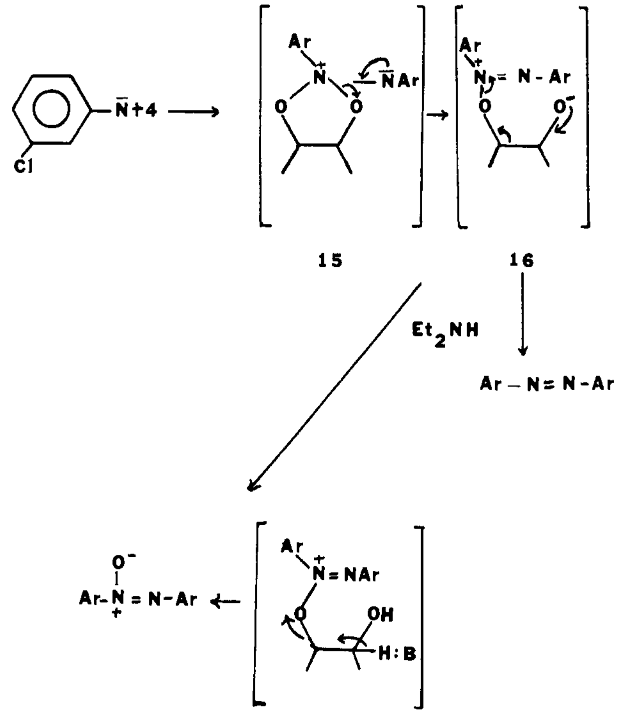


The problem of the mode of formation of the azobenzene (in nonprotic solvents) and of azoxybenzene (in diethylamine) remains. There is no doubt that the combination of nitrenes is diffusion controlled[41] and that this process could account satisfactorily for the formation of azobenzene. It was not excluded, however, that attack of the nitrene on the adduct might also occur. Under such circumstances an alternative pathway could be envisaged passing through an azoxy ether **15**. If, in the presence of diethylamine, **16** may be protonated to **17**, an alternative elimination may ensue, giving azoxybenzene.

(43) M. J. Jorgensen and A. F. Thacher, *Chem. Commun.*, 1290 (1969).

(44) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, 91, 5176 (1969); P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).

(45) D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 47, 1961 (1964).



17

Experimental Section

General Procedures. Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were determined on Beckman IR-5A and -10 spectrophotometers, uv spectra on a Cary 14 spectrophotometer, nmr on Varian A-60, T-60, and HA-100 spectrometers, and mass spectroscopy was done on a Varian M-66 spectrometer. *m*-Chloronitrobenzene was zone refined for quenching studies. Cyclohexene and cyclopentenone were purified as described previously.[46] Liquid nitrobenzenes were distilled once, and solid aromatic nitro compounds were recrystallized at least once.

Preparative Irradiations. A typical example was that of nitrobenzene in cyclohexene: a solution of 430 mg (3.5 mmol) of nitrobenzene in 50 ml of cyclohexene-diethyl ether mixture (1:2) was irradiated under nitrogen with a Hanovia 450-W medium-pressure lamp through Pyrex at −78° for 5 hr. The progress of the irradiation was followed by glc analysis until complete disappearance of the nitrobenzene. After removing solvent and excess cyclohexene at −20° (0.005 mm) the residue was recrystallized several times from ethyl acetate-*n*-pentane. A yield of 120 mg (17%) of adduct was obtained, but this in no way represents a maximum.

Other photocycloadditions were performed in a similar manner with adjustments in concentration and solvent dependent on the solubility of the various nitrobenzenes.

Hydrogenation of Adducts. A typical procedure was as follows. Platinum oxide (200 mg) in 10 ml of ethyl acetate was hydrogenated at room temperature, then cooled to −20°. A solution of 205 mg (1.0 mmol) of nitrobenzene–cyclohexene adduct in 5 ml of ethyl acetate was then added and the mixture shaken under hydrogen for 2 hr at −20° and 1 hr at room temperature. Filtration and evaporation of the solvent gave a residue which on crystallization from benzene gave *cis*-cyclohexane-1,2-diol, mp 96–97°, undepressed on a mixture with an authentic specimen. The nmr and infrared spectra were identical with those of the authentic specimen.

The mother liquor remaining was extracted with 1 *N* hydrochloric acid and the base was isolated after neutralization and identified (infrared) as aniline. It was characterized as the benzenesulfonamide (mp and mmp 109–110°). The yields of the diol and aniline were obtained by glc analysis on a 6 ft × 0.25 in. column of 2.5% FFAP on Chromosorb P using acenaphthene and 2-methylnaphthalene, respectively, as calibrating compounds. The results from this and other hydrogenations are given in Table I.

Other hydrogenations were performed in a similar manner and the glycols identified by comparison with authentic specimens in glc retention time, and infrared and nmr spectra.

Relative Rates of Nitrobenzene Photoaddition. Solutions of nitrobenzene (0.1 *M*) in the alkenes were degassed by nitrogen purge in Bausch and Lomb Spectronic 20 tubes. After stoppering, the solutions were irradiated in a merry-go-round[47] at 15° using a Hanovia 450-W arc and a Pyrex filter. The irradiations were carried to about 10% conversion of nitrobenzene. The solutions were analyzed by glc using a 5 ft × 0.25 in. column of 20% SE-30 on Chromosorb W at 115°. Naphthalene was used as calibrating compound. A solution of nitrobenzene in (1:1) isopropyl alcohol–6 *N* hydrochloric acid was used as actinometer and irradiated simultaneously.

Quenching Studies. Solutions of *m*-chloronitrobenzene (0.1 *M*) in 1:1 cyclohexene–ether containing appropriate concentrations of octafluoronaphthalene (0.01–0.09 *M*) were degassed (nitrogen purge) and stoppered. The solutions were irradiated at −15 ± 1° in a merry-go-round with a Hanovia 450-W lamp. The 366-nm light was isolated using a combination of Corning O-52 and 7-60 filters. Irradiations were carried to 6–12% conversion, and the solutions were analyzed with a 6 ft × 0.25 in. column of 10% FFAP on Chromosorb P at 160°. Naphthalene was used as calibrating compound, and a solution of cyclopentenone in 1:1 cyclohexene–ether was used as actinometer and irradiated simultaneously. (The photoadducts were analyzed at 170° using acenaphthylene as calibrating compound.) The results are plotted in Figure 2. The slope is a least-squares plot.

Sensitization of *m*-Chloronitrobenzene Reaction. Solutions of *m*-chloronitrobenzene in cyclohexene–ether (1:1) were prepared and benzophenone (0.5 *M*) was added. The benzophenone absorbed >90% of the light. The irradiation was performed as described for quenching experiments and taken to 5–6% conversion.

Relative Decomposition Rates. Solutions of 50 mg of the photoadduct of *m*-chloronitrobenzene and cyclohexene in 1 ml of solvent (0.21 *M*) were prepared at 0°. The solutions were immediately transferred to a variable low-temperature unit VLT-2 Beckman infrared cell (0.1 mm) at 21.0 ± 0.5°. The absorbances of the carbonyl stretch were measured every 10 min and are shown plotted against time in Figure 2. The relative rates of decomposition of different adducts (0.21 *M*) in carbon tetrachloride were determined in the same manner (see Figure 6).

Decomposition of the *m*-Chloronitrobenzene–Cyclohexene Adduct in Diethyl Ether. The adduct (550 mg, 2.3 mmol) in 30 ml of diethyl ether at −78° was added slowly over 45 min to 5.0 ml of refluxing diethylamine. The solvent and some amine were then removed at −5° (40 mm) and the residue was chromatographed over silica gel (30 g) using benzene as eluent. After the elution of orange-yellow material the eluent was changed to ethyl acetate–benzene (1:9). The benzene eluate (112 mg after evaporation of the solvent) was separated by thick-layer chromatography using benzene–light petroleum (1:3) as eluent. Two main visible zones ($R_f \approx 0.9$ and 0.65) were isolated. That of R_f 0.65 after extraction with chloroform gave 63 mg (0.23 mmol, 20%) of 3,3′-dichloroazoxybenzene, mp (from ethanol) and mmp 96–97°. Its infrared spectrum was identical with that of an authentic specimen. The fraction of R_f 0.9 gave 11 mg of 3,3′-dichloroazobenzene, mp and mmp 100–101° after crystallization from ethanol. Its infrared and mass spectra were identical with those of an authentic specimen. The ethyl acetate–benzene eluate was evaporated and the residue was distilled at 0° (0.01 mm) to give a small amount of cyclopentenaldehyde. This was identified by comparison of its infrared, nmr, and mass spectra with those of an authentic specimen. In a separate experiment the yield of aldehyde was estimated (glc), using *n*-dodecane as calibrating compound, as 8–9%.

The residue after removal of the aldehyde was separated by thick-layer chromatography using ethyl acetate–benzene (1:19) as eluent. The crude product (R_f 0.26) was isolated and subjected to a second separation. Isolation and crystallization from ethyl acetate–*n*-hexane gave 30 mg of **8**: mp 88–89°; M^+ 239, $(M + 2)^+$ 241 (31% of 239); ir $\nu_{\max}^{CCl_4}$ 3600, 3400, 1590, 1570, and 1470 cm^{-1}; nmr δ 1.4–2.0 (6 H, m), 2.95 (1 H), 3.9 (1 H, OH), 4.25 (1 H, m), 5.18 (1 H, –C*H*O), 6.7–7.3 (4 H, Ar). *Anal.* Calcd for $C_{12}H_{11}NOCl$: C, 60.11; H, 5.89; N, 5.85. Found: C, 60.33; H, 5.70; N, 5.88.

The alcohol (12 mg) was acetylated (acetic anhydride–pyridine, room temperature, 24 hr). The crude product, after removal of the reagents, was purified by thin-layer chromatography (eluent,

---

(46) P. de Mayo, J. P. Pete, and M. Tchir, *Can. J. Chem.*, 22, 2535 (1968).

(47) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

ethyl acetate–light petroleum, 1:19) and crystallized from ethyl acetate–*n*-hexane to give the corresponding acetate: mp 72–73°; M^+ 281, $(M + 2)^+$ 283 (32% of M^+); $\nu_{max}^{CCl_4}$ 1750, 1590, 1570, 1475, and 1220 cm^{-1}; nmr ($CDCl_3$) δ 1.74 (3 H, CH_3CO–), 1.76 (CH), 2.95 (1 H, m), 4.25 (1 H, m) 6.00 (1 H, s, *H*COAc), 7.30–6.40 (4 H, aromatic). *Anal.* Calcd for $C_{14}H_{16}NO_3Cl$: C, 59.66; H, 5.73; N, 4.97. Found: C, 59.10; H, 5.92; N, 4.83.

Reduction of Alcohol 8. The alcohol **8** (25 mg) in 1 ml of ether was added to a solution of lithium aluminum hydride (30 mg) in ether (3 ml). After stirring for 2 hr, the excess hydride was decomposed with saturated potassium sodium tartrate. Isolation of the product gave 22 mg showing two spots on thin-layer chromatography. Separation by thick-layer chromatography (eluent, ethyl acetate–benzene, 1:4) gave 18 mg of *cis*-2-(3′-chloroanilino)-cyclopentanylcarbinol (**9**). This was identical in every way with a synthetic specimen prepared as described below, as was the derived monoacetate and bis-*p*-nitrobenzoate.

Synthesis of *cis*-2-(3′-Chloroanilino)cyclopentanylcarbinol. A mixture of methyl and ethyl esters of 2-cyclopentanonecarboxylic acid (Aldrich) (800 mg) and 660 mg of *m*-chloroaniline in 20 ml of benzene was refluxed for 20 hr under a Dean–Stark apparatus. The product was chromatographed on silica gel (70 g) to give 650 mg of a mixture of methyl and ethyl esters of 2-(3′-chloroanilino)-cyclopent-1-enecarboxylic acid. This mixture (600 mg) in ethyl acetate (20 ml) was hydrogenated over platinum oxide until an uptake of 120 ml of hydrogen was observed (5.36 mmol). After concentration, the product was added to 60 g of silica gel. Benzene eluted unreacted starting material (130 mg). Ethyl acetate–benzene (1:19) then eluted 340 mg of the dihydro ester mixture. This showed the expected physical properties in the infrared and nmr spectrum. The mixed esters (100 mg) in ether (5 ml) were then added to lithium aluminum hydride (80 mg) in ether (5 ml) and the mixture was stirred for 2 hr. After decomposition (potassium sodium tartrate) the carbinol **9** was isolated: $\nu_{max}^{CHCl_3}$ 3590, 3380, 1590, 1570, 1480 cm^{-1}; nmr δ 1.67 (7 H), 2.23 (1 H, m, C*H*N), 3.3 (2 H, N*H*, O*H*), 3.70 (2 H, d, $J \sim 6$ Hz CH_2O), 6.40–7.30 (4 H, aromatic); mol wt (mass spectrum) 225, 227 (32% of 225). *Anal.* Calcd for $C_{12}H_{16}NOCl$: C, 63.84; H, 7.15; N, 6.2. Found: C, 64.32; H, 7.38; N, 6.34. The acetate (acetic anhydride–pyridine, room temperature, 24) had $\nu_{max}^{CHCl_3}$ 3430, 1735, 1600, 1575, 1500, 1485, and 1220 cm^{-1}; nmr ($CDCl_3$) δ 1.67 (7 H), 2.46 (1 H, m, C*H*N), 3.80 (1 H, NH), 4.07 (2 H, d, $J \sim 7$ Hz), 6.3–7.2 (4 H, aromatic); mol wt (mass spectrum) 267,269. *Anal.* Calcd for $C_{14}H_{18}NO_2Cl$: C, 62.68; H, 6.78; N, 5.23. Found: C, 63.27; H, 6.53; N, 5.13. The bis-*p*-nitrobenzoate had the following characteristics: mp 117–118°; $\nu_{max}^{CCl_4}$ 1725, 1660, 1600, 1590, 1475, 1530, 1270, and 1100 cm^{-1}; nmr δ 1.85 (7 H), 3.0 (1 H, C*H*N), 4.5 (2 H, CH_2O), and 7.0–8.3 (12 H, aromatic). *Anal.* Calcd for $C_{26}H_{22}N_3O_7Cl$: C, 59.58; H, 4.23; N, 8.02. Found: C, 59.45; H, 4.00; N, 7.89.

Thiabenzenes. III. Synthesis and Properties of Thiabenzene 1-Oxides[1a]

Alfred G. Hortmann* and Ronald L. Harris[1b]

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130. *Received October 2, 1970*

Abstract: The synthesis of a representative series of 1-methyl-3,5-disubstituted thiabenzene 1-oxides (**2**) by the reaction of dimethyloxosulfonium methylide with 1,3-disubstituted 2-propynones (**1**) is described. In several cases, the initially formed allylides (**3**) were isolated and converted to the 1-oxides (**2**) under basic as well as neutral conditions. Alkylation of the 1-oxide **2a** on the *S*-methyl group was effected in stages *via* generation of the anion and treatment with methyl iodide to yield the *S*-ethyl and *S*-isopropyl derivatives **6a** and **6b**. Reduction of **2a** with hydrogen over platinum or zinc in acetic acid lead to reductive cleavage of the S-ring yielding **11** or **12**. Nmr (^1H, ^{13}C) and proton exchange data are described and discussed in relation to the types of bonding possible for thiabenzene 1-oxides. An ylide-like bonding structure is proposed for the thiabenzene 1-oxides.

The existence of bonds of the pπ–dπ type, formed by interaction of d AO's of second-row elements with p AO's of first-row elements, is generally accepted.[2] However, due to the directional character associated with the d AO's having proper symmetry for such interaction, several modes of overlap of d AO's with p AO's have been proposed, and consequently the nature of pπ–dπ bonds is still a subject of speculation. In addition, the question of the degree to which conjugative effects can be transmitted through such bonds in potentially "aromatic" cyclic conjugated systems is an intriguing one which continues to receive attention.[2-4]

Our interest in this area was stimulated by the discovery that the reaction of dimethyloxosulfonium methylide[5] with disubstituted acetylenic ketones (**1**) affords a route to 1,3,5-trisubstituted thiabenzene 1-oxides (**2**),[6] a novel class of cyclic compounds containing a conjugated six π-electron system. Through-conjugation at sulfur, if it is possible, can occur only *via* 2pπ–3dπ bonds in the thiabenzene 1-oxides (assuming that only 3s and 3p valence orbitals are used in the tetrahedrally oriented σ bonds at sulfur). Thus, from the standpoint of bonding in the C_2–S–C_6 moiety in the thiabenzene 1-oxides, these compounds may be formally compared with the cyclotriphosphazines,[2-4,7] cyclotrithiatriazene trioxides,[8] phosphabenzenes,[9] and related substances. Since most published studies on the properties of thiabenzenes,[10] thianaphthalenes,[11]

---

(1) (a) Abstracted in part from the Ph.D. Dissertation of Ronald Lee Harris, Washington University, 1970; (b) National Science Foundation Trainee, 1968–1969.

(2) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969), and references cited therein.

(3) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, pp 158–176.

(4) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 430–436.

(5) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965); **84**, 867 (1962).

(6) A preliminary report describing the preparation and some properties of **2a** has been published: A. G. Hortmann, *ibid.*, **87**, 4972 (1965).

(7) H. R. Allcock and W. J. Birdsall, *ibid.*, **91**, 7541 (1969).

(8) T. J. Maricich, *ibid.*, **90**, 7179 (1968).

(9) G. Märkl, *Angew. Chem.*, **77**, 1109 (1965).

(10) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969), and previous papers in this series. See also ref 25 below.

(11) C. C. Price and D. M. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).