Photochemical Reactions of Azine Monoxides. IV. Cyclic Azine Monoxides[1]

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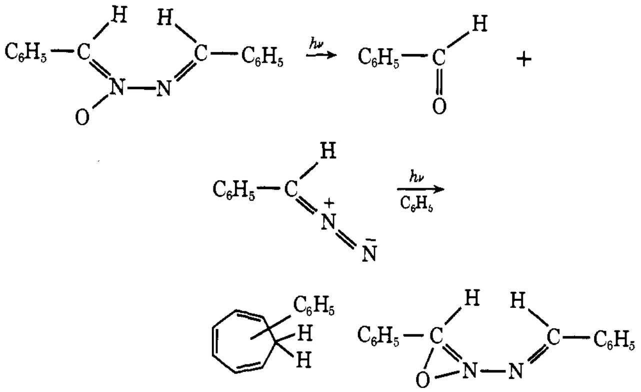
Abstract: Azine monoxides are observed to undergo smooth photochemical decomposition *via* two different pathways: (1) oxygen migration with ultimate formation of diazo compounds plus carbonyl compounds, or diazo ketones (cyclic azine monoxides); and (2) electrocyclic disrotary ring closure with formation of novel four-membered ring azoxy compounds. Acyclic and six-membered ring cyclic azine monoxides apparently undergo only process 1; five-membered ring systems, only process 2; and seven-membered ring systems, both processes 1 and 2.

Azine monoxides show a high susceptibility to undergo light-induced reactions unlike the analogous azines.[3a] Kirmse and coworkers have reported that benzophenone azine monoxide and benzaldehyde azine monoxides, upon photolysis, lead to benzophenone and benzaldehyde, respectively, with diazo compound intermediates being suggested by the transient red-orange colored solutions during the photolysis.[3b] With this in mind, it was hoped that photolysis of saturated *cyclic* azine monoxides might lead to the yet unexplored β, γ, and δ diazo ketones.

Results and Discussion

Formation of diazo compound intermediates in Kirmse's systems was verified by the photolysis of benzaldehyde azine monoxide which, in addition to providing a quantitative yield of benzaldehyde, led to a >60% yield of a mixture of phenylcycloheptatrienes, ostensibly formed from addition of phenyl carbene to benzene. This oxygen migration process is analogous to that observed in the photolysis of nitrones.[4] Oxaziridine intermediates such as 1 are postulated as intermediates in such reactions. Photolysis of unsymmetrical azine monoxide 2 provided good evidence for the specificity of oxygen migration in these systems, since benzophenone was formed to the total exclusion of benzaldehyde, which could not be detected by glpc or by nmr.



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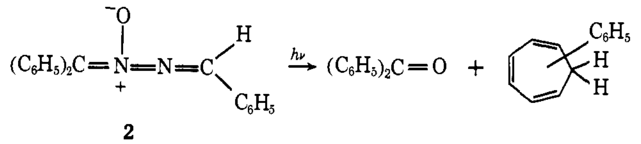
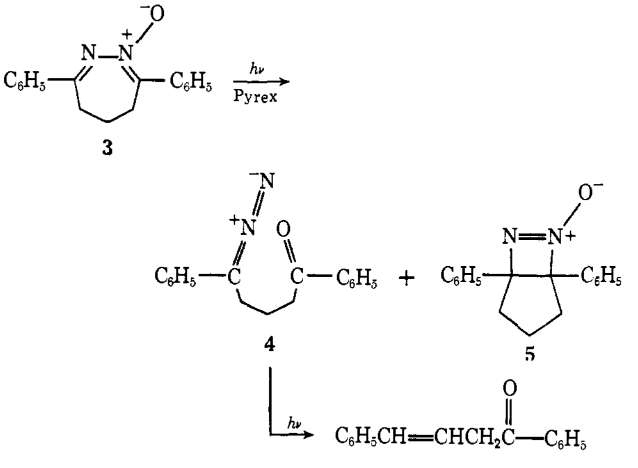


2

Irradiation of a CH_2Cl_2 solution of the seven-membered ring azine monoxide 3 with a 450-W, medium-pressure mercury lamp, equipped with a Pyrex filter, produced an intense, red-colored solution. The presence of diazo ketone intermediate 4 was suggested strongly by the presence of both a λ_{max} 508 mμ absorption in the uv and a strong absorption at 2040 cm^{-1} in the ir spectrum. Continued irradiation caused a disappearance of the red color and elution chromatography led to the isolation of two products, one an isomer of the starting material and the other having lost N_2. The latter product, isolated in 43% yield, was shown to be the unsaturated ketone 6, which would be expected from decomposition of diazo ketone 4.[5]



3

4

5

6

The product isomeric with starting material was isolated in 28% yield and was assigned the four-membered ring azoxy structure 5 on the basis of both its

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[1] Some of this work has been reported previously in communication form: W. R. Dolbier, Jr., and W. M. Williams, *J. Amer. Chem. Soc.*, **91**, 2818 (1969); *J. Chem. Soc. D*, 289 (1970).

[2] (a) Taken in part from the Ph.D. dissertation of W. M. W., University of Florida, June 1971; (b) Fellow of the Alfred Sloan Foundation, 1970–1972.

[3] (a) D. R. Arnold, V. Y. Abraitys, and D. McLeod, Jr., *Can. J. Chem.*, **49**, 923 (1971); (b) W. Kirmse, L. Horner, and H. Fernekess, *Chem. Ber.*, **94**, 279 (1961).

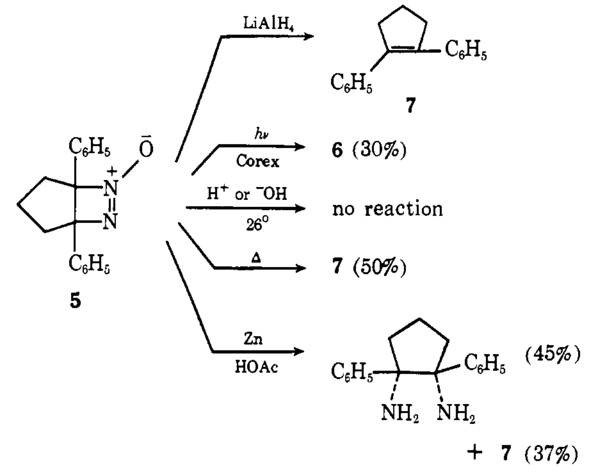
[4] E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, New York, N. Y., 1967, p 14.

[5] A. Padwa, E. Alexander, and M. Niemczyk, *J. Amer. Chem. Soc.*, **91**, 456 (1969); we thank Dr. Padwa both for spectra and a sample of **6**.

spectroscopic (including ^{13}C nmr spectrum)[6] and chemical properties.

The chemistry of **5**, shown in Scheme I, is also clearly in agreement with the assigned structure.[8] The remarkable thermal stability of **5** (14-hr half-life in diglyme at 161°) is consistent with Lemal's similar observations for four-membered ring azo compounds.[9]

Scheme I

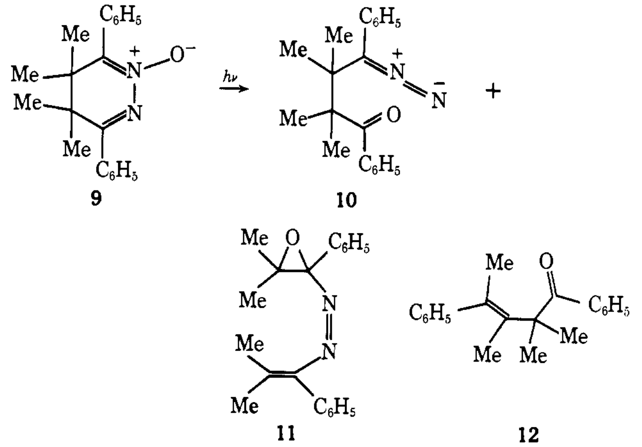


Although a thorough investigation of the excited state responsible for the observed reactions was not carried out, it seems likely that a $\pi \rightarrow \pi^*$, singlet state is responsible for *both* photoproducts.

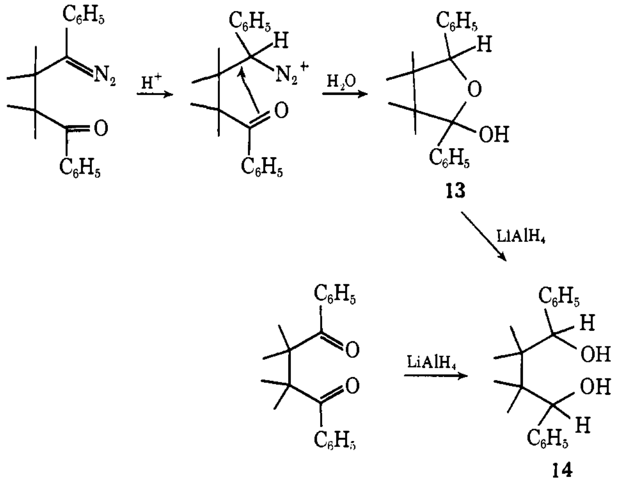
Two closely related systems, nitrones[10] and aromatic amine oxides,[11] have been observed to react *via* $\pi \rightarrow \pi^*$ singlet states to form oxaziridines, while triplet states in these systems led only to photodeoxygenations. An examination of the uv spectrum of **3** showed the lowest energy transition to apparently be a $\pi \rightarrow \pi^*$ transition; *i.e.*, it had a large extinction coefficient, ϵ 7690.

The importance of the singlet state was also inferred when piperylene, an excellent, low-energy triplet quencher, failed to quench either photolytic process. Actually the yields of **5** (31%) and **6** (54%) were increased when **3** was photolyzed in piperylene solution. Quenching of side reactions which occurred from triplet states would account for the increased yields. Such quenching experiments, however, do not rigorously exclude the possibility of a triplet state reaction since the triplet energy could conceivably be lower than that of piperylene (E_t = 58 kcal/mol),[12] or the rate of product formation might be *faster* than diffusion-controlled quenching. In all likelihood, however, *both* processes are derived from the singlet state.

Similar irradiation of the six-membered ring monoxide, **9**, led to a reddish-brown solution which spectroscopically showed a uv λ_{max} 493 mμ and an intense ir absorption at 2050 cm^{-1}, thus indicating the presence of diazo ketone **10**. Further irradiation of the solution, while leading to disappearance of the color, led to none of the expected unsaturated ketone **12**. A low yield of an unidentified, impure ketone which did not react with ozone could be obtained by elution chromatography (see Experimental Section).



By using a sun lamp one could moniter the photolysis easily by nmr. So doing, one could determine that there were only *two* primary products from the photolysis. Two, equal intensity, singlet absorptions at τ 8.64 and 8.56 were assigned to the two different pairs of methyl groups of the diazo ketone intermediate. Addition of a few drops of acidified methanol to the nmr tube resulted in immediate gas evolution, loss of reddish-brown color and loss of these two absorptions. Destruction of this solution with dilute H_2SO_4 led to the isolation of much **13**. Besides spectroscopic evidence, the structure of **13** was deduced by its $LiAlH_4$ reduction to diol **14**, which could be independently prepared as shown.



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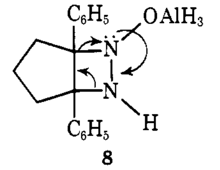
[6] The ^{13}C nmr spectrum gave five absorptions (86.5, 117.5, 158.5, 161.8, and 171.0 ppm upfield from CS_2 as an internal standard) of equal intensity, which indicated the presence of two different quaternary and three secondary aliphatic carbon atoms in the molecule.[7]

[7] We thank Dr. Leroy Johnson of Varian Associates, Palo Alto, Calif., for running the 220-MHz proton and ^{13}C nmr spectra of **5** and **19**.

[8] The uniqueness of the $LiAlH_4$ reduction of **5** to **7**, a process which generally leads only to deoxygenation, can be rationalized mechanistically in terms of a relief of ring strain in the reduced intermediate **8**.



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[9] N. Rieber, J. Alberts, J. Lipsky, and D. M. Lemal, *J. Amer. Chem. Soc.*, 91, 5668 (1969).

[10] J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 3995 (1970).

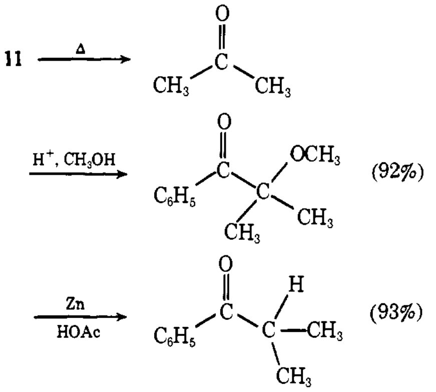
[11] O. Buchardt, G. G. Spence, and E. C. Taylor, *Chem. Rev.*, 70, 231 (1970).

[12] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 1245 (1966).

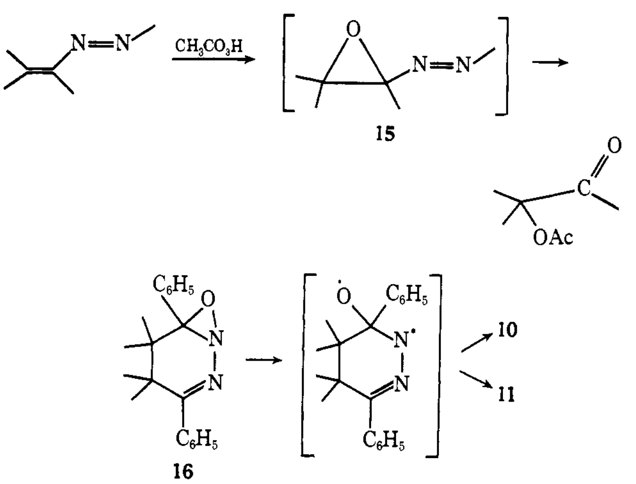
The other primary photoproduct could be isolated in 19% yield as a yellow-green oil from elution chromatography of the crude photolysis mixture. It was shown to be isomeric with starting material and on the basis of its spectroscopic and chemical properties was assigned the structure **11**. The nmr showed the methyl groups as four singlets at τ 9.17, 9.10, 8.47, and 8.45 (in CH_2Cl_2); the mass spectrum showed no parent, but small (p − H_2O) and (p − acetone) peaks at m/e 288 and 248;[13] the uv spectrum showed continuous weak absorption from 380 mμ (quite typical of acyclic azo compounds)[14] and had λ_{max} 237 (ϵ 18,300) which agreed reasonably with that of a rare α,β-unsaturated azo compound.[15] The ir had two dominant absorptions at 1450 and 1435 cm^{-1} and a medium one at 1485 cm^{-1}. While azo compounds absorb generally at about 1600 cm^{-1}, Gillis has recently shown that conjugation, as in α,β-unsaturated azo compounds, shifts the absorption to around 1500 cm^{-1}.[15a]

The chemistry of **11** was also strongly indicative of its structure. The products shown in Scheme II as isolated from these chemical reactions of **11** can best be envisioned as arising from the epoxy portion of the molecule, while the remaining portion apparently leads only to tars in each case. Nevertheless, the composite data *cannot* be rationalized reasonably using any alternative structure for **11**. Especially interesting was the smooth pyrolytic cleavage of **11** to acetone at temperatures below 80°. There are similarities between this reaction and those of *p*-toluenesulfonylhydrazones of α,β-epoxy ketones, which have been investigated by Eschenmoser.[16] This type of cleavage process is presently being investigated in further detail.

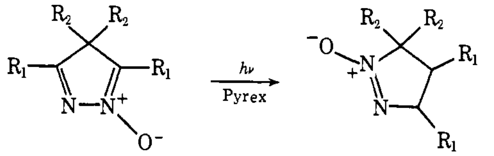
Scheme II



No isolable compound analogous to **11** has been reported previously although Gillis hypothesized the intermediacy of epoxy-azo compound **15**, in the reaction below.[15b] Both products of this reaction can be envisioned as deriving from the same *photochemical* process, that of forming the oxaziridine intermediate **16**, which then converts both to diazo ketone **10** and epoxy-azo compound **11** by competing ground state reactions.



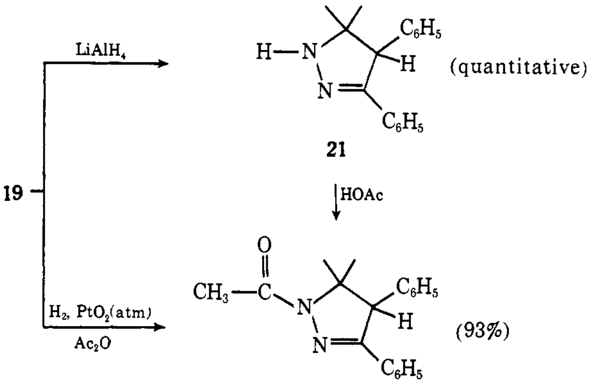
Photolysis of the five-membered ring analog **17** led to a single product in 70% yield which was found to be isomeric with starting material. Structure **19** was assigned to this product on the basis of its spectroscopic[17] and chemical properties. In addition, an independent synthesis of **19** was accomplished. Scheme III depicts some pertinent chemistry of **19**. The independent synthesis was accomplished as in Scheme IV.



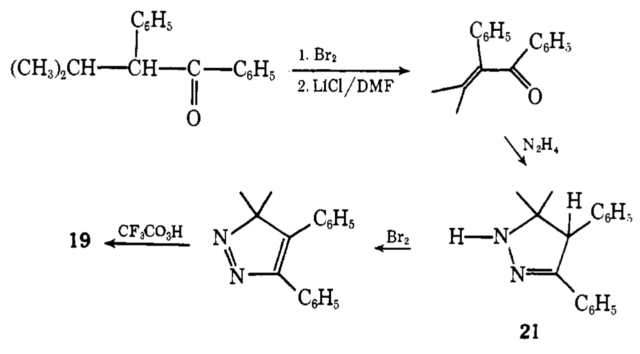
17, $R_1 = C_6H_5$; R_2 = Me
18, R_1 = Me; R_2 = Et

19, $R_1 = C_6H_5$; R_2 = Me
20, R_1 = Me; R_2 = Et

Scheme III



Scheme IV



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[13] It should be noted that the loss of acetone from a somewhat analogous compound, 1,2-epoxy-2-methylpropylbenzene, upon electron impact, was a feature of its mass spectrum.

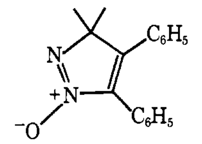
[14] P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 276.

[15] (a) B. T. Gillis, *J. Amer. Chem. Soc.*, **87**, 4576 (1965); (b) *J. Org. Chem.*, **32**, 95 (1967).

[16] (a) A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, **50**, 708 (1967); (b) D. Felix, H. Schreiber, K. Piers, V. Horn, and A. Eschenmoser, *ibid.*, **51**, 1461 (1968).

[17] The ^{13}C nmr spectrum showed two different phenyl groups, three different ring carbons, and two identical methyl carbons.[7]

Each of the intermediates in the synthesis were characterized, with pyrazoline **21** being identical with the $LiAlH_4$ product from **19**. None of the isomeric *N*-oxide, **22**, could be detected from the oxidation step.



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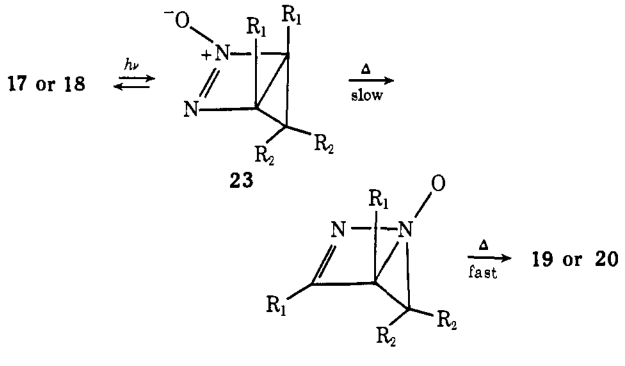
Evidence that the structure of the photoisomer was indeed **19** and not **22** was derived from spectroscopic data of Freeman[18] on analogous systems where both isomers *were* known.

To use his data it was preferable for us to have a nonphenyl-substituted system and thus **18** was photolyzed to produce photoisomer **20**. Assignment of the 1-oxide structure in this case was unambiguous since its uv spectrum showed λ_{max} 315 (ϵ 3530) and 227 (2380), while that of Freeman's 3,4,5,5-tetramethyl-5*H*-pyrazole 1-oxide was almost identical (λ_{max} 305 (ϵ 3800) and 226 (2100)).[19]

A reasonable mechanism which would give rise to the 1- but not the 2-oxides involves an initial electrocyclic ring closure as shown in Scheme V.

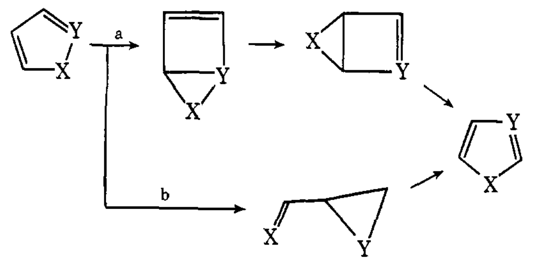
Scheme V



In a low-temperature photolysis (−78°) of **18**, intermediate **23** could be detected in the nmr by the appearance of two new singlet methyl group absorptions at τ 8.82 and 8.24. These remained indefinitely at temperatures up to about −20° where they began to decrease with concomitant increase in intensity of starting material and formation of product (**20**) which had *not* been present at the lower temperatures. Both starting material and product could be isolated from this reaction and characterized as before.

It should be noted that the photolysis of the five-membered ring system follows a pathway which is analogous to that observed for a number of heteroaromatic systems[20] seen in Scheme VI as process a and in contrast to many other reported processes which apparently follow pathway b.[21]

Scheme VI



In summary, all of the photochemical transformations which have been thus far observed for acyclic, five-, six-, and seven-membered ring azine monoxides seem to be able to rationalized on the basis of two basic rearrangement pathways each probably originating from the singlet state. Oxygen migration *via* probable oxaziridine intermediates is the *exclusive* pathway for acyclic and six-membered ring azine monoxides, while five-membered ring systems apparently are transformed entirely *via* an electrocyclic ring closure process. The seven-membered ring system partitions between the two pathways.

γ- and δ- but not β-diazo ketones were formed in this study, and some information was garnered as to the chemistry of such new systems. Perhaps most interesting, however, was the observation of the electrocyclic process which formed heretofore unknown four-membered ring azoxy compounds. This relatively great photochemical lability of azine monoxides is of course in complete contrast to the relative inertness of the analogous azine compounds.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and were uncorrected. Ir spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer; uv spectra on a Cary Model 15 spectrometer; nmr spectra from a Varian Model A-60 spectrometer, utilizing TMS as an internal standard; and mass spectral data from a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV. Elemental analyses were determined by Atlantic Microlab, Inc. The glpc analyses were carried out on a Varian Aerograph Model A-90-P3 gas chromatographs combined with a Leeds and Northrup Model H recorder equipped with a Disc integrator using 6 ft × 0.25 in. 10% Carbowax 20M on Chromosorb P column. All common reagents which are not referenced were commercially available.

3,7-Diphenylhexahydro-1,2-diazepine 1-Oxide (3). To 5.0 g (0.0202 mol) of 3,7-diphenylhexahydro-1,2-diazepine[22] in 100 ml of Et_2O and 50 ml of CH_2Cl_2 was added 14.8 g (0.014 mol) of Na_2CO_3. To it was added at 0° 0.0505 mol of CF_3CO_3H[23] in Et_2O. The stirring was continued for 1.5 hr after all the peracid had been added. Water was added and the solution was then washed with a 15% K_2CO_3 solution and water, dried, and evaporated. The residue was subjected to column chromatography on silica gel, eluting with CCl_4–Et_2O (10:1) to remove impurities, with the pure oxide (1.0 g, 19%) being eluted with CH_2Cl_2–Et_2O (1:1): mp 168–169°; ir (KBr) 3000, 2910, 1570, 1550, 1505, 1485, 1450, 1440, 1350, 1335, 1310, 1300, 1290, 1270, 1230, 1195, 1160, 1150, 1145, 1080, 1045, 1015, 990, 980, 880, 785, 765, 742, 725, 710, 700, 695 cm^{-1}; nmr (CH_2Cl_2) τ 7.32 (6 H, m), 2.53 (6 H, m), 1.98 (4 H, m); uv (EtOH) λ_{max} 317 mμ, s (ϵ 7690), 285 (12,300), 255 (12,500); mass spectrum, *m/e* (%) 264 (31.5), 248 (21.8), 236 (28.8), 234 (41.5), 117 (55.5), 115 (27.9), 105 (95.9), 104 (55.8), 103 (56.1), 91 (40.0), 77 (100), 51 (32.8).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.60. Found: C, 77.32; H, 6.30; N, 10.72.

4,4-Dimethyl-3,5-diphenyl-4*H*-pyrazole. 2,2-Dibenzoylpropane[24] (20 g, 0.0794 mol) in 600 ml of MeOH and 1 ml of concentrated HCl were heated to reflux and treated dropwise with a solution of 3.10 g (0.092 mol) of 95% N_2H_4 in 50 ml of MeOH. After refluxing overnight, the solution was poured onto 1500 g of ice and extracted with ether. The ethereal layers were washed with H_2O,

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[18] J. P. Freeman, *J. Org. Chem.*, **27**, 1309 (1962).

[19] The analogous 2-oxide had a very different uv spectrum: λ_{max} 241 mμ (ϵ 6300).

[20] (a) P. Beak, J. J. Miesal, and W. R. Messer, *Tetrahedron Lett.*, 5315 (1967); (b) P. Beak and W. Messer, *Tetrahedron*, **25**, 3287 (1969).

[21] B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, **89**, 6911 (1967).

[22] C. G. Overberger and J. J. Monagle, *ibid.*, **78**, 4470 (1956).

[23] W. D. Emmons and A. S. Pagano, *ibid.*, **77**, 89 (1955).

[24] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1961 (1949).

dried, and evaporated *in vacuo* yielding 18.7 g of crude product. Recrystallization from hexane–benzene (4:1) gave 16.5 g (88%) of long, white flakes: mp 125.5–126.5°; ir (KBr) 3030, 2970, 1505, 1490, 1450, 1440, 1365, 1345, 1155, 1075, 1035, 1005, 925, 835, 780, 770, 700, 680 cm^{-1}; nmr (CH_2Cl_2) τ 8.35 (6 H, s), 2.57 (6 H, m), 1.96 (4 H, m); uv (EtOH) λ_{max} 313 mμ (ϵ 18,770), 222 (8330), 205 (16,600); mass spectrum, *m/e* (%) 248 (100), 205 (78.4), 145 (70.1), 144 (48.8), 130 (34.3), 104 (87.0), 103 (29.0), 77 (61.5).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 81.90; H, 6.87; N, 11.24. Found: C, 81.95; H, 6.51; N, 11.35.

4,4-Dimethyl-3,5-diphenyl-4*H*-pyrazole 1-Oxide (17). In a manner similar to that of preparing **3**, 5.0 g (0.0202 mol) of 4,4-dimethyl-3,5-diphenyl-4*H*-pyrazole was oxidized with 0.0505 mol of CF_3CO_3H to produce a gummy oil which upon elution chromatography on silica gel using first CH_2Cl_2, then $CHCl_3$, and then $CHCl_3$–Et_2O (3:1) yielded 200 mg (4%) of pure oxide: mp 120°; ir (KBr) 1585, 1550, 1515, 1490, 1455, 1440, 1370, 1305, 1140, 1080, 1000, 770, 695 cm^{-1}; nmr (CH_2Cl_2) τ 8.18 (6 H, s), 2.46 (6 H, m), 2.00 (2 H, m), 1.65 (2 H, m); uv (EtOH) λ_{max} 344 mμ (ϵ 10,200), 263 (13,600), 221 (30,500); mass spectrum, *m/e* (%) 264 (64.0), 248 (38.9), 234 (71.4), 205 (39.3), 149 (36.3), 145 (39.2), 144 (32.8), 131 (75.5), 130 (24.6), 116 (44.5), 115 (56.5), 105 (58.0), 104 (66.7), 91 (71.0), 77 (100), 76 (32.0), 51 (53.3), 50 (21.0), 45 (41.8), 41 (29.2), 39 (29.9).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.60. Found: C, 77.05; H, 6.10; N, 10.29.

3,3,4,4-Tetramethyl-1,2-diphenylcyclobutene Ozonide. Into 4.8 g of 3,3,4,4-tetramethyl-1,2-diphenylcyclobutene[25] in 75 ml of CH_2Cl_2, cooled to −20°, was bubbled ozone, generated from a Wellsbach generator, until the exit gases liberated iodine from an aqueous solution of KI. Evaporation of solvent *in vacuo* at 26° gave a quantitative yield of the stable ozonide: white solid, mp 150–151° (EtOH); ir (KBr) 300, 2970, 2900, 1480, 1465, 1455, 1400, 1375, 1295, 1155, 1100, 1070, 1045, 1015, 990, 920, 785, 765, 720, 700, 690, 595, 515 cm^{-1}; nmr (CH_2Cl_2) τ 9.25 (6 H, s), 8.71 (6 H, s), 2.60 (10 H, m).

2,2,3,3-Tetramethyl-1,4-diphenylbutane-1,4-dione. 3,3,4,4-Tetramethyl-1,2-diphenylcyclobutene ozonide (5.6 g) in 50 ml of diglyme and 10 ml of concentrated HCl was heated on a steam bath for 5.5 hr with occasional swirling. After diluting with H_2O, aqueous NaOH was added and the organic products were taken up in ether. After washing with water, the ether was dried and evaporated to yield 4.8 g of solid. Chromatography on silica gel eluting with CH_2Cl_2 removed a liquid impurity, followed by 3.9 g (72.4%) of the diketone: mp 113–114° (EtOH); ir (KBr) 2995, 2940, 1680, 1470, 1445, 1400, 1385, 1365, 1265, 1210, 1195, 1155, 1085, 1005, 975, 965, 925, 800, 790, 775, 760, 745, 710, 670, 630, 545 cm^{-1}; nmr (CH_2Cl_2) τ 8.61 (12 H, s), 2.61 (10 H, m); uv (EtOH) λ_{max} 236 mμ (ϵ 10,450); mass spectrum, *m/e* (%) 294 (1.6), 237 (1.6), 172 (6.6), 105 (100), 77 (23.6).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.70; H, 7.59.

4,4,5,5-Tetramethyl-3,6-diphenyl-4,5-dihydropyridazine. To 3.9 g (0.0132 mol) of 2,2,3,3-tetramethyl-1,4-diphenylbutane-1,4-dione in 50 ml of benzene was added 0.60 g (0.018 mol) of anhydrous hydrazine and the solution was refluxed overnight. The solution was cooled, washed with water, and diluted with ether. After drying, the solvent was evaporated *in vacuo* yielding 3.7 g (97.3%) product: mp 178° (lit.[26] 177.5–179°); ir (KBr) 2950, 1570, 1540, 1520, 1450, 1430, 1400, 1380, 1360, 1300, 1140, 1080, 1035, 1015, 1000, 990, 970, 925, 780, 765, 755, 700, 685 cm^{-1}; nmr (CH_2Cl_2) τ 8.98 (12 H, s), 2.63 (10 H, s).

4,4,5,5-Tetramethyl-2,6-diphenyl-4,5-dihydropyridazine 1-Oxide (9). To 0.5302 g (0.00183 mol) of azine in 30 ml of CH_2Cl_2 was added 0.395 g (0.00194 mol) of 85% *m*-chloroperbenzoic acid. After stirring at 26° for 20 hr the solution was washed with K_2CO_3 solution and then water and dried. Solvent was evaporated and the residue chromatographed on silica gel, eluting first with CH_2Cl_2, then with ether to remove the impurities, with the pure oxide (0.365 g, 68%) eluting from the column with methanol as a light yellow solid: mp 235–236° dec; ir (KBr) 3000, 2940, 1595, 1560, 1500, 1450, 1430, 1325, 1250, 1140, 1000, 780, 765, 745, 710, 705, 695 cm^{-1}; nmr (CH_2Cl_2) τ 8.90 (6 H, s), 8.77 (6 H, s), 2.59 (3 H, s), 2.53 (7 H, s); uv (EtOH) λ_{max} 304 mμ (ϵ 4140), 255 (6670); mass spectrum *m/e* (%) 306 (40.8), 305 (42.0), 145 (25.8), 144 (25.8), 131 (100), 115 (27.0), 105 (37.8), 104 (46.8), 91 (53.4), 84 (42.0), 77 (44.4), 41 (49.2).

Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.58; H, 7.32; N, 9.32.

Photolysis of Benaldazine Monoxide in Benzene. A solution of 0.7636 g of the monoxide[27] in 100 ml of benzene was photolyzed through quartz for 25 min with a 450-W, medium-pressure mercury lamp (Hanovia) under N_2. Tlc revealed the presence of two products. Evaporation of solvent yielded an oil which was chromatographed on silica gel. Elution with pentane removed 0.3525 g (61.5%) of a mixture of phenylcycloheptatrienes[28] identified from ir, nmr, and mass spectra. Further elution with CH_2Cl_2 yielded 0.3656 g (quantitative) of benzaldehyde which was identified from its ir spectra.

Photolysis of *N*-Benzylidene-*N*′-diphenyleneazine *N*′-Oxide (2) in Benzene. A solution of 0.7931 g of the monoxide[27] in 100 ml of benzene was photolyzed in a similar manner. Evaporation of solvent yielded an oil which was chromatographed as above to yield 0.2984 g (67.2%) of a mixture of phenylcycloheptatrienes and benzophenone [2,4-DNP, mp 238–239° (lit.[29] 239°)].

Photolysis of 3,7-Diphenylhexahydro-1,2-diazepine 1-Oxide (3). A solution of 1.50 g of **3** in 100 ml of CH_2Cl_2 was photolyzed under N_2, through Pyrex, with the 450-W lamp. Interruption of the photolysis after about 10 min revealed a red solution due to the presence of **4** (λ_{max} 508 mμ and strong ir absorbance at 2040 cm^{-1}). Continued photolysis of this solution resulted in gradual decoloration until after 25 min there remained only a light yellow solution. Tlc indicated that two products were present. Evaporation yielded a brownish oil which was chromatographed on silica gel [CH_2Cl_2–pentane (1:1)] to yield 0.575 g (42.8%) of **6**.[5] Further elution with CH_2Cl_2 yielded 0.430 g (28.7%) of **5**: white solid; mp 135°; ir (KBr) 3061, 3028, 2983, 2933, 1600, 1581, 1565, 1553, 1548, 1538, 1533, 1528, 1519, 1515, 1500, 1489, 1449, 1444, 1422, 1346, 1328, 1318, 1310, 1271, 1208, 1178, 1172, 1165, 1161, 1122, 1091, 1084, 1069, 1033, 999, 991, 973, 939, 902, 882, 767, 751, 701, 693 cm^{-1}; nmr (CH_2Cl_2) τ 7.80 (6 H, m),[30] 2.86 (10 H, s); uv (EtOH) λ_{max} 270 mμ (ϵ 452), 264 (735), 258 (958), 210 (17,800); mass spectrum, *m/e* (%) 264 (56.5), 235 (13.5), 234 (62.0), 220 (100), 219 (31.9), 129 (33.3), 117 (36.5), 115 (40.6), 105 (81.2), 104 (53.8), 103 (79.1), 102 (23.2), 91 (68.5), 77 (82.0), 51 (36.0).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.60. Found: C, 77.06; H, 5.92; N, 10.86.

Reduction of 1,4-Diphenyl-2,3-diazabicyclo[3.2.0]hept-2-ene 2-Oxide (5) with $LiAlH_4$. A mixture of 192 mg of **5** in 15 ml of Et_2O and 1.0 g of $LiAlH_4$ was stirred at 26° for 2 hr. After pouring onto chipped ice, extracting with Et_2O, washing with water, drying, and evaporating, 155 mg (97%) of **7**[31] was obtained.

Photolysis of 5. A solution of 91.5 mg of **5** in 100 ml of CH_2Cl_2 was photolyzed under N_2 through Pyrex for 10 min with the 450-W lamp. No reaction was observed (tlc). A Corex filter was substituted for the Pyrex filter and the photolysis was continued for 15 min. Four products were detected by tlc, and the residue obtained after evaporation of solvent was chromatographed on silica gel [pentane–CH_2Cl_2] to yield 12 mg of a mixture of two unknown compounds plus 10 mg (35%) of **6**. Further elution with CH_2Cl removed 60 mg of unreacted **5**.

Reaction of 5 with Zinc in Glacial Acetic Acid. To a suspension of excess Zn in glacial HOAc was added 100 mg of **5**, and the mixture was refluxed for 45 min. Filtration was followed by neutralization of the filtrate and extraction with ether. After washing the ether solution with water, drying and evaporation, chromatography of the residue on silica gel [CH_2Cl_2] yielded 33 mg (39%) of **7**. Further elution with methanol provided 43 mg (45%) of a very polar compound, *cis*-1,2-diamino-1,2-diphenylcyclopentane as a white solid: mp 69–72°; ir (CCl_4) 3390, 3300, 3095, 3060, 3030, 2960, 2880, 1600, 1595, 1445, 1320, 1075, 1035, 700, 590, 575 cm^{-1}; nmr (CCl_4) τ 8.25 (4 H, s), 7.78 (6 H, m), 3.06 (10 H, s); mass spec-

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[30] A 220-MHz proton nmr spectrum of compound **5** indicated that this multiplet was made up of at least 31 peaks.

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trum, *m/e* (%) 252 (4.9), 235 (45.1), 144 (40.2), 143 (20.7), 133 (20.7), 132 (100), 104 (64.6), 77 (37.2), 38 (20.1), 36 (53.7).

The dihydrochloride could be prepared by treating the diamine with gaseous HCl in anhydrous Et_2O: mp (MeOH–MeCN) 260–262° dec.

Anal. Calcd for $C_{17}H_{22}Cl_2N_2$: C, 62.76; H, 8.61; N, 6.82. Found: C, 62.52; H, 8.64; N, 6.86.

Pyrolysis of 5. A 117-mg portion of **5** in 30 ml of dry diglyme was stirred and refluxed for 11 hr. Water was added, and the organic products were taken up in CH_2Cl. After washing thoroughly with H_2O the solution was dried and evaporated. The residue was chromatographed on silica gel [pentane] to yield 14 mg (37%) of **7**. Further elution with CH_2Cl_2 provided 71 mg of unreacted **5**.

Photolysis of 3,7-Diphenylhexahydro-1,2-diazepine 1-Oxide (3) in Piperylene. To 75 ml of freshly distilled piperylene and 10 ml of CH_2Cl_2 was added 194.8 mg of **3**. The solution was irradiated with a 100-W lamp through Pyrex until the red color, which appeared after about 5 min, had completely disappeared (35 min). As the photolysis continued, all of **3** slowly dissolved and reacted. Evaporation of solvent yielded an oil which was chromatographed on silica gel [pentane–CH_2Cl_2 (1:1)] which removed 94.4 mg (54.2%) of **6**. Continued elution with CH_2Cl_2 removed 60.1 mg (30.8%) of **5**.

Photolysis of 4,4,5,5-Tetramethyl-3,6-diphenyl-4,5-dihydropyridazine 1-Oxide (9). A solution of 0.3160 g of **9** in 100 ml of CH_2Cl_2 was photolyzed through Pyrex for 30 min with the 100-W lamp under N_2. After a few minutes the otherwise colorless or light yellow colored solution had become reddish brown due to formation of **10**: ir (film) 2050, 1660 cm^{-1}; nmr (CH_2Cl_2) τ 8.66 (6 H, s), 8.56 (6 H, s); uv (CH_2Cl_2) λ_{max} 493 mμ.

Solvent was evaporated and the reddish-brown residue was placed on a silica gel column with moist CH_2Cl_2. Instantly, gaseous evolution of N_2 occurred and the reddish-brown color of the diazo ketone disappeared. CH_2Cl_2 quickly eluted 0.2203 g of a product mixture. On standing overnight, this mixture slowly solidified to a brown solid which was washed with pentane to yield 100 mg of **13**, as a white solid: mp 161°; ir (KBr) 3540, 2980, 2965, 1465, 1445, 1400, 1365, 1245, 1150, 1140, 1055, 1040, 1025, 990, 960, 920, 800, 775, 700, 600, 565, 520, 495 cm^{-1}; nmr (CCl_4) τ 9.48 (3 H, s), 9.21 (3 H, s), 9.08 (3 H, s), 8.95 (3 H, s), 7.42 (1 H, s), 2.78 (8 H, s), 247 (2 H, m); uv (EtOH) λ_{max} 217 mμ (ϵ 13,400); mass spectrum, *m/e* (%) 296 (1.4), 278 (5.6), 263 (7.0), 190 (40.8), 175 (40.8), 174 (81.7), 159 (100), 131 (19.0), 117 (26.8), 91 (23.2), 77 (42.2).

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.17. Found: C, 80.87; H, 8.39.

Continued elution of the silica gel column with CH_2Cl_2 slowly removed 0.0603 g (19%) of **11** as a yellow-green oil: ir (film) 3030, 2980, 2900, 1595, 1560, 1485, 1450, 1435, 1365, 1360, 1330, 1310, 1295, 1260, 1210, 1180, 1160, 1140, 1070, 1050, 1030, 960, 940, 920, 830, 755, 700 cm^{-1}; nmr (CCl_4) τ 9.19 (3 H, s), 9.13 (3 H, s), 8.47 (6 H, s), 2.70 (10 H, m); uv (EtOH) λ_{max} 235 mμ (ϵ 18,300); mass spectrum, *m/e* (%) 288 (1.1), 248 (3.3), 220 (6.6), 205 (8.2), 148 (22.0), 119 (35.2), 117 (37.4), 105 (100), 77 (42.3), 58 (34.1), 43 (86.8).

2,2,3,3-Tetramethyl-1,4-diphenylbutane-1,4-diol (14). An ether solution of 0.1209 g of 2,2,3,3-tetramethyl-1,4-diphenylbutane-1,4-dione was added dropwise to a stirred suspension of 0.3 g of $LiAlH_4$ in anhydrous Et_2O. After stirring at 26° for 3.3 hr, the mixture was cautiously poured onto ice, and was extracted with Et_2O. The Et_2O solution was then washed with water, dried, and evaporated to yield 0.0981 g (82%) of a white solid: mp (acetonitrile) 158–163°; ir (KBr) 3200, 2950, 1490, 1470, 1445, 1390, 1375, 1355, 1290, 1255, 1195, 1130, 1075, 1055, 1040, 1025, 1000, 910, 885, 865, 765, 700 cm^{-1}; nmr (CCl_4) τ 9.47 (6 H, s), 9.07 (6 H, s), 5.22 (2 H, s), 5.00 (2 H, broad), 2.81 (10 H, s); mass spectrum *m/e* (%) 280 (2.2), 175 (20.0), 174 (100), 159 (100), 132 (31.9), 108 (50.3), 107 (96.8), 105 (21.6), 79 (25.7), 77 (23.2).

Reduction of 2-Hydroxy-3,3,4,4-tetramethyl-2,4-diphenyltetrahydrofuran (13) with $LiAlH_4$. To 41 mg of **13** in 25 ml of anhydrous ether was added an excess of $LiAlH_4$, and the mixture was stirred for 1.5 hr. The mixture was then cautiously poured onto ice and extracted with ether. The ether extracts were washed with H_2O, dried, and evaporated to yield 34 mg (83%) of **14**, mp 154–157°.

Pyrolysis of 2,3-Epoxy-2,7-dimethyl-3,6-diphenyl-4,5-diaza-4,6-octadiene (11). A CCl_4 solution of 20.3 mg of **11** was placed in an nmr tube, and slowly heated over a 10-min period to 100°. The heating was continued for 5 min after which time, an nmr spectrum showed a decrease in the absorptions of **11** and a new sharp singlet absorption at τ 7.92. Continued heating at 100° for 45 min resulted in the disappearance of the nmr signals of **11** and an increase of the absorption at τ 7.92. The solution was divided into two portions. To one was added a dilute solution of acetone–CCl_4, resulting in an increase in the intensity of the absorption at τ 7.92. The other portion was evaporated at 0.25 mm, and all volatile materials were collected in a liquid N_2 trap. An acidified solution of 2,4-DNP was added and the solution was shaken for several minutes. All volatiles were removed *in vacuo* and water was added, which caused precipitation of an orange solid, mp ($EtOH-H_2O$) 123°. An authentic sample of acetone 2,4-DNP melted at 124°[32] and had a mixture melting point at 123–124°

Reduction of 11 with Zn–HOAc. A suspension of excess powdered Zn in 3 ml of glacial HOAc was added to 60.3 g of **11**, and the mixture heated on a steam bath for 5 min with occasional swirling. The mixture was filtered and the filtrate neutralized with aqueous NaOH solution and extracted with ether. The ether solution was washed with water and dried. Evaporation yielded 43 mg of crude oil which contained one major component (tlc). Elution chromatography on silica gel [CH_2Cl_2] purified the oil (27 mg, 93%) which was positively identified as isobutyrophenone.[33]

Acid Hydrolysis of 11 in Acidified Anhydrous Methanol. To 0.307 g of **11** in an nmr tube was added 1 ml of acidified anhydrous MeOH. The color of the solution became much darker and heat was evolved. The progress of the reaction was monitored by nmr spectroscopy, and no acetone was observed at any time during the reaction. After about 15 min the reaction was essentially complete. After evaporation to dryness, the tlc of the residual oil showed that it consisted of only one major component. Chromatography on silica gel [CH_2Cl] eluted 0.0163 g (92%) of 2-methoxy-2-methylpropiophenone: ir (film) 3010, 2930, 2890, 1675, 1600, 1580, 1460, 1445, 1370, 1350, 1260, 1225, 1160, 1070, 1000, 980, 905, 815, 795, 715, 690 cm^{-1}; nmr (CCl_4) τ 8.56 (6 H, s), 6.85 (3 H, s), 2.60 (3 H, m), 1.75 (2 H, m); uv (EtOH) λ_{max} 278 mμ (ϵ 1280), 245 (11,160); mass spectrum, *m/e* (%) 178 (< 1.0), 105 (19.5), 77 (15.1), 73 (100).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.85; H, 8.03.

Photolysis of 4,4-Dimethyl-3,5-diphenyl-4*H*-pyrazole 1-Oxide (17). A solution of 138 mg of **17** in 100 ml of CH_2Cl_2 was photolyzed through Pyrex under N_2 with the 450-W lamp. There was no color change evident and tlc showed only one compound to have formed. After evaporation of solvent the residue was chromatographed on silica gel (CH_2Cl_2). Evaporation gave 98 mg (71%) of a white solid, **19**: mp (EtOH) 136.5°; ir (KBr) 1570, 1510, 1500, 1490, 1480, 1445, 1435, 1345, 1195, 1160, 1155, 1070, 965, 915, 805, 800, 780, 765, 705, 690, 670, 640, 625, 615 cm^{-1}; nmr (CH_2Cl_2) τ 8.44 (6 H, s), 2.67 (10 H, m); uv (EtOH) λ_{max} 337 mμ (ϵ 4430), 248 (20,300); mass spectrum, *m/e* (%) 264 (27.2), 234 (10.0), 132 (12.5), 131 (100), 115 (20.0), 91 (41.3).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.60. Found: C, 77.25; H, 5.97; N, 10.44.

Reduction of 5,5-Dimethyl-3,4-diphenyl-5*H*-pyrazole 1-Oxide (19) with $LiAlH_4$. To a suspension of 1 g of $LiAlH_4$ in 35 ml of dry ether was slowly added 134 mg of **19**. After stirring at 26° for 2 hr, the mixture was poured onto ice and the products were taken up in ether. After the ether solution was washed with water and dried, evaporation yielded 123 mg (97%) of **21**: mp 112–114° (decomposed on standing overnight); ir (KBr) 3360, 3050, 2960, 1560, 1490, 1455, 1380, 1340, 1195, 1065, 950, 925, 890, 760, 740, 690, 590, 500 cm^{-1}; nmr (CCl_4) τ 9.20 (3 H, s), 8.72 (3 H, s), 6.21 (1 H, s), 5.35 (1 H, broad), 2.90 (8 H, m), 2.62 (2 H, m); uv (EtOH) λ_{max} 291 mμ (ϵ 10,260); mass spectrum, *m/e* (%) 250 (100), 236 (25.3), 235 (98.3), 193 (86.9), 56 (36.6).

Acetylation of 5,5-Dimethyl-3,4-diphenyl-Δ^2-pyrazoline (21). To 70 mg of **21** was added 10 ml of Ac_2O, and the solution was heated on a steam bath under a N_2 purge for 0.5 hr with occasional swirling. Aqueous KOH was added to neutralize the excess Ac_2O, and the organic products were taken up in ether, which was washed with water, dried, and evaporated to yield 78 mg (95%) of 1-acetyl-5,5-dimethyl-3,4-diphenyl-Δ^2-pyrazoline as a colorless oil: ir (film) 3065, 3030, 3010, 2990, 1940, 1665, 1600, 1570, 1495, 1405, 1365, 1320, 1305, 1190, 1140, 1080, 1040, 950, 925, 865, 770, 735, 705, 695, 650, 630, 600, 520, 475, 425, 380, 365, 350 cm^{-1}; nmr (CCl_4) τ 8.82 (3 H, s), 8.42 (3 H, s), 7.68 (3 H, s), 5.82 (1 H, s), 2.90 (8 H, m), 2.52 (2 H, m); uv (EtOH) λ_{max} 296 mμ (ϵ 18,200), 288 (18,100); mass spectrum, *m/e* (%) 292 (99.0), 250 (74.3), 236 (22.2), 235 (100), 193 (30.5).

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(32) R. L. Shriner in ref 29, p 362.

(33) H. Leuchs, A. Heller, and H. Hoffmann, *Ber.*, **62**, 871 (1929).

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.04; H, 6.90; N, 9.58. Found: C, 78.16; H, 6.84; N, 9.36.

Hydrogenation of 5,5-Dimethyl-3,4-diphenyl-5*H*-pyrazole 1-Oxide (19). **19** (121 mg) was hydrogenated using PtO_2 in 5 ml of Ac_2O and 7 ml of HOAc at 1 atm. Products were taken up in ether which was washed with water and dried. Evaporation yielded 123 mg (85%) of oil, identified from its spectra as 1-acetyl-5,5-dimethyl-3,4-diphenyl-Δ^2-pyrazoline.

2-Bromo-3-methyl-1,2-diphenylbutan-1-one. To a solution of 5.9 g (0.025 mol) of 3-methyl-1,2-diphenylbutan-1-one[34] in 60 ml of CCl_4 was added 4.0 g (0.025 mol) of Br_2, and the solution was stirred at 26° for 2 days until the reddish color of the Br_2 had disappeared and gaseous evolution had ceased. Evaporation yielded 7.9 g (quantities) of the crude bromide as a light green oil: ir (film) 3060, 2980, 2940, 2880, 1680, 1600, 1580, 1495, 1445, 1390, 1370, 1230, 1185, 1030, 935, 845, 825, 755, 700, 660, 630, 530, 475 cm^{-1}; nmr (CCl_4) τ 9.31 (3 H, d), 8.90 (3 H, d), 7.30 (1 H, septet). 2.91 (6 H, m), 2.50 (4 H, m).

3-Methyl-1,2-diphenyl-2-buten-1-one. To 7.9 g (0.025 mol) of 2-bromo-3-methyl-1,2-diphenylbutan-1-one in 50 ml of dry DMF was added 4.25 g (0.10 mol) of LiCl, and the mixture was heated to 125–130° under N_2 for 1.5 hr. The solution was poured into water and extracted with two 200-ml portions of ether. The extracts were combined, and washed with four 500-ml portions of water, and dried over $MgSO_4$. Evaporation yielded a highly colored oil, which was distilled through a short column to yield 5.4 g (92%) of very light yellow oil: bp 140–142° (1 mm); ir (film) 2990, 2960, 2930, 2890, 2820, 2760, 1665, 1600, 1580, 1490, 1445, 1375, 1320, 1295, 1275, 1230. 1165, 1045, 1025, 860, 795, 765, 705, 730, 474 cm^{-1}; nmr (CCl_4) τ 8.31 (3 H, s), 822 (3 H, s), 2.78 (8 H, m), 2.09 (2 H, m); uv (EtOH) λ_{max} 279 mμ (ϵ 2720), 246 (14,210); mass spectrum *m/e* (%) 236 (75.9), 235 (48.4), 221 (35.1), 131 (34.6), 105 (100), 91 (34.0), 77 (31.4),

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.55; H, 7.01.

5,5-Dimethyl-3,4-diphenyl-Δ^2-pyrazoline (21). To 0.236 g (0.001 mol) of 3-methyl-1,2-diphenyl-2-buten-1-one in 5 ml of methanol was added 0.289 g (0.009 mol) of 97% hydrazine, and the resulting solution was stirred at ambient temperature under N_2 for 30 hr. Evaporation gave 0.246 g (99%) of the white solid, **21**.

5,5-Dimethyl-3,4-diphenyl-5*H*-pyrazole. To 1.7 g (0.007 mol) of **21** were added 25 ml of CH_2Cl_2 and 15 ml of water containing 1 g of KOH. To this rapidly stirred mixture was added dropwise, over a 10-min period at 26°, a solution of 1.27 g (0.007 mol) of Br_2 in 3 ml of CH_2Cl_2. After stirring for 4 hr the aqueous solution was removed and the CH_2Cl_2 layer was washed with water and dried. Evaporation yielded an impure solid product which was recrystallized from hexane to give 1.1 g (65%) of pure product: mp 124°; ir (KBr) 3000, 2900, 1630, 1590, 1550, 1480, 1445, 1420, 1325, 1245, 1170, 1155, 1075, 1065, 1030, 1015, 955, 915, 850, 780, 760, 718, 710, 690 cm^{-1}; nmr (CCl_4) τ 8.57 (6 H, s), 2.80 (8 H, m), 2.40 (2 H, m); uv (EtOH) λ_{max} 303 mμ (ϵ 4190) 232 (14,900); mass spectrum, *m/e* (%) 248 (4.9), 220 (72.9), 206 (31.6), 205 (100), 204 (23.4), 203 (25.7), 77 (20.8).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.40; H, 6.46; N, 11.17.

5,5-Dimethyl-3,4-diphenyl-5*H*-pyrazole 1-Oxide (19). To 248 mg (0.0010 mol) of 5,5-dimethyl-3,4-diphenyl-5*H*-pyrazole in 15 ml of Et_2O was added 1 g of solid K_2CO_3, and the solution was cooled to 0°. A solution of 0.0019 mol of CF_3CO_3H (**24**) in 4 ml of ether was then added dropwise to the rapidly stirred solution. After 1 hr, the solution was poured into an aqueous solution of K_2CO_3 and additional ether was added. The ether solution was then washed with water and dried. Evaporation gave 250 mg of the virtually pure oxide. Chromatography on silica gel with CH_2Cl_2 yielded 200 mg (76%) of analytically pure **19**.

Photolysis of 4,4-Diethyl-3,5-dimethyl-4*H*-pyrazole 1-Oxide[35] (18). A solution of 1.20 g of **18** in 100 ml of CH_2Cl_2 was photolyzed through Corex and under N_2 with a 450-W lamp. Samples were periodically withdrawn and checked on the ir spectrometer until the characteristic stretch at 1580 cm^{-1} had disappeared (about 2.5 hr). After concentration of the solution a glpc analysis on a 5-ft Carbowax column at 180° revealed the presence of at least seven products, although there was one very dominant component. Column chromatography on silica gel (CH_2Cl_2) removed many of the impurities and the major component, **20**, was removed from the column with $CHCl_3$ as a light yellow oil (0.344 g, 29%): ir (film) 2975. 2930, 2880, 1650, 1495, 1440, 1390, 1265, 675, 625 cm^{-1}; nmr (CCl_4) τ 9.47 (6 H, t), 8.30 (4 H, m), 8.25 (3 H, m), 7.95 (3 H, m); uv (EtOH) λ_{max} 315 mμ (ϵ 3530), 227 (2380); mass spectrum, *m/e* (%) 168 (37.0), 97 (28.6), 69 (25.2), 55 (100), 41 (28.6).

Anal. Calcd for $C_9H_{16}N_2O$: C, 64.25; H, 9.59. Found: C, 64.00; H, 9.78.

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Methyl Migration in the Aromatization of *p*-Xylene 1,2-Oxide[1]

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Abstract: *p*-Xylene 1,2-oxide (**4a**) has been prepared and its rearrangement to mixtures of 2,4- and 2,5-xylenol in aqueous solutions at various pH values has been investigated. When the reaction was carried out in basic, neutral, and weakly acidic solutions, the major product was found to be 2,4-xylenol, the formation of which involves migration of the methyl substituent on the oxirane ring from C-1 to C-2. The relative amount of 2,5-xylenol formed in the aromatization tended to increase with decreasing pH of the reaction medium, but only when the reaction was carried out in strongly acidic solution did the 2,5 isomer become the predominant product. The rearrangement to 2,4-xylenol provides a chemical model for a number of enzymatic hydroxylations which involve concomitant 1,2 shifts of alkyl side chains and which have been postulated to proceed *via* arene oxide intermediates.

The enzymatic hydroxylation of aromatic rings has been shown to be accompanied by intramolecular migration of the atom or group originally present at the site of substitution (the "NIH shift").[2] A mechanism involving the enzyme-catalyzed formation of an arene

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(2) (a) G. Guroff, J. W. Daly, D. M. Jerina, J. Renson, B. Witkop, and S. Udenfriend, *Science*, **157**, 1524 (1967); (b) J. Daly, G. Guroff, S. Udenfriend, and B. Witkop, *Arch. Biochem. Biophys.*, **122**, 218 (1967); (c) J. Daly and G. Guroff, *ibid.*, **125**, 136 (1968); (d) J. Daly,