Table I. Quantum Yield of Photoreduction for Irradiation at 254 nm[a]

Compound	Solvent	Initial concn, M	Intensity, quanta/sec	Rate, R, molecules/sec	ϕ_{av}[b]
Ni(AA)$_2$	Ethanol	5.20×10^{-3}	1.98×10^{16}	5.64×10^{13}	1.8×10^{-2}
Ni(AA)$_2$	95% ethanol–water	5.20×10^{-3}	2.37×10^{16}	2.35×10^{14}	2.3×10^{-2}
Ni(TFA)$_2$[c]	Ethanol	5×10^{-3}	2.35×10^{16}	5.64×10^{13}	4.6×10^{-3}

[a] Results obtained at $23 \pm 1°$ in ethanol. The ethanol was degassed by freeze–thaw techniques. [b] The quantum yields shown are calculated from $R/\{(I_i{}^Q)(I_i{}^f)\}^{1/2}$, where $I_i{}^Q$ is the incident light intensity and $I_i{}^f$ is the final incident corrected for the absorbance of the deposited nickel film as described in ref 2. [c] TFA is 1,1,1-trifluoro-2,4-pentanedionato anion.

The wavelength dependence of the quantum yield was determined by irradiating ethanolic solutions of Ni(AA)$_2$ at 312 nm. This mercury line was isolated by filtering with Corex glass which has 0% T at wavelengths shorter than 260 nm. The degassed solutions showed no detectable photochemical reaction after irradiating for 17.5 hr at 312 nm. The ultraviolet spectrum of Ni(AA)$_2$ in dry ethanol consists of a complex, strong absorption whose maximum is at 295–300 nm [$\epsilon \sim 3 \times 10^4$ l./(mol cm)]. The band has a low-energy shoulder at about 312 nm and a high-energy shoulder at about 250–260 nm. The high-energy shoulder is quite weak [$\epsilon \sim 100$ l./(mol cm)]. The intense absorption at ca. 300 nm is undoubtedly due to a $\pi \rightarrow \pi^*$ transition primarily localized on the ligands. Since the photoreduction takes place from the high-energy side of the intense band (254 nm) but not from the low-energy side (312 nm), the reaction must occur from a specific high-energy state. The exact nature of this state is not known as yet. However, the reaction does not take place from the ligand π^* vibrational ground state which is on the low-energy side of the 300-nm band. The photoreduction of tris(hexafluoroacetylacetonato)iron(III), on the other hand, does occur by such a mechanism.[1] Since there are no readily observable charge-transfer bands for the Ni(II) chelates in this spectral region, the reduction may take place from vibrationally excited ligand π^* states or from ligand states resulting from loss of π-level degeneracy due to chelation.[4] It is also possible that the broad band has considerable ligand-to-metal charge-transfer character.

Cotton and Fackler[5] have assigned an absorption at 260 nm to the trimer Ni$_3$(AA)$_6$ which is stable in noncoordinating solvents. This band decreases in intensity in coordinating solvents in which the solvated monomer has been shown to be present. The appearance of this band in ethanol may be due to low concentrations of the timer. Therefore, the possibility exists that only the trimer is photoactive. To investigate this possibility, we have photolyzed ethanolic solutions of bis(dipivaloylmethane)nickel(II), Ni(DPM)$_2$, which is known to be monomeric both in the solid and in solution.[5,6] Preliminary results show that Ni(DPM)$_2$ undergoes the same photoreduction as Ni(AA)$_2$ at 254 nm with similar efficiency.

The effect of oxygen on these photoreductions is pronounced. Ethanolic solutions of Ni(AA)$_2$ where no effort had been made to remove dissolved air showed no photochemical activity.

(4) K. DeArmond and L. S. Forster, Spectrochim. Acta, 19, 1393 (1963).
(5) F. A. Cotton and J. P. Fackler, J. Amer. Chem. Soc., 83, 2818 (1961).
(6) F. A. Cotton and J. J. Wise, Inorg. Chem., 5, 1300 (1966).

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The Mechanism of Photoisomerization in a 1,3-Diazabicyclo[3.1.0]hex-3-ene[1a]

Sir:

In a recent communication, Padwa, Clough, and Glazer[1b] reported that 2,4,6-triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (1 and 2) photoisomerized to enediimine 3 which thermally cyclized to dihydropyrazine 4. The reactions were discussed in terms of possible applicability of the Woodward–Hoffman orbital symmetry rules. We have independently found a similar photo-


1, R$_1$ = Ph; R$_2$ = H
2, R$_2$ = H; R$_1$ = Ph
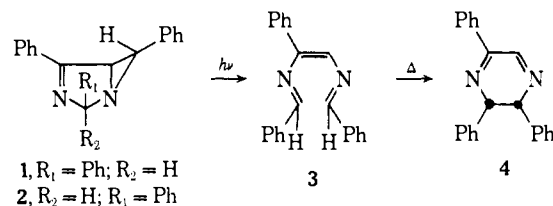
isomerization with 2,2-dimethyl-4-phenyl-6-p-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene, but now have trapped a 1,3-dipolar intermediate by cycloaddition with a dipolarophile and by matrix isolation. This new evidence demonstrates that the reaction occurs stepwise via the formation of an azomethine ylide which subsequently opens to the enediimine.

Aziridine 5 was prepared according to the procedure of Heine, et al.[2] (λ_{max}^{EtOH} 283 nm, ϵ 23,000). Irradiation of an argon-purged solution of 5 in benzene (150 mg in 30 ml, 450-W Hanovia lamp, Pyrex filter) at room temperature for 10 sec produced a bright red color (λ_{max} 565 nm) which faded after several minutes to yellow. Continued irradiation regenerated the red-colored species, but after 3 hr, the reaction mixture became quite yellow and most of the aziridine had reacted to give enediimine 7 in 40% yield. The

(1) (a) A portion of this work was presented at the CIC–ACS Joint Conference, Toronto, Ontario, Canada, May 1970; (b) A. Padwa, S. Clough, and E. Glazer, J. Amer. Chem. Soc., 92, 1778 (1970).
(2) H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, J. Org. Chem., 32, 2708 (1966).

identification of **7** was based on uv, ir, nmr, and mass spectral data which are in agreement with those de-

5
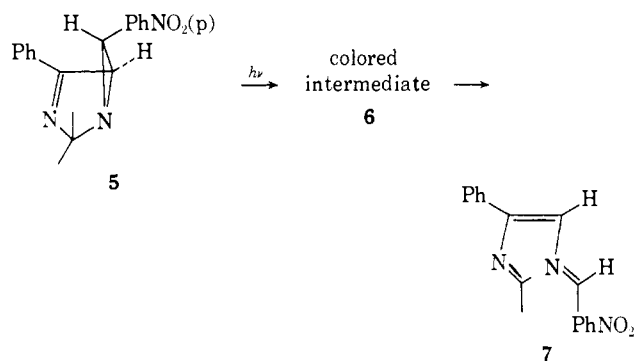
scribed by Padwa, *et al.*,[1b] for enediimine **3**: molecular ion at *m/e* 307; uv λ_{max}^{EtOH} 260 (ϵ 18,800), 395 nm (ϵ 10,700); ir (CHCl$_3$) 6.26 μ; nmr (CDCl$_3$) τ 8.45 (s, 6 H), 2.75 (s, 1 H), 2.00–2.60 (m, 9 H), 1.65 (s, 1 H).

The nature of the red-colored intermediate was revealed by trapping experiments. The color formed upon irradiation of the stirred benzene solution of **5** was immediately discharged by the addition of dimethyl acetylenedicarboxylate. Further irradiation after 1 equiv of the dipolarophile had been added (71 mg for 150 mg of **5**) no longer produced the coloration, and in 2 hr, gave 68% yield of adduct **9**. The structure of **9** was characterized by its uv, ir, nmr,
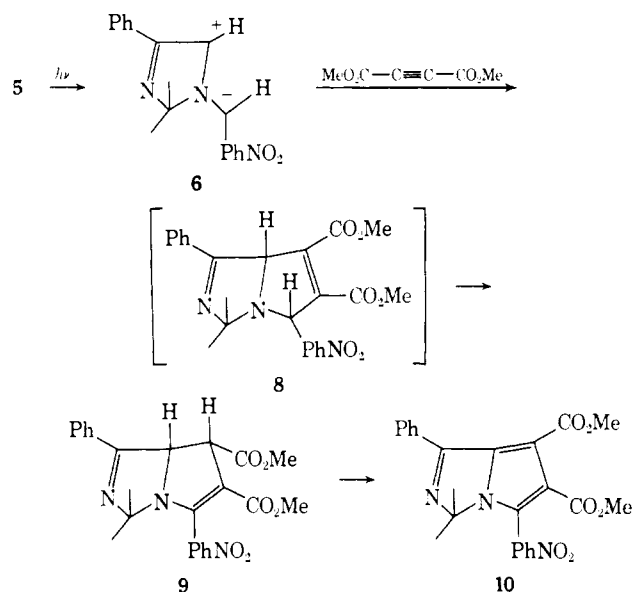

and mass spectral data: mp 150–152°; molecular ion at *m/e* 447; uv λ_{max}^{EtOH} 247 (ϵ 19,500), 300 nm (ϵ 12,500); ir (CHCl$_3$) 5.77 and 5.83 (C=O), 6.25 μ (C=N); nmr (CDCl$_3$) τ 8.60 (s, 3 H) and 8.42 (s, 3 H, geminal methyls), 6.56 (s, 3 H) and 6.37 (s, 3 H, ester methyls), 4.40 (d, *J* = 4.4 Hz, 1 H) and 3.95 (d, *J* = 4.4 Hz, 1 H, methine hydrogens), 1.70–2.70 (m, 9 H, aromatic hydrogens). Structure **9** rather than **8** was assigned to the adduct on the basis of the nmr spectrum which shows the two methine hydrogens as an AB quartet with *J* = 4.4 Hz. In a substituted 3-pyrroline such as **8**, a much smaller coupling constant would be expected.[3] The stereochemistry of **9** (and of **8** assuming

a suprafacial 1,3-hydrogen shift[4]), is determined by applying the Karplus equation[5] to the dihedral angles measured on a Dreiding model. The observed coupling constant is in good agreement with the value calculated for a cis configuration of **9**. This assignment is further supported by the fact that catalytic dehydrogenation of **9** occurred with remarkable ease.[6] Thus, refluxing **9** in benzene with palladium on charcoal for 15 min afforded **10** in quantitative yield (mp 205°). The nmr spectrum of **10** shows the equivalent geminal methyls as a sharp singlet at τ 8.45. When **5** and dimethyl acetylenedicarboxylate were refluxed in toluene for 3 hr, the products were a mixture of **9** and **10** in the ratio 70:30 (total yield 69%). Previously Heine, *et al.*, have reported a similar thermal cycloaddition of **5** with diethyl acetylenedicarboxylate to give the homolog of **10**.[7]

The colored intermediate was also trapped with tetracyanoethylene (TCNE). When a solution of **5** and TCNE in methylene chloride was irradiated, no color was observed and after 1 hr, the aziridine had disappeared to give adduct **11** in 95% yield (mp 186–187°; λ_{max}^{EtOH} 249 nm, ϵ 25,200). In agreement with the

11
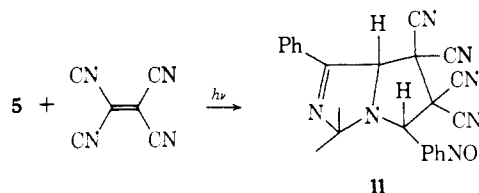
assigned structure, the nmr of **11** exhibits a pair of singlets at τ 4.05 and 4.69 for the two methine hydrogens. Acetylenedicarboxylate esters and TCNE are highly reactive dipolarophiles and their stereospecific cycloaddition with azomethine ylides from aziridines have been well documented.[8]

Irradiation of **5** in ethanol glass at liquid nitrogen temperature produced a bright red intermediate which was identical spectroscopically with the one from room-temperature photolysis. On warming to 220°K, the color faded, more rapidly on exposure to visible light, to give **7**. Photolysis of **5** and dimethyl acetylenedicarboxylate in ethanol glass at 77°K still gave the red color, but on warming it was rapidly discharged to give **9** identified by tlc. These observations are reminiscent of the colored intermediates from low-temperature photolysis of aryloxiranes which have been shown to be the related carbonyl ylides.[9]

Our results strongly suggest the intermediacy of azomethine ylide **6** formed by a cleavage of the aziridine C–C bond prior to the formation of enediimine **7**. The

(4) Conceivably a photoinduced process.

(5) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(6) The thermal cycloaddition of 2-phenyl-3-benzoylaziridine to dimethyl acetylenedicarboxylate has been reported by Padwa and Hamilton to give a pyrrole and a 2-pyrroline whose stereochemistry was believed to be trans: A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 4363 (1965).

(7) H. W. Heine, B. B. Smith, III, and J. D. Bower, *J. Org. Chem.*, **33**, 1097 (1968).

(8) (a) R. Huisgen, W. Scheer, and H. Hubert, *J. Amer. Chem. Soc.*, **89**, 1753 (1967); (b) R. Huisgen, W. Scheer, H. Mäder, and E. Brunn, *Angew. Chem., Int. Ed. Engl.*, **8**, 604 (1969). For other examples see: (c) A. Padwa and L. Hamilton, ref 3c and 6; (d) H. W. Heine and R. Peavy, *Tetrahedron Lett.*, 3123 (1965); (e) R. Huisgen, W. Scheer, G. Szeimies, and H. Hubert, *ibid.*, 397 (1966).

(9) T. DoMinh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970); D. R. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970).

(3) H. W. Heine and R. P. Hanzel, *J. Org. Chem.*, **34**, 171 (1969); (b) A. M. Trozzolo and T. DoMinh, unpublished results, see also adduct **11**; (c) A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, **4**, 118 (1967).

possibility of a triplet diradical was excluded by failure to detect an epr signal at 77°K from the colored intermediate. Two possible ylides, 6a and 6b, may be derived from 5. From the structure of 9, it seems reasonable to assign the cis structure 6a to the ylide ob-

6a   6b
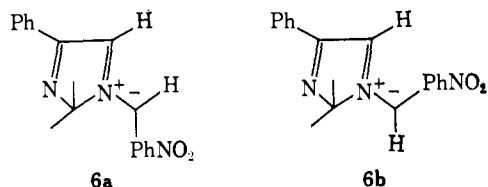
served.[10] Consequently, the photoinduced ring opening appears to involve a conrotatory motion which is allowed from the ground state[11] in contrast to a disrotation described by Huisgen and coworkers for a simpler aziridine–azomethine ylide system.[8a] Experiments are under way to investigate the possibility of a "hot" ground-state reaction analogous to the one suggested by Ullman and Henderson for the indenone–pyrylium oxide system.[12,13]

Acknowledgment. We are indebted to Professor H. W. Heine for stimulating discussions and a generous supply of the aziridine.

(10) It can be seen that 6 and 6a are only two of several resonance structures contributing to the ground state of the ylide.
(11) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(12) E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, **86**, 5050 (1966).
(13) We have also examined isomeric aziridines of type 1 and 2 whose ylides would be expected to be mirror images of each other. In agreement with the proposed mechanism, irradiation in ethanol glass at

Ar = Ph, PhNO₂(p)
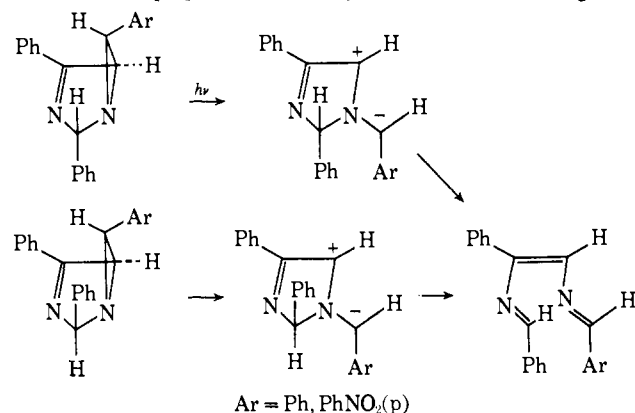
77°K was found to produce spectroscopically identical colored intermediates which on warming to room temperature gave the same enediimine. Irradiation of 5 in 2-methyltetrahydrofuran glass at 77°K gave a blue intermediate, which, upon warming, was converted to 6. The nature of this intermediate and its relation to the solid-state photochromism of 5 and related compounds will be discussed in a future report.

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d,l-Malabaricanediol. The First Cyclic Natural Product Derived from Squalene in a Nonenzymic Process

Sir:

Recently Chawla and Dev reported the isolation of the unique triterpene malabaricanediol (I).[1] The

II

I, R = R′ = H
III, R = R′ = TMS
V, R = Ac; R′ = H
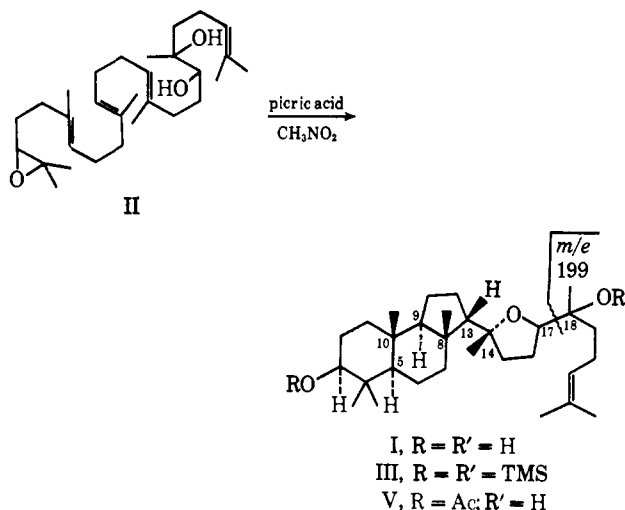
unusual perhydrocyclopenta[a]napthalene skeleton of I, although previously unknown among natural triterpenoids, had been observed in nonenzymic cyclizations of squalene 2,3-oxide by van Tamelen and coworkers at Stanford.[2] We now report that acid-catalyzed cyclization of the epoxydiol II produces *d,l*-malabaracanediol (I) in 7% yield. This is the first natural compound ever derived from nonenzymatic cyclization of a squalene derivative and the yield is remarkable if one considers that the molecule has nine asymmetric centers, six of which must be formed stereospecifically during the course of the cyclization. Picric acid was used for the first time as a cyclization catalyst and was found to have dramatic advantages over all previously employed acidic agents.

The required epoxydiol II was prepared from the intact squalene molecule. The synthetic sequence involves some novel new chemistry and chromatographic separations of squalene derivatives and is described elsewhere.[3] The diol function in II derives from trans hydration of a corresponding epoxide and thus has the erythro configuration. Assuming that the two sites of asymmetry in II have formed independently of one another, then there are equal amounts of the four possible stereoisomers, and only 50% of the material (*i.e.*, one pair of enantiomers) can lead to racemic I. The 7% yield was calculated using this correction.

Polyene epoxide cyclizations have to date been accomplished only with strong acid catalysts.[4] These strong acids (SnCl₄, BF₃ etherate, etc.) readily attack olefins and other functional groups as well as epoxides. In spite of numerous attempts at cyclization of diol epoxide II with these harsh catalysts, no trace of the desired natural product I was detected. Malabaricanediol I was found to cyclize further under the conditions employed. Clearly what was needed here was a protonic acid (Lewis acids can irreversibly tie up the diol) strong enough to protonate epoxides, but not double bonds. Weaker acids, however, are better nucleophiles and could interfere with cyclization. Picric acid, being of reasonable acidity and hopefully

(1) A. Chawla and S. Dev, *Tetrahedron Lett.*, 4837 (1967).
(2) E. E. van Tamelen, J. Willet, M. Schwartz, and R. Nadeau, *J. Amer. Chem. Soc.*, **88**, 5937 (1966).
(3) K. B. Sharpless, *Chem. Commum.*, in press.
(4) E. E. van Tamelen, *Accounts Chem. Res.*, **1**, 111 (1968);   W. S. Johnson, *ibid.*, **1**, 1 (1968).