PPO (2,5-diphenyloxazole, 1.0 g), and dimethyl-POPOP (1,4-di[2-(4-methyl-5-phenyloxazolyl)]benzene, 0.01 g). All samples except benzylamine hydrochloride were soluble in this medium. Benzylamine hydrochloride was solubilized using Hyamine hydroxide (*p*-[diisobutylcresoxyethoxyethyl]dimethylbenzylammonium hydroxide) by addition of 3 ml to the above solution. The quenching of the scintillation caused by this latter component was monitored by counting a sample of methyl phenylacetate both with and without the equivalent amount of Hyamine hydroxide. Each sample was counted for 1 min, and the results are shown in Table II.

Acknowledgment. We are indebted to Eli Lilly and Co., the Ciba Pharmaceutical Co., and G. D. Searle and Co. for providing partial financial support of this work. B. P. S. wishes to acknowledge receipt of an S. R. C. fellowship.

Mechanism of Ozonolysis. A New Route to Ozonides[1]

Robert W. Murray* and Akio Suzui

Contribution from the Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121. Received October 20, 1972

Abstract: The photooxidation of diaryl diazo compounds in the presence of aldehydes leads to the formation of ozonides. In the case of 1-(1-naphthyl)-1-phenyl-1-propene the photooxidation method gives an ozonide cis/trans ratio which is the same as that obtained from the trans olefin and different from that obtained from the cis olefin. Ozonolysis of *cis*- and *trans*-1-(1-naphthyl)-1-phenyl-1-propene leads to stereospecific formation of the corresponding epoxides as the major products.

Several observations in apparent conflict with the Criegee[2] mechanism of ozonolysis have led to additional suggestions for the mechanism.[3–9] Most of these additional suggestions have been concerned with the stereochemical consequences of the reaction, that is, the ability of the olefin stereochemistry to somehow affect the amounts and stereochemistry of the ozonide products. An important element of one of these proposals is that the Criegee zwitterion–carbonyl recombination pathway to ozonide formation can be accompanied by varying amounts of one or more additional pathways also leading to ozonide.[3–7] The amount and nature of these additional pathways would then be dependent upon such factors as olefin steric requirements, concentration and geometry, solvent, and other parameters.

Because the olefin–ozonide stereochemical dependence plays such an important role in interpreting the mechanism, it seemed to us that it would be useful to try and determine, by some independent pathway, the ozonide stereochemistry produced in a pure zwitterion plus carbonyl compound reaction pathway. Such an approach requires a nonozone production of the zwitterion in an environment where ozonide might be expected to form. We report here the results of some work in which we have found such a route to ozonide, as well as determined, in some cases, the ozonide stereoisomer ratio and related it to the mechanism problem.

Results and Discussion

The suggestion that the photooxidation of diphenyldiazomethane proceeds through the intermediacy of a carbonyl oxide was first made by Kirmse, Horner, and Hoffman.[10] The suggestion later received support from two groups. Bartlett and Traylor reported[11] that such photooxidations lead to the formation of benzophenone diperoxide, a product which they concluded arose from dimerization of the carbonyl oxide. Hamilton and Giacin, on the other hand, found that an intermediate present in the photooxidation of diphenyldiazomethane was capable of oxidizing the hydrocarbon solvent used.[12] They concluded that the intermediate was the carbonyl oxide in its diradical form as opposed to the dipolar form postulated by Bartlett and Traylor.

If these reactions are proceeding through the Criegee carbonyl oxide or zwitterion then they could provide independent evidence for the involvement of the zwitterion in ozonide formation. Using a photooxidation apparatus similar to one described in the literature,[13] we have photolyzed diazo compounds in the presence of oxygen and aldehydes hoping to form ozonides *via* the Criegee pathway. When diphenyldiazomethane was photolyzed in chlorobenzene alone the product was benzophenone diperoxide thus confirming the results of Bartlett and Traylor.[11] When the photooxidation was carried out in the presence of acetaldehyde, propionaldehyde, or benzaldehyde as solvent then the

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(1) Portions of this work have been reported in preliminary form: R. W. Murray and A. Suzui, *J. Amer. Chem. Soc.*, **93**, 4963 (1971).

(2) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(3) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **88**, 3144 (1966).

(4) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

(5) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(6) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).

(7) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *J. Amer. Chem. Soc.*, **93**, 3044 (1971).

(8) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

(9) S. Fliszár and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).

(10) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 22 (1958).

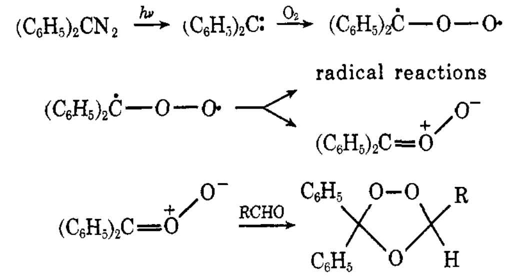
(11) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962).

(12) G. A. Hamilton and J. R. Giacin, *ibid.*, **88**, 1584 (1966).

(13) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *ibid.*, **90**, 975 (1968).

ozonide of 1,1-diphenylpropene, 1,1-diphenyl-1-butene or triphenylethylene, respectively, could be isolated. In the latter cases no diperoxide was formed and the other major product was benzophenone. The ozonide is presumably formed from reaction of the carbonyl oxide with aldehyde which reaction competes successfully with diperoxide formation. Results to date indicate that the reaction is limited to diazo compounds containing two aryl substituents. When one of the aryl groups is substituted by methyl or hydrogen then no ozonide is formed. The ozonide yields are low, the highest yield being 11.8% for the triphenylethylene ozonide.

These results provide a unique confirmation of the Criegee proposal for ozonide formation. The current limitation of the reaction to diaryldiazo compounds is presumably related to the relative tendency of the carbenes to form triplets.[14] Triplet carbenes are known to react more readily with oxygen.[14,15] Likewise, Hamilton and Giacin found that the carbenes which gave the most hydrocarbon oxidation were those with the greatest tendency to form triplets.[12] At present then the reaction is best described as involving photolysis of the diazo compound to give triplet carbene followed by reaction of triplet carbene with oxygen to give the diradical form of the carbonyl oxide. Presumably, a portion of the diradical carbonyl oxide then populates the dipolar form which reacts with aldehyde to give ozonide. The low ozonide yields are presumably due to leakage of the carbonyl oxide into free-radical processes at the diradical state.

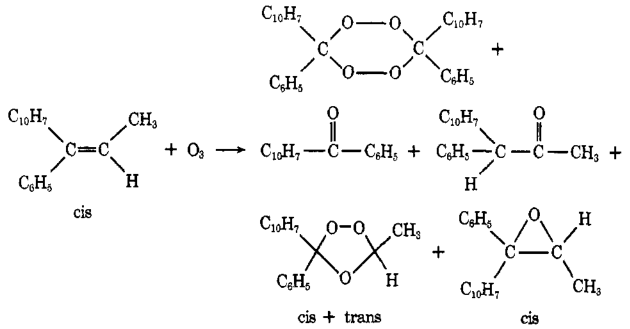


We then searched for a system which would give an ozonide capable of having cis–trans isomers. Because of the aryl substituent limitation this choice is rather restricted. The diazo compound chosen, 1-naphthylphenyldiazomethane, was photolyzed first in benzene as in the previous case. This photolysis leads to the formation of 1-naphthyl phenyl ketone diperoxide, a white crystalline material with mp 207° dec. The stereochemistry of this material was not determined.

Photooxidation of the diazo compound in acetaldehyde or benzaldehyde as solvent led to the formation of 1-(1-naphthyl)-1-phenyl-1-propene or 1-(1-naphthyl)-stilbene ozonide, respectively. In both cases the ozonide was obtained as a cis–trans pair.

The stereoisomers of 1-(1-naphthyl)-1-phenyl-1-propene were obtained by the iodine dehydration of 1-naphthylphenylcarbinol. The carbinol was synthesized from ethylmagnesium bromide and 1-naphthyl phenyl ketone. The dehydration gave a mixture of the cis and trans isomers. Through the use of a combination of distillation, column chromatography, recrystallization, and glpc the isomers were ultimately separated. The olefin stereochemical assignments were made by analogy to a previously observed nmr correlation in 1,1-diarylpropenes. According to this correlation, substitution into one of the aryl groups causes it to rotate out of the plane of the double bond more than the unsubstituted aryl group. While the aryl groups can have both an inductive and a direct (ring current) influence on the olefinic proton and methyl group, the latter was found to be predominant.[16a] Thus deshielding is at a maximum for those olefinic protons which are directly adjacent to the aryl group more nearly coplanar with the double bond. When the naphthyl group is taken as the substituted aryl group in the olefins of interest then the cis[16b] configuration is assigned to the olefin with nmr absorptions at 3.58 and 8.48 for the olefinic and methyl absorptions, respectively. The trans olefin then has the same absorptions at 4.08 and 8.00, respectively.

Ozonolysis of either olefin stereoisomer led to the same mixture of products. The products include 1-naphthyl phenyl ketone diperoxide, parent ozonide, the epoxide corresponding to the olefin, 1-naphthyl phenyl ketone, and 1-(1-naphthyl)-1-phenyl-2-propanone. In addition, a low boiling fraction was removed from the crude reaction mixture in each case and shown by glpc to contain 2-butene ozonide, a cross ozonide.



In the case of the cis olefin, the ozonide had a cis/trans ratio of 1.08 while the trans olefin gave an ozonide cis/trans ratio of 0.78. These ratios were determined from the nmr spectra and were based on ozonide stereochemical assignments which used the previously observed[5] nmr spectral correlation. According to this correlation, the cis ozonide methine hydrogen will absorb at lower magnetic field. The olefins dealt with here are, strictly speaking, in a structural class for which little nmr data are available. The stereochemical assignments must therefore be regarded as tentative. There appear to be only two violations of the cited[5] correlation. In these cases the trans ozonide isomer has the methine hydrogen at lower magnetic field. The two cases are the ozonides of stilbene[17,18] and 1,4-dichloro-2-butene.[18] It should be noted that both of these cases contain substitutents which are magnetically anisotropic.

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[14] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 83.

[15] M. Jones, Jr., and K. R. Bettig, *J. Amer. Chem. Soc.*, **87**, 4015 (1965).

[16] (a) R. van der Linde, O. Korver, P. K. Korver, P. J. van der Haak, J. U. Veenland, and Th. J. de Boer, *Spectrochim. Acta*, **21**, 1893 (1965). (b) The cis designation is assigned to the isomer in which the naphthyl and methyl groups are on the same side of the double bond. This same isomer would be assigned the *Z* designation by the IUPAC 1968 Tentative Rules, Section E.

[17] C. E. Bishop, D. D. Denison, and P. R. Story, *Tetrahedron Lett.*, 5739 (1968).

[18] R. Criegee and H. Korber, *Chem. Ber.*, **104**, 1807 (1971).

Establishing the stereochemistry of the ozonides in the present case is not a trivial problem. Unequivocal stereochemical assignments have now been made for several other ozonides. Such assignments have relied on partial resolution of a *dl* pair in the trans isomer.[18,19] Unfortunately, this route is not available here, since both isomers are *dl*. As is the case with the stilbene ozonide pair,[17,18] the ozonide isomers here cocrystallize. A single isomer can be obtained by preferential destruction of the other, but both isomers are not available for dipole moment measurements. The previously cited[20] infrared band correlations also cannot be used here since the useful bands do not appear.

Ozonide stereochemical assignments have been based on the rate of reaction with triphenylphosphine,[17,18] the assumption being made that the cis compound will react faster than the trans. If the same assumption is made here then reaction with triphenylphosphine leads to a different stereochemical assignment than that made from the nmr data. Based on the partial resolution of the *dl* compound technique, Criegee and Korber[18] have pointed out that assignment based on rate of reaction with triphenylphosphine also fails in the case of 1,4-dichloro-2-butene. Indeed, based on a survey of the available cases where more than one method has been used to make stereochemical assignments, Criegee and Korber[18] have concluded that only an assignment based on the rate of elution from a silica gel column correlates completely with the resolution method. In our judgment that conclusion may be too restrictive, particularly if one views the nmr spectral technique as producing two correlations depending upon whether the ozonide contains magnetically anisotropic groups or not. We have, however, subjected the ozonide cis/trans mixture to column chromatography using the conditions of Criegee and Korber,[18] namely, using a 1-m column of silica gel and eluting with ether–pentane (2:98). Under these conditions a partial separation of the ozonides is obtained. If the stereochemical assignment based on nmr is used then the trans ozonide has the longer retention time. While it is more difficult to make predictions regarding dipole moments in this case than in the cases studied by Criegee and Korber, a crude prediction based on the expected contributions of the various substituents to the dipole moment is that the trans ozonide would have the higher dipole moment. On this basis the nmr and chromatography data are supportive.

Accepting the tentative ozonide stereochemical assignments given above, then the photooxidation of 1-naphthylphenyldiazomethane in acetaldehyde gives 1-(1-naphthyl)-1-phenyl-1-propene ozonide with a cis/trans ratio of 0.75.

Regardless of what stereochemical assignments are made, the photooxidation method has given an ozonide cis/trans ratio (0.75) which is essentially the same as that obtained (0.78) from the trans olefin isomer. This conclusion is consistent with our hypothesis[6] that trans olefins are more likely to involve a higher percentage of the zwitterion–aldehyde pathway. If the tentative stereochemical assignments given are correct then the cis olefin has produced an ozonide distribution (1.08) which contains more cis ozonide than that obtained from the trans olefin (0.78). Again this is consistent with the previous observations[6] that cis olefins generally give more cis ozonide. It should also be pointed out that the cis olefin has given a higher total yield (12%) of 1-(1-naphthyl)-1-phenyl-1-propene ozonide than the trans olefin (5.2%), a correlation which has been observed quite consistently.[6]

Despite the fact that there appeared to be very little overlap between the wavelength output of the lamp used and the ultraviolet spectrum of the ozonides, this ratio was found to alter in favor of the presumed trans ozonide with prolonged photolysis. By altering photolysis times it was found that the ratio of 0.75 remained constant at times of 50 min or less. At these times the reaction mixture contains unreacted diazo compound.

The assignment of ozonide stereochemistry in the 1-(1-naphthyl)stilbene ozonide obtained from the photolysis of 1-naphthylphenyldiazomethane in benzaldehyde is also a difficult problem. As in the case of the 1-(1-naphthyl)-1-phenyl-1-propene ozonide, many of the methods usually employed for making the assignment are not applicable here. If the nmr correlation for ozonides containing magnetically anistropic groups described above is used then the ozonide was produced with a cis/trans ratio of 1.49/1. Reduction with triphenylphosphine does proceed more rapidly with one isomer, which isomer is the one assigned the cis stereochemistry on the basis of nmr. While a faster rate of reaction with triphenylphosphine has usually been associated with the cis isomer, the structure of the ozonide involved is such that it is not obvious that one would expect a similar correlation here. Use of the silica gel chromatography technique did provide a partial separation of isomers. The isomer with the longer retention time is the one assigned the trans configuration on the basis of the nmr data. In this case, it is even more difficult to make a prediction regarding the relative dipole moments of the cis and trans isomers. Until more data are available on related ozonides, we are unable to go any further than making the very tentative stereochemical assignment given above based on the nmr absorptions.

Formation of Epoxides. Ozonolysis of *cis*- and *trans*-1-(1-naphthyl)-1-phenyl-1-propene gave other data which is of some significance to the ozonolysis mechanism problem. The major products of the ozonolysis in both cases were the epoxides and not the ozonides of the olefins. More importantly, the epoxides were formed stereospecifically. The cis olefin gave only cis epoxide in 31.2% yield and the trans olefin gave only trans epoxide in 23.6% yield. The authentic epoxides, for comparison purposes, were obtained by oxidation of the olefins with *m*-chloroperbenzoic acid. Both olefins gave a small amount of 1-(1-naphthyl)-1-phenyl-2-propanone, which was shown in a separate experiment to be a rearrangement product of the epoxides. In addition, both olefins gave small yields of 1-naphthyl phenyl ketone diperoxide.

There are now a number of reports[5,21–24] in the litera-

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(19) L. D. Loan, R. W. Murray, and P. R. Story, *J. Amer. Chem. Soc.*, **87**, 737 (1965).

(20) R. W. Murray in "Techniques and Methods of Organic and Organometallic Chemistry," D. B. Denney, Ed., Marcel Dekker, New York, N. Y., 1969, p 1.

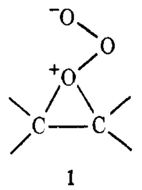
(21) R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley, *J. Amer. Chem. Soc.*, **66**, 1274 (1944).

(22) P. D. Bartlett and M. Stiles, *ibid.*, 77, 2806 (1955).

(23) R. Criegee, *Advan. Chem. Ser.*, **No. 21**, 133 (1959).

(24) P. S. Bailey and A. G. Lane, *J. Amer. Chem. Soc.*, **89**, 4473 (1967).

ture of epoxides being produced in the ozonolysis reaction. In the case of 1-olefins containing bulky substituents the epoxide is the major product.[24] This departure from the normal ozonolysis product has been explained by postulating a different structure for the initial adduct between ozone and the olefin. We have suggested[3] that the σ adduct, **1**, is important in such cases while Bailey and Lane[24] have suggested that either **1** or an open form of the σ adduct **2**, may be involved.



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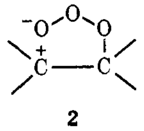

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The observation that *cis*- and *trans*-1-(1-naphthyl)-1-phenyl-1-propene give epoxides stereospecifically and with retention of configuration suggests that **1** may be the preferred structure of the adduct in these cases. The open form **2** permits rotation about the C–C bond and would only be consistent with the results if closure to **1** occurred more rapidly than C–C bond rotation.

Summary

The photooxidation of diazo compounds in the presence of aldehydes has provided a new route to ozonides as well as a unique confirmation of the Criegee zwitterion mechanism for ozonide formation. In the case of 1-(1-naphthyl)-1-phenyl-1-propene the photooxidation method gives an ozonide cis/trans ratio which is the same as that obtained from the trans olefin and different from that obtained from the cis olefin. This observation could indicate that the trans olefin utilizes the zwitterion pathway to a greater extent in producing ozonide.

While ozonide stereoisomer ratios can be determined and compared, only tentative stereochemical assignments can be made for the ozonides involved here.

Experimental Section

The nmr spectra were determined on a Varian T-60 high resolution nmr spectrometer. The spectra were taken in CCl_4 solution except as otherwise indicated. Chemical shift values given are τ values relative to internal TMS. Melting points were taken on a Fisher Melting Point Apparatus and are uncorrected. Elemental analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The glpc analyses were carried out on a Varian Aerograph Model A-705 gas chromatograph using various lengths and percentages of cyanosilicone. Column chromatographic analyses were carried out on a 25-mm diameter column packed with 100–300 mesh silica gel. Thin layer chromatographic analyses were carried out using Brinkman silica gel G on 0.25-mm precoated glass plates (5 × 10 cm, analytical) and 2-mm precoated glass plates (20 × 20 cm, preparative). The plates were developed using mixtures of benzene and hexane. The photolysis apparatus was similar to the one described in the literature[13] and used a General Electric DWY 650-W lamp without filter.

Ozonolyses. A Welsbach Model T-408 ozonator was used as a source of ozone. Ozone was delivered at a rate of 0.15 mmol/min. Ozonolyses were carried out at 0° in ether solution and were continued until the theoretical amount of ozone had been delivered.

Diphenyldiazomethane. A mixture of 19.6 g (100 mmol) of benzophenone hydrazone, 25 g (115 mmol) of yellow mercuric oxide, 100 ml of hexane, and 1 ml of KOH–methanol solution was stirred vigorously at room temperature for 6 hr. The reaction mixture was filtered and the solvent evaporated from the filtrate under reduced pressure. The dark red residue was used immediately in this form.

Photooxidation of Diphenyldiazomethane in Chlorobenzene. A solution of 18.9 g (97.7 mmol) of diphenyldiazomethane in 125 ml of chlorobenzene was placed in the photolysis apparatus with an oxygen flow of 240 ml/min. Photolysis at 10–15° was continued (75 V) for 2 hr at which time the characteristic color of the diazo compound had disappeared. Solvent was removed *in vacuo* to give 21.9 g of a yellow residue. The methanol-insoluble portion of the residue was recrystallized from acetone to give yellow crystals of benzophenone diperoxide. Repeated recrystallization gave a sample with mp 210–212°, lit.[11] mp 213.5–214°.

Photooxidation of Diphenyldiazomethane in Acetaldehyde. A solution of 9.70 g (50 mmol) of diphenyldiazomethane in 200 ml of freshly distilled acetaldehyde was placed in the photolysis apparatus with an oxygen flow rate of 300 ml/min. The solution was photolyzed (50 V) at 10–15° for 130 min at which time the color of the diazo compound had disappeared. Removal of excess acetaldehyde *in vacuo* gave 11.4 g of a light yellow residue. The residue was chromatographed on silica gel. Elution with benzene–hexane (20:80) gave 0.95 g (7.8%) of 1,1-diphenylpropene ozonide. This material was identical with that obtained from ozonolysis of 1,1-diphenylpropene and had nmr absorptions at 2.7 (multiplet, 10 H), 4.50 (quartet, 1 H), and 8.60 (doublet, 3 H), and infrared absorption at 1220 and 1120 cm^{-1}. Further elution of the column with benzene–hexane (50:50) gave 8.23 g (90.5%) of benzophenone.

Photooxidation of Diphenyldiazomethane in Benzaldehyde. A solution of 9.7 g (50 mmol) of diphenyldiazomethane in 125 ml of freshly distilled benzaldehyde was placed in the photolysis apparatus with an oxygen flow rate of 240 ml/min. The solution was photolyzed (70 V) for 55 min at 10–15° at which time the color of the diazo compound had disappeared. After removal of excess benzaldehyde *in vacuo* 11.5 g of a yellow residue remained. The methanol soluble portion was chromatographed on silica gel. Elution with benzene–hexane (50:50) gave 1.80 g (11.8%) of triphenylethylene ozonide, mp 97°, lit.[25] mp 95°. The ozonide had nmr absorptions at 2.7 (multiplet, 15 H) and 3.73 (singlet, 1 H). Continued elution with benzene–hexane (50:50) gave 7.18 g (79%) of benzophenone.

Photooxidation of Diphenyldiazomethane in Propionaldehyde. A solution of 9.70 g (50 mmol) of diphenyldiazomethane in 200 ml of freshly distilled propionaldehyde was placed in the photolysis apparatus with an oxygen flow rate of 300 ml/min. The solution was photolyzed (50 V) for 120 min at 10–15° at which time the color of the diazo compound had disappeared. After removal of excess propionaldehyde *in vacuo* 9.8 g of a light yellow residue was obtained. This residue was chromatographed on silica gel. Elution with benzene–hexane (20:80) gave 0.11 g (0.84%) of 1,1-diphenylbutene ozonide. The ozonide had nmr absorptions at 2.7 (multiplet, 10 H), 4.57 (triplet, 1 H), 8.0–8.9 (multiplet, 2 H), and 9.02 (triplet, 3 H).

Ozonolysis of 1,1-Diphenylpropene. A solution of 5.0 g (25.8 mmol) of 1,1-diphenylpropene (from acetic acid dehydration of 1,1-diphenylpropanol) in 30 ml of freshly distilled acetaldehyde was ozonized at 0–1° to the theoretical amount of ozone. Excess acetaldehyde was removed under reduced pressure to give 5.1 g of a yellow liquid. The crude product was chromatographed on silica gel. Elution with benzene–hexane (20:80) gave the 1,1-diphenylpropene ozonide. Repetition of the chromatography gave a pure sample for comparison purposes.

1-Naphthyl Phenyl Ketone Hydrazone.[26] 1-Naphthyl phenyl ketone was made according to the method of Baddeley.[27] A solution of 58.0 g (0.25 mol) of the ketone in 50.0 g (1.0 mol) of 85% hydrazone hydrate, 15 g of acetic acid, and 200 ml of butanol was refluxed for 10 hr. The reaction mixture was concentrated under reduced pressure and extracted with ether. The ether was evaporated and the residue recrystallized from methanol to give 48.0 g (78%) of 1-naphthyl phenyl ketone hydrazone, mp 85–86°.

1-Naphthylphenyldiazomethane.[26] A solution of 2.50 g (10 mmol) of 1-naphthyl phenyl ketone hydrazone in 50 ml of hexane was stirred with 2.50 g of yellow mercuric oxide and 0.5 ml of saturated KOH–methanol solution at room temperature for 1 hr. The reaction mixture was filtered and concentrated under reduced pressure to give red crystals (2.45 g) of 1-naphthylphenyldiazomethane, mp 78–79°.

1-Naphthylphenylethylcarbinol. A solution of ethylmagnesium bromide in ether, prepared from 48.0 g of Mg turnings and 230 g (2.1 mol) of ethyl bromide, was added to a solution of 116 g (0.5 mol)

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(25) J. Castonguay, M. Bertrand, J. Carles, S. Fliszar, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969).

(26) H. Reimlinger, *Chem. Ber.*, **97**, 3493 (1964).

(27) G. Baddeley, *J. Chem. Soc.*, 99 (supplement) (1949).

of 1-naphthyl phenyl ketone in 200 ml of dry benzene with stirring and under reflux. The reaction mixture was allowed to stand overnight and was then poured over cracked ice. A saturated NH_4Cl solution was added and the organic layer separated. The aqueous layer was extracted with ether. The combined organic layers were dried with $MgSO_4$ and then filtered. The solvent was removed to give 125 g of the light yellow carbinol. This material was used in the dehydration step without further purification.

cis- **and** *trans*-**1-(1-Naphthyl)-1-phenyl-1-propene.** The 1-naphthylphenylethylcarbinol was heated at 200° for 30 min with a trace of iodine and under water aspirator vacuum. The residual liquid was distilled *in vacuo* and the distillate (33 g, bp 142–149° (0.02 mm)) chromatographed on alumina. Elution with hexane gave 22 g (39.6%) of 1-(1-naphthyl)-1-phenyl-1-propene. This material, which proved to be a mixture of the cis and trans isomers, had nmr absorptions at 2.2 and 2.8 (multiplets, 12 H), 3.61 and 4.12 (quartets, 1 H), and 8.08 and 8.52 (doublets, 3 H). Reasoning by analogy with similar systems,[16] the absorptions at 3.61 and 8.52 are assigned to the cis isomer and those at 4.12 and 8.08 to the trans isomer. On the basis of this assignment the liquid material contained a 52/48, cis/trans mixture of the olefins. This liquid was redistilled *in vacuo*. Trituration of the distillate with methanol gave two fractions, a solid fraction containing a 64/36 cis/trans ratio of the olefins and a liquid fraction containing a 45/55 cis/trans ratio of the olefins.

The solid fraction (5.0 g) was refluxed for 2 hr in 10 ml of acetic acid containing 0.5 g of *p*-toluenesulfonic acid. After removal of acetic acid the residue was distilled *in vacuo*. The distillate (bp 128–133 (0.2 mm), 4.3 g) was recrystallized from methanol to give white crystals of *cis*-1-(1-naphthyl)-1-phenyl-1-propene, mp 68–69°, lit.[28] mp 72–73°. The pure cis compound had nmr absorptions at 3.58 (quartet, 1 H) and 8.48 (doublet, 3 H), in addition to aromatic absorptions.

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.32; H, 6.66.

The liquid fraction was analyzed by glpc at 200° using a 30 ft × $^3/_8$ in. column packed with 5% XF-1150 cyanosilicone on Chromosorb G and using a He flow of 30 ml/sec. The olefin with the longer retention time was collected and recrystallized from methanol to give white crystals of *trans*-1-(1-naphthyl)-1-phenyl-1-propene, mp 61–62°. The pure trans compound had nmr absorptions at 4.08 (quartet, 1 H) and 8.00 (doublet, 3 H), in addition to aromatic absorptions.

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.34; H, 6.54.

Photooxidation of 1-Naphthylphenyldiazomethane in Benzene. A solution of 2.45 g (10 mmol) of 1-naphthylphenyldiazomethane in 100 ml of benzene was photooxidized at 10–15° for 10 hr using an oxygen input of 100 ml/min and operating the lamp at 50 V. At the end of this time the characteristic color of the diazo compound had completely disappeared. After removal of solvent the residual liquid was chromatographed on silica gel. Elution was carried out with benzene–hexane (20:80) and benzene–hexane (50:50). Seven fractions were eluted and analyzed further by analytical tlc. The fractions containing diperoxide (3–5) were combined and chromatographed on preparative tlc plates. The plates were developed using benzene–hexane (80:20). The diperoxide bands were recovered using benzene as solvent. The recovered material was recrystallized from chloroform to give white crystals of 1-naphthyl phenyl ketone diperoxide, mp 207° dec. The diperoxide had nmr (CD_3Cl) absorptions at 2.0 and 2.8 (multiplets). The stereochemistry of the diperoxide was not determined.

Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.25; H, 4.87. Found: C, 82.74; H, 5.01.

Photooxidation of 1-Naphthylphenyldiazomethane in Acetaldehyde. A solution of 2.45 g (10 mmol) of 1-naphthylphenyldiazomethane in 100 ml of freshly distilled acetaldehyde was photooxidized at 10–15° using an oxygen input of 100 ml/min and operating the lamp at 50 V. Several runs were made with irradiation times varying from 50 to 80 min. After 80 min irradiation the diazo compound was completely decomposed. After removing acetaldehyde under reduced pressure the residual liquid was chromatographed on silica gel. Elution was carried out with benzene–hexane (20:80) followed by benzene–hexane (50:50). The chromatography was followed by checking each fraction for the presence of ozonide by tlc. Fractions containing ozonide were then combined and chromatographed on preparative tlc plates with benzene–hexane (80:20) used for development. The ozonide was extracted with benzene and recrystallized from benzene–hexane to give white crystals, mp 103–105°. This sample of ozonide had a cis–trans ratio of 4.3/1 as determined by the nmr spectrum. The nmr spectrum has absorptions at 2.2 and 2.8 (multiplets, 12 H), 4.32 and 4.60 (quartets, 1 H), and 8.49 and 8.71 (doublets, 3 H). Reasoning by analogy with similar systems[5] the absorptions at 4.32 and 8.71 are assigned to the cis stereoisomer and those at 4.60 and 8.49 to the trans stereoisomer.

Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.00; H, 5.51.

As determined by nmr spectra the ozonide had a varying cis/trans ratio depending upon the photolysis time (all at 50 V). Thus at 50 and 60 min photolysis times the ozonide obtained had cis/trans ratios respectively of 0.75 (*ca.* 5.5%) and 0.82 (*ca.* 7.9%). While more ozonide is produced at longer photolysis times the ozonide ratio alters in favor of the cis ozonide reaching a cis/trans ratio of 2.52 at 80 min (prior to recrystallization). By varying the photolysis time it was determined that the cis/trans ratio remains essentially constant at and below 50 min.

Ozonolysis of *cis*-**1-(1-Naphthyl)-1-phenyl-1-propene.** A solution of 2.0 g (8.18 mmol, 0.2 *M*) of *cis*-1-(1-naphthyl)-1-phenyl-1-propene in 41 ml of diethyl ether was ozonized at 0° to the theoretical amount of ozone. Most of the diethyl ether was removed under reduced pressure (180 mm) at 0° and the residual liquid was distilled (30 mm) to give a fraction for glpc analysis. The analysis indicated the presence of 2-butene ozonide. The undistilled liquid, which indicated the presence of six substances by tlc, was chromatographed on silica gel. Elution was carried out with benzene–hexane mixtures from benzene–hexane (20:80) to 100% benzene. Fifteen fractions were collected and analyzed further by analytical tlc. The first five fractions contained unreacted olefin. Fractions 6 and 7 contained the ozonide with cis/trans ratio = 1.07. Fractions 6–15 were combined and rechromatographed by preparative tlc using benzene–hexane (80:20) to develop and benzene to elute. Five products were obtained. The first of these was recrystallized from chloroform–benzene to give 20 mg (1.1%) of 1-naphthyl phenyl ketone diperoxide, mp 207° dec. The second fraction (260 mg, 12.0%) was the ozonide with a cis/trans ratio of 1.08. The third fraction (600 mg, 31.2%) was identical with the authentic epoxide obtained by peracid oxidation of *cis*-1-(1-naphthyl)-1-phenyl-1-propene. The fourth fraction was identified as 1-naphthyl phenyl ketone (700 mg, 45.5%) by comparison with authentic ketone. The fifth product was identified as 1-(1-naphthyl)-1-phenyl-2-propanone (10 mg, 0.5%), a transformation product of the epoxide.

Ozonolysis of *trans*-**1-(1-Naphthyl)-1-phenyl-1-propene.** The procedure and quantities used were identical with those given for the cis olefin. The final preparative tlc analysis gave five products as follows: 1-naphthyl phenyl ketone diperoxide (10 mg, 0.6%), ozonide (100 mg, 5.2%, cis/trans ratio = 0.78), epoxide of *trans*-1-(1-naphthyl)-1-phenyl-1-propene (400 mg, 23.6%), 1-naphthyl phenyl ketone (800 mg, 49.5%), and 1-(1-naphthyl)-1-phenyl-2-propanone (10 mg, 0.6%).

Epoxidation of *cis*- **and** *trans*-**1-(1-Naphthyl)-1-phenyl-1-propene.** The olefins (244 mg, 1 mmol) were treated individually with 85% *m*-chlorobenzoic acid (200 mg, 1 mmol) in 25 ml of chloroform at 0° overnight. The chloroform solution was washed with excess 10% NaOH solution and then dried with K_2CO_3. The chloroform was evaporated off and the residue analyzed by preparative tlc using benzene–hexane (80:20) for development and benzene for elution. The product from the cis olefin solidified upon trituration with hexane and was recrystallized from benzene–hexane to give colorless crystals: mp 92–93°; nmr 2.3 and 2.8 (multiplet, 12 H), 6.41 (quartet, 1 H), 9.03 (doublet, 3 H); ir 1320, 1005, and 890 cm^{-1}.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.65; H, 6.22.

The product from the trans olefin solidified on trituration with hexane to give colorless crystals: mp 79–80°; nmr 2.0, 2.4, 2.8 (multiplet, 12 H), 6.48 (quartet, 1 H), 8.78 (doublet, 3 H); ir 1296, 1005, and 890 cm^{-1}.

Anal. Calcd for $C_{19}H_{10}O$: C, 87.66; H, 6.19. Found: C, 87.63; H, 6.34.

Rearrangement of *cis*- **and** *trans*-**1,2-Epoxy-1-(1-naphthyl)-1-phenylpropane.** The epoxides were treated individually with a trace of *p*-toluenesulfonic acid or *m*-chlorobenzoic acid in ether at room temperature overnight. After removal of solvent the residual liquid was chromatographed on preparative tlc plates using benzene–hexane (80:20) for development and benzene for elution. The eluted material from both epoxides solidified on trituration

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(28) A. M. Khaletskii and A. Ya. Kaplan, *Zh. Obshch. Khim.*, **26**, 434 (1956).

with methanol to give colorless crystals of 1-(1-naphthyl)-1-phenyl-2-propanone: mp 83–84°, lit.[29] mp 84.5–85°; nmr 2.2, 2.8 (multiplet, 12 H), 4.31 (singlet, 1 H), 7.86 (singlet, 3 H); ir 1708 cm^{-1} (C–O).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.27; H, 6.36.

Photooxidation of 1-Naphthylphenyldiazomethane in Benzaldehyde. A solution of 2.45 g (10 mmol) of 1-naphthylphenyldiazomethane in 100 ml of benzaldehyde was photooxidized at 10–15° using an oxygen input of 100 ml/min and operating the lamp at 50 V for 50 min. After removing excess benzaldehyde under reduced pressure, the remaining liquid was chromatographed on silica gel (60 g silica gel, 3 g H_2O). Elution was carried out with benzene–hexane (20:80) and then benzene–hexane (50:50). All fractions were analyzed for ozonide using analytical tlc. Fractions containing ozonide were combined and chromatographed on preparative tlc plates using benzene–hexene (80:20) for development and benzene for recovery. The recovered ozonide (2.20 g, 5.6%) had a cis/trans ratio of 1.49. In this case the tentative stereochemical assignment is also based on the nmr spectrum. In ozonides with groups having diamagnetic anisotropies attached to the carbon containing the methine hydrogen it is found that the previously cited correlation is reversed and the trans isomer is the one with the methine hydrogen at lower field.[17,18] Both of the ozonides have a multiplet absorption at 1.8–3.0 (17 H) while the cis isomer has a singlet at 3.86 (1 H) and the trans has a singlet at 3.56 (1 H).

When the ozonide was allowed to stand for 11 months, rechromatographed by preparative tlc, and the recovered material recrystallized from benzene–hexane, colorless crystals of the pure trans compound were obtained. This material had mp 116–117° and nmr absorptions at 1.8–2.7 (multiplet, 7 H), 2.78 (singlet, 5 H), 2.96 (singlet, 5 H), and 3.56 (singlet, 1 H).

Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.31; H, 5.14.

Reduction of 1-(1-Naphthyl)-1-phenyl-1-propene and 1-(1-Naphthyl)stilbene Ozonides with Triphenylphosphine. Solutions of the ozonides in carbon tetrachloride were treated dropwise with a carbon tetrachloride solution of triphenylphosphine directly in an nmr tube. The tube contents were mixed for 1 min using a vibrator and then allowed to stand for 10 min before recording the nmr spectrum. In the case of 1-(1-naphthyl)-1-phenyl-1-propene ozonide the ozonide had an initial cis–trans ratio of 0.84 and ratios of 0.92, 1.15, and 1.32 after 8.8, 21.6, and 26.8% reaction, respectively. For 1-(1-naphthyl)stilbene ozonide the starting ozonide had a cis–trans ratio of 1.64 and ratios of 1.06, 0.91, and 0.74 after 8.8, 21.6, and 26.8% reaction, respectively.

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Enolene Rearrangements. III. Investigation of Charge Distribution in the Transition State of the Enolene Rearrangement

James M. Watson, John L. Irvine, and Royston M. Roberts*

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received October 3, 1972*

Abstract: The electronic nature of the transition state of the enolene rearrangement has been probed by the determination of substituent effects on the rates of rearrangement of 4′-R-4-pentenophenone-*2*-d_2 (R = H, CH_3, CH_3O, Cl, CN), 2,2-dimethyl-1-(4′-R-benzoyl)cyclopropane (R = H, CH_3, CH_3O, Cl), and 2,2-dimethyl-1-(3′-R-benzoyl)cyclopropane (R = H, CH_3O, Cl). The effects of various substituents on the rate of rearrangement have been correlated with Hammett[1] plots.

Having previously demonstrated[2–6] that the enolene rearrangement (**1** $\rightleftarrows$ **3**) of homoallylic ketones (**1**) proceeds *via* a reversible 1,5-hydrogen shift concerted with ring closure to an alkylacylcyclopropane intermediate (**3**), we desired to investigate the electronic nature of the transition state leading to and from **3**. We now report the results of two separate approaches to the study of this transition state which involve Hammett correlations of rearrangement rates of appropriately substituted 2,2-dideuterio-4-pentenophenones (**1a–e**, R′ = H) and of appropriately substituted alkylacylcyclopropanes (**3a–d, f, g**, R′ = CH_3).

Results

I. Syntheses of Compounds for Rearrangement. 4-Pentenophenones. With the exception of the parent compound of the series (**1a**, R′ = H),[4] the substituted 4-pentenophenones employed have not been previously reported. 4-Pentenophenone, 4′-methyl-4-pentenophenone, 4′-methoxy-4-pentenophenone, and 4′-chloro-4-pentenophenone were prepared by the imine alkylation procedure of Stork and Dowd[7] using the appropriate para-substituted acetophenone and alkyl bromide. As acetophenones bearing a strong electron-withdrawing group (*e.g.*, NO_2, CN) on the aromatic ring are not compatible with the Grignard reagent involved in imine alkylations, other approaches to the synthesis of 4-pentenophenones bearing such

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