# 1,3-Dipolar Cycloaddition Reactions of the Azomethine Ylide Derived from the 1,3-Diazabicyclo[3.1.0]hex-3-ene System[1]

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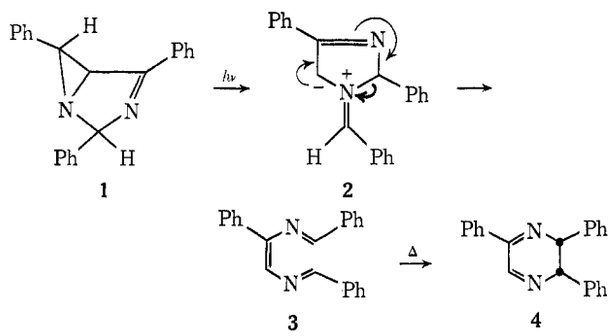
*endo*-2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene reacts stereospecifically with dimethyl maleate and dimethyl fumarate in refluxing xylene or on irradiation to give $\Delta^2$-pyrrolines as cycloadducts. The base-catalyzed epimerization of the various adducts supports the stereochemical structure assignments. A likely mechanism for these additions is the conversion of the diazabicyclo system into an azomethine ylide, which subsequently reacts with the unsaturated substrate. The photochemical results imply that the opening of the aziridine ring proceeds by a conrotatory motion in contrast to the disrotatory motion predicted from orbital symmetry considerations. Three possible explanations to account for these results are presented.

Cyclopropyl anions are predicted by Woodward and Hoffmann to open thermally to allyl anions by a conrotatory course.[3] To date, no clear-cut example of this electrocyclic process is known.[4] However, Huisgen and coworkers have recently established that the thermal ring cleavage of the isoelectronic aziridine system proceeds by conrotatory motion.[5] The azomethine ylide formed can undergo subsequent 1,3-dipolar cycloaddition with homo and hetero multiple bonds to give a variety of heterocyclic rings.[6-10] It has also been found that irradiation of aziridines[11-14] and oxiranes[15-17] frequently yields products derived from related 1,3-dipole intermediates. These reactions may be envisioned as electrocyclic processes proceeding by disrotatory ring opening.

As part of a broad program on the photochemical transformation of small ring heterocycles,[18] we recently described some characteristics of the 1,3-diazabicyclo-[3.1.0]hex-3-ene system.[19] The photoconversion of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**1**) into *cis*-2,3-dihydro-2,3,5-triphenylpyrazine (**4**) was formulated as proceeding *via* enediimine **3**, which thermally cyclized to *cis*-dihydropyrazine **4**.




1 2 3 4

The ring opening was suggested to proceed *via* the azomethine ylide **2**, formed by cleavage of the aziridine C–C bond.[20] One of the interesting features observed with this system is that azomethine ylide **2** could be trapped by 1,3-dipolar cycloaddition with an added dipolarophile prior to the formation of enediimine **3**.[14,21] Irradiation of a sample of **1** in an ethanol glass at liquid nitrogen temperature produced a bright red color which could be attributed to azomethine ylide **2**. Photolysis of **1** and dimethyl acetylenedicarboxylate at 77°K still gave the red color, but on warming it was rapidly discharged to give a single cycloadduct.[21] The structure of the adduct was assigned as (3*R**,7*R**,7a*S**)-dimethyl-7,7a-dihydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**6**). The stereochemical assignment rests on the magnitude of the coupling constants and their relationship to appropriate model systems[6,7,10,14] and was further supported by the facile oxidation of **6** with palladium on charcoal to **7**. The related *trans*-$\Delta^2$-pyrroline system is known to be markedly resistant to further oxidation.[7]

The formation of cycloadduct **6** presumably proceeds by way of a transient $\Delta^3$-pyrroline intermediate **5**, which undergoes a subsequent 1,3-suprafacial hydrogen shift.[22] It is particularly interesting to note that cycloadduct **6** is not the product expected on the basis of orbital symmetry considerations. Thermolysis of a solution of **1** and dimethyl acetylenedicarboxylate also resulted

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. XLV. For part XLIV, see A. Padwa, D. Dean, and J. Smolanoff, *Tetrahedron Lett.*, 4087 (1972).

(2) Alfred P. Sloan Foundation Fellow, 1968–1972; National Institute of Health Special Postdoctoral Fellow, 1972–1973.

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) For some attempts see R. Huisgen and P. Eberhard, *J. Amer. Chem. Soc.*, **94**, 1348 (1972).

(5) R. Huisgen, W. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967).

(6) H. W. Heine and R. Peavy, *Tetrahedron Lett.*, 3123 (1965); *J. Org. Chem.*, **31**, 3924 (1966); W. H. Heine and R. Henzel, *ibid.*, **34**, 171 (1969).

(7) A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 4363 (1965); *J. Heterocycl. Chem.*, **4**, 118 (1967); A. Padwa and W. Eisenhardt, *Chem. Commun.*, 380 (1968).

(8) R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Lett.*, 397 (1966); R. Huisgen, W. Scheer, and H. Mader, *Angew. Chem., Int. Ed. Engl.*, **8**, 602 (1969); **2**, 633, 644 (1963); R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, **100**, 1802 (1967); J. H. Hall and R. Huisgen, *Chem. Commun.*, 1187, 1188 (1971).

(9) J. W. Lown, G. Dallas, and T. W. Maloney, *Can. J. Chem.*, **47**, 3557, 4335 (1969); *Chem. Commun.*, 1543 (1968); 247 (1971); J. W. Lown, *Rec. Chem. Progr.*, **32**, 51 (1971).

(10) P. B. Woller and N. H. Cromwell, *J. Heterocycl. Chem.*, **5**, 579 (1968); *J. Org. Chem.*, **35**, 888 (1970).

(11) J. W. Lown and K. Matsumoto, *ibid.*, **36**, 1405 (1971).

(12) R. Huisgen and H. Mader, *Angew. Chem., Int. Ed. Engl.*, **8**, 604 (1969).

(13) S. Oida and E. Ohki, *Chem. Pharm. Bull.*, **16**, 764 (1968).

(14) T. DoMinh and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970); **94**, 4046 (1972).

(15) T. DoMinh, A. M. Trozzolo, and G. W. Griffin, *ibid.*, **92**, 1402 (1970).

(16) D. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970).

(17) H. Hamberger and R. Huisgen, *Chem. Commun.*, 1190 (1971); A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).

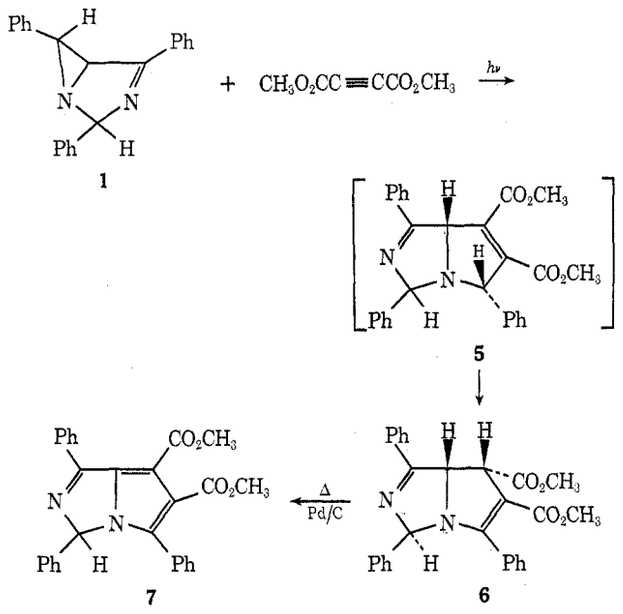
(18) For a review see A. Padwa, *Accounts Chem. Res.* **4**, 48 (1971).

(19) A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970); A. Padwa and E. Glazer, *Chem. Commun.*, 838 (1971).

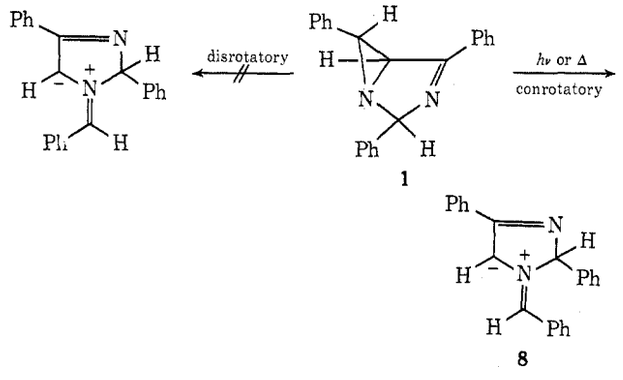
(20) For a review on C–C bond cleavage of the aziridine ring, see H. Heine in "Mechanism of Molecular Migrations," Vol. III, B. S. Thyagarajan, Ed., Interscience New York, N. Y., 1971, p 145.

(21) A. Padwa and E. Glazer, *J. Amer. Chem. Soc.*, **94**, 7788 (1972).

(22) Similar results have been reported by Trozzolo and DoMinh with the related 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene system.[14] As was pointed out by these authors, the conversion of **5** to **6** may be a photoinduced process.



in the formation of the same product. From the structure of the cycloadduct **6**, it seems reasonable to assign the cis structure **8** to the azomethine ylide obtained

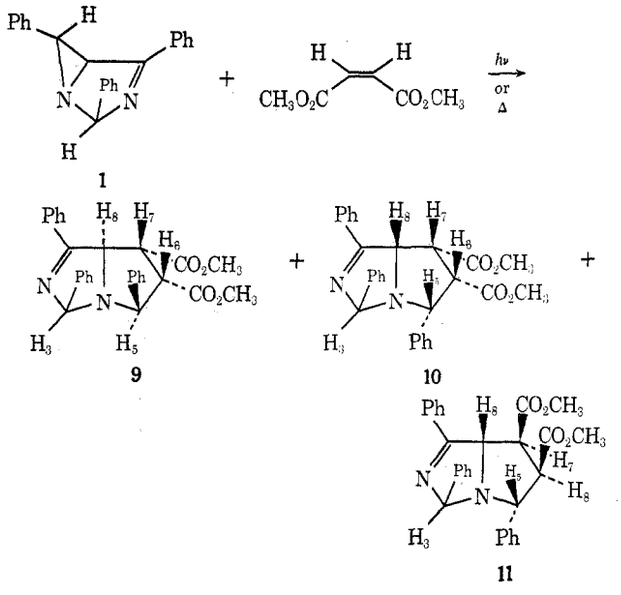


from both the thermolysis and photolysis of **1**.[23] Consequently, the photoinduced ring opening of **1** appears to proceed *via* a conrotatory opening, which is in direct contrast with the results described by Huisgen and coworkers.[5] In this paper we describe some additional experiments which confirm the photochemically disallowed valence tautomerization of **1** to **8** and offer a possible rationalization for its behavior.

Irradiation of a nitrogen-purged solution of *endo*-2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene and dimethyl maleate in benzene for 3.5 hr afforded a mixture of three cycloadducts, **9** (mp 221–222°, 9%), **10** (mp 172–173°, 9%), and **11** (mp 158–159°, 51%). Dimethyl maleate was also found to react with diazabicyclohexene **1** in refluxing xylene to produce the same three cycloadducts in the same relative yields.

The thermally induced ring opening of **1** to *cis*-azomethine ylide **8** can be assumed to occur according to the selection rules.[5] Huisgen and coworkers have convincingly demonstrated that the stereochemistry about the olefinic dipolarophile is always retained in

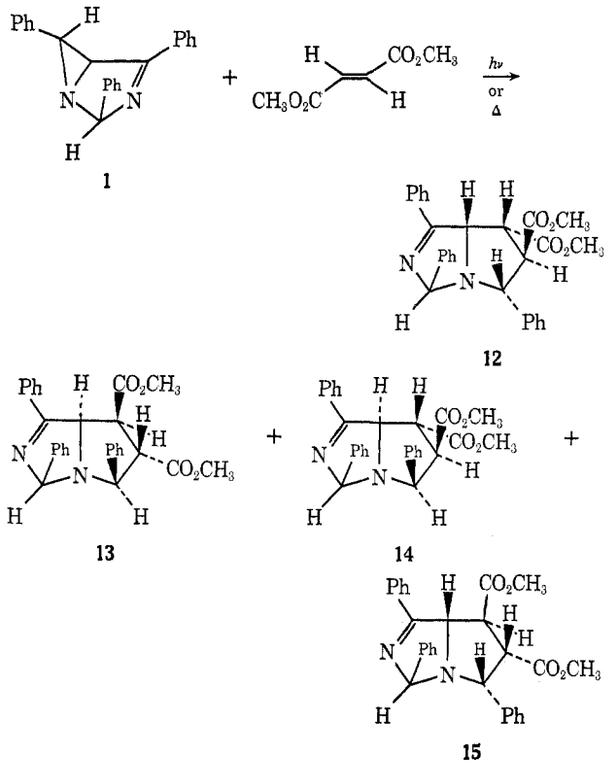
(23) We have examined the photocycloaddition of dimethyl acetylenedicarboxylate with both *exo*- and *endo*-2,4,6-triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene. Both photocycloadditions were found to produce the same cycloadduct (*i.e.*, **6**). This observation is consistent with the intermediacy of cis ylide **8**, which is subsequently trapped by attack of the dipolarophile from the less hindered side.



1,3-dipolar cycloadditions.[24] The three cycloadducts obtained can be attributed to the two possible orientation complexes for concerted cycloaddition of the azomethine ylide **8** to the dipolarophile. The assignment of configuration for adducts **9–11** rests on their characteristic nmr spectra (see Experimental Section). The most useful criterion for assigning configurations is that the ester methyl signal moves to higher fields when it is adjacent to a *cis*-phenyl ring. The appearance of a carbomethoxy signal at $\tau$ 6.82 in adduct **10** is consistent with this principle. Protons $H_5$ and $H_8$ in the various maleate adducts are cis to each other by virtue of the concerted cycloaddition. Assuming retention of dipolarophile stereochemistry, it follows that protons $H_6$ and $H_7$ must also be in a cis configuration. This reasoning suggests that all the protons are cis to one another in adduct **10**. The location of a carbomethoxy group at $\tau$ 6.76 in adduct **11** is also consistent with the stereochemical assignment. The configuration at $C_5$ in adducts **10** and **11** was shown to be the same but opposite to that of adduct **9**. This was demonstrated by some base-catalyzed epimerization experiments which will be discussed at a later point. The remaining adduct is assigned as pyrrolidine **9**. The splitting patterns observed with adducts **9–11** are in accord with first-order coupling patterns. The conformational mobility of the pyrrolidine ring however, deprives the coupling constants of their diagnostic value; trans couplings can reach larger values than are found for cis vicinal ring protons. For example, the trans coupling constant in adducts **9** and **11** for protons $H_7$ and $H_8$ has a value of 3.0 and 6.5 Hz, while the trans coupling constant for protons $H_5$ and $H_6$ is 10.0 Hz. The cis coupling constants ($J_{5,6}$ and $J_{7,8}$) for adduct **10** were found to be 6.0 Hz. A similar lack of consistency in the magnitude of the couplings was also found with the corresponding fumarate adducts (see below). These contradictions were not totally unexpected. The difficulties encountered in making assignments in the pyrrolidine ring based on the magnitude of the coupling constants was pointed out earlier by Huisgen and coworkers.[8]

(24) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633, 637 (1963).

When the irradiation of diazabicyclohexene **1** was carried out with dimethyl fumarate, a mixture of four isomeric cycloadducts **12** (mp 147–149°, 27%), **13** (oil,



13%), **14** (mp 196–197°, 27%), and **15** (mp 137–139°, 13%) was obtained. The thermal reaction of **1** with dimethyl fumarate also gave the same four isomeric adducts.

The stereochemical assignments for adducts **12–15** were based on the same considerations used in the dimethyl maleate system. In line with the previous discussion, thermal cycloaddition of dimethyl fumarate with *cis*-azomethine ylide **8** should result in protons $H_5$ and $H_8$ being cis to one another in each of the four adducts. The appearance of a carbomethoxy signal at relatively high field in adducts **14** and **15** is consistent with the vicinal shielding effect of the neighboring *cis*-phenyl ring. Protons $H_6$ and $H_7$ can be fixed as being trans in adducts **12–15** if one assumes retention of stereochemistry about the dipolarophile. As was noted previously, the vast spread of the vicinal coupling constants deprives them of their diagnostic value.

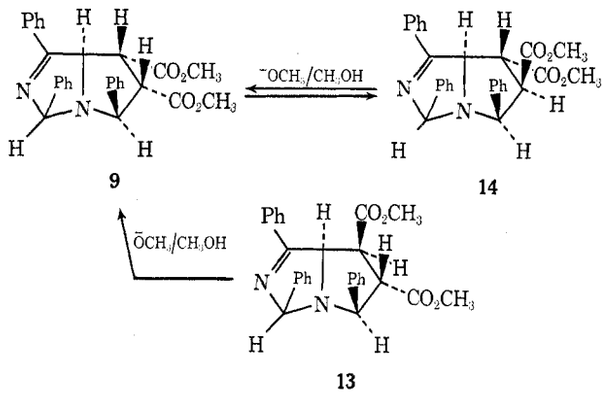
Additional information which supports the stereochemical assignments was obtained from some base-catalyzed epimerization experiments. Schemes I and II summarize the results obtained.

Fumarate adduct **13** was found to isomerize to maleate adduct **9** which, in turn, is in equilibrium with fumarate adduct **14**. Treatment of adducts **10**, **11**, or **15** with base results in the exclusive formation of adduct **12**.[25] These experiments clearly establish that compounds **9**, **13**, and **14** have configurations at $C_5$ and $C_8$ which are different from those of **10**, **11**, **12**, and **15**.

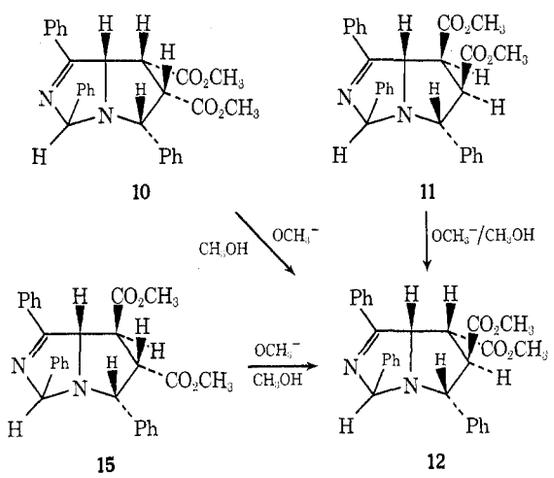
In an attempt to further interrelate the fumarate and maleate adducts, these compounds were heated in the presence of an oxidizing agent. Thus oxidation of maleate adduct **11** with palladium on charcoal in boiling

(25) The fact that adduct **12** is stable to further epimerization provides additional support for its stereochemical assignment.

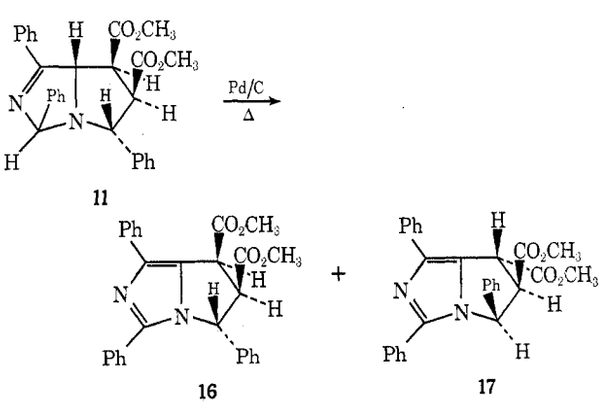
SCHEME I



SCHEME II



benzene produced a mixture of (5*R**,6*R**,7*S**)- (**16**, 78%) and (5*R**,6*S**,7*S**)-dimethyl-5,6,7-trihydro-1,3,5-triphenylpyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**17**, 16%). The structure and stereochemistry of compounds **16** and **17** were assigned on the basis of nmr



spectroscopy. The appearance of a carbomethoxy absorption in **17** at high field relative to **16** is compatible with the vicinal shielding effect of the neighboring *cis*-phenyl ring. The failure of both **16** and **17** to undergo further oxidation, even under more forcing conditions, is indicative of the extremely stable nature of the imidazole ring present in these systems. The fact that compound **17** is also formed in the oxidation of **11** suggests that epimerization occurs during the course of the reaction. This suggestion is supported by the

observation that **16** is stable under the reaction conditions. Furthermore, oxidation of adduct **14** also results in a mixture of **16** and **17** (1:5). As a result of the oxidative epimerization, we are not able to use this procedure for elucidating the stereochemistry of the various cycloadducts.

All of the aforementioned reactions of diazabicyclohexene **1** with the activated dipolarophiles conform to the concept of 1,3-dipolar cycloaddition as proposed by Huisgen and coworkers.[26] The thermal ring cleavage of **1** involves stereospecific, conrotatory ring opening.[27] Our results, as well as those of DoMinh and Trozzolo,[14] on the photochemically induced 1,3-dipolar cycloaddition of **1** imply a conrotatory motion in contrast to the disrotatory motion described by Huisgen and coworkers for the simpler aziridine–azomethine ylide system.[5] The mechanism for formation of *cis*-azomethine ylide **8** from the irradiation of **1** remains an intriguing puzzle. One possibility to account for these results is that electron demotion in **1** occurs prior to molecular change and leads to an electronically unexcited but vibrationally excited molecule which ring opens by the equivalent of a pyrolytic process. This would be analogous to the "hot" ground-state reaction suggested by Ullman and Henderson for the indenone–pyrylium oxide system.[28] An alternate explanation involves the excited state of **1** undergoing a disrotatory ring opening to give a *trans*-azomethine ylide in its excited state. The electronically excited trans ylide may isomerize to ground-state cis ylide **8**, or react with the dipolarophile by a photochemically allowed $_4\pi_a + _2\pi_s$ process. This type of cycloaddition will give cycloadducts whose stereochemistry are equivalent to those produced from the thermal cycloaddition of yilde **8**. Reaction from an electronically excited state manifold of product has been suggested to occur in the photodeprotonation of phenols[29] and in the photoenolization of *o*-methylbenzophenone[30] and provides reasonable chemical precedent for the above suggestion. Still another possibility is that the photoinduced ring opening of **1** is not controlled by orbital symmetry factors but rather involves reaction of the thermodynamically more stable azomethine ylide.[31] This is not unreasonable, since, in this system, the three-membered ring is incorporated in a fused ring system where strain is relieved on bond heterolysis. The resulting 1,3 dipole will be more stable, relative to starting material, than the analogous acyclic system. Consequently, the passage of **1** to **8** will be significantly assisted by relief of ring strain and may proceed by a nonconcerted path. This possibility may be considered to be analogous to the thermally disallowed valence tautomerism of 6-cyclohexylimino-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirene to an isoquinolinium imine[32] and also to the tautomerization of 2,3-diphenylindenone oxide into the corresponding benzopyrylium 4-oxide.[33] The available data do not decisively distinguish among the three possibilities.

(26) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968), and leading references.

(27) The thermal cycloaddition of 1,3-diazabicyclo[3.1.0]hex-3-enes to activated dipolarophiles was first reported by Heine and coworkers: H. Heine, A. B. Smith, and J. D. Bowers, *ibid.*, **33**, 1097 (1968). These authors did not report on the direction of ring opening.

(28) E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, **86**, 5050 (1964).

(29) A. Weller, *Progr. React. Kinet.*, **1**, 199 (1961).

(30) E. F. Ullman, *Accounts Chem. Res.*, **1**, 353 (1968).

(31) See W. T. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969), for criticism of the applicability of the Woodward–Hoffmann rules in photochemical reactions.

(32) J. W. Lown and K. Matsumoto, *Chem. Commun.*, 692 (1970).

(33) E. F. Ullman and J. E. Milks, *J. Amer. Chem. Soc.*, **86**, 3814 (1964).

## Experimental Section[34]

**Irradiation of *endo*- and *exo*-2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene with Dimethyl Acetylenedicarboxylate.**—A solution containing 300 mg of diazabicyclohexene **1** and 140 mg of dimethyl acetylenedicarboxylate in 60 ml of benzene was irradiated with a 450-W Hanovia mercury lamp for 2.5 hr. Removal of the solvent at 50° under reduced pressure gave a dark oil whose nmr spectrum indicated the complete absence of 2,3-dihydro-2,3,5-triphenylpyrazine (**4**). Recrystallization of the oil from 95% ethanol gave (3*R**,7*R**,7a*S**)-dimethyl-7,7a-dihydro-1,3,5-triphenyl-3-*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**6**) as a white, crystalline solid (72%): mp 123–124°; ir (KBr) 5.80, 6.15, 6.95, 7.95, 10.60, 12.30, 13.40, 14.10, 14.40 $\mu$; uv (95% ethanol) 240 nm ($\epsilon$ 19,000); nmr (100 MHz, pyridine-$d_5$) $\tau$ 6.62 (3 H, s), 6.58 (3 H, s), 4.54 (d, 1 H, $J$ = 4.0 Hz), 3.80 (d, 1 H, $J$ = 4.0 Hz), 3.62 (t, 1 H, $J$ = 4.0 Hz), 1.96–3.02 (m, 15 H); mass spectrum *m/e* 452 ($M^+$), 450, 391, 285, 105, and 104 (base).

*Anal.* Calcd for $C_{28}H_{24}O_4N_2$: C, 74.32; H, 5.35; N, 6.19. Found: C, 73.94; H, 5.12; N, 6.15.

**Dimethyl-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (7).**—A solution of 100 mg of photoadduct **6** in 50 ml of benzene was refluxed over palladium on charcoal for 1 hr. The catalyst was removed by filtration and the solution was concentrated under reduced pressure to give 65 mg (68%) of dimethyl-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**7**) as a yellow solid: mp 151–152°; ir (KBr) 5.90, 6.35, 6.50, 6.98, 7.20, 7.88, 8.35, 8.90, 9.12, 12.00 and 13.24 $\mu$; uv (95% ethanol) 265, 290, and 378 nm ($\epsilon$ 17,350, 14,000, 15,300); nmr ($CDCl_3$, 100 MHz) singlets at $\tau$ 6.32 (3 H), 6.16 (3 H), and 3.80 (1 H), and a multiplet at 2.92–2.16 (15 H); mass spectrum *m/e* 450 ($M^+$), 391 (base), 105, and 77.

*Anal.* Calcd for $C_{28}H_{22}O_5N_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.47; H, 5.12; N, 6.26.

**Thermal and Photochemical Cycloaddition of *endo*-2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene with Dimethyl Maleate.**—A solution containing 620 mg of endo aziridine **1** and 288 mg of dimethyl maleate in 50 ml of xylene was heated at reflux for 3 days. Removal of the solvent *in vacuo* gave a crude solid which showed a complex mixture of carbomethoxy adducts in the nmr. The mixture was separated by scanning liquid–liquid partition chromatography.[35] The optical density trace showed three peaks. The first peak contained 20 mg (2%) of 2,3,5-triphenylpyrazine, mp 152–153°. The second peak contained 170 mg (19%) of a crude solid that proved to be a two-component mixture (ratio 1:1). The mixture could be separated by fractional crystallization from ethanol and the more insoluble component was a white, crystalline solid whose structure is assigned as (3*R**,5*S**,6*S**,7*R**,7a*R**)-dimethyl-5,6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**9**): mp 221–222°; ir (KBr) 5.82, 6.15, 6.95, 7.25, 7.92, 8.22, 8.90, 9.46, 9.65, 11.32, 12.96, and 14.40 $\mu$; uv (95% ethanol) 247 nm ($\epsilon$ 17,300); nmr ($CDCl_3$, 100 MHz) $\tau$ 6.44 (5 H), 6.24 (s, 3 H), 5.00 (d, 1 H, $J$ = 10.0 Hz), 4.68 (dd, 1 H, $J$ = 5.0 and 3.0 Hz), 4.36 (d, 1 H, $J$ = 5.0 Hz), 3.36–2.16 (m, 15 H); mass spectrum *m/e* 454 ($M^+$), 351, 292, 260, 193, and 174 (base).

*Anal.* Calcd for $C_{28}H_{26}O_4N_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.83; H, 5.69; N, 6.12.

The second and less soluble component of the mixture was a white solid, mp 172–173°, whose structure is assigned as (3*R**,5*R**,6*S**,7*R**,7a*S**)-dimethyl-5,6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**10**): ir (KBr) 5.75, 6.90–7.00, 8.29, 8.50, 9.08, 10.28, 10.82, 13.30, and 14.38 $\mu$; uv (95% ethanol) 245 nm ($\epsilon$ 15,100); nmr ($CDCl_3$, 100 MHz) $\tau$ 6.82 (4 H), 6.38 (4 H), 5.72 (d, 1 H, $J$ = 6.0 Hz),

(34) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavia Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with a Varian Associates high-resolution spectrometer and at 100 MHz using a Jeolco-MH-100 spectrometer.

(35) A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 102 (1967).

4.44 (dd, 1 H, $J$ = 6.0 and 3.0 Hz), 4.26 (d, 1 H, $J$ = 3.0 Hz), 3.34–1.96 (m, 15 H); mass spectrum $m/e$ 454 ($M^+$), 351, 292, 193, 189, and 174 (base).

*Anal.* Calcd for $C_{28}H_{26}O_4N_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.65; H, 5.89; N, 6.06.

The third and largest peak present in the liquid–liquid partition chromatogram amounted to 462 mg (51%) of a white solid, mp 158–159°, whose structure is assigned as (3*R**,5*R**,6*R**,7*S**,7a*S**)-dimethyl-5,6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]-imidazole-6,7-dicarboxylate (**11**): ir (KBr) 5.80, 6.98, 8.30, 9.48, 9.90, 13.35, and 14.40 $\mu$; uv (95% ethanol) 247 nm ($\epsilon$ 16,700); nmr ($CDCl_3$, 100 MHz) $\tau$ 6.76 (s, 3 H), 6.46 (4 H), 6.20 (t, 1 H, $J$ = 6.5 Hz), 5.16 (d, 1 H, $J$ = 10.0 Hz), 4.60 (dd, 1 H, $J$ = 6.5 and 5.0 Hz), 3.94 (d, 1 H, $J$ = 5.0 Hz), and 2.04–2.96 (m, 15 H); mass spectrum $m/e$ 454 ($M^+$), 452, 393, 311, 310 (base), 309, 193, and 174.

*Anal.* Calcd for $C_{28}H_{26}O_4N_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.27; H, 5.65; N, 6.23.

When the irradiation of *endo*-aziridine **1** (972 mg) and dimethyl maleate (120 mg) was carried out in 180 ml of benzene for 3.5 hr the same three adducts were isolated from the liquid–liquid partition chromatogram. There were no detectable signs of any other isomers.

**Thermal and Photochemical Cycloaddition of *endo*-2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene with Dimethyl Fumarate.**—A solution containing 620 mg of the *endo*-diazabicycloaziridine **1** and 288 mg of dimethyl fumarate in 50 ml of xylene was heated at reflux for 3 days. Removal of the solvent *in vacuo* left a crude oil whose nmr spectrum indicated the existence of a complex mixture of carbomethoxy adducts. The mixture was subjected to scanning liquid–liquid partition chromatography and the optical density trace consisted of three peaks. The first peak contained 350 mg (39%) of a white solid whose nmr spectrum indicated it to be a mixture of two carbomethoxy adducts (ratio 2:1). The major component of the mixture was obtained by fractional crystallization from 95% ethanol. This material was assigned as (3*R**,5*R**,6*R**,7*R**,7a*S**)-dimethyl-5,-6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,-7-dicarboxylate (**12**): mp 147–149°; ir (KBr) 5.80, 6.18, 6.95, 7.30, 7.88, 8.30, 9.12, 9.78, 10.89, 13.08, 13.42, and 14.50 $\mu$; uv (95% ethanol) 244 nm ($\epsilon$ 15,600); nmr ($CDCl_3$, 100 MHz) $\tau$ 6.50 (5 H), 6.34 (s, 3 H), 5.84 (d, 1 H, $J$ = 10.0 Hz), 4.74 (dd, 1 H, $J$ = 6.0 and 3.0 Hz), 4.10 (d, 1 H, $J$ = 3.0 Hz), and 2.04–2.96 (m, 15 H); mass spectrum $m/e$ 454 ($M^+$), 452, 393, 351, 310, 292, 193, and 174 (base).

*Anal.* Calcd for $C_{28}H_{26}O_4N_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.91; H, 5.71; N, 6.10.

The minor component of the mixture could not be cleanly separated from **12** but was characterized as (3*R**,5*S**,-6*S**,7*S**,7a*R**)-dimethyl-5,6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**13**) by its nmr spectrum ($CDCl_3$), which showed peaks at $\tau$ 6.28 (4 H), 6.32 (4 H), 5.08 (d, 1 H, $J$ = 8.0 Hz), 4.74 (m, 1 H), 4.18 (d, 1 H, $J$ = 4.0 Hz), and 2.2–3.1 (m, 15 H).

The second peak in the liquid–liquid partition chromatogram amounted to 360 mg (40%) of a solid whose nmr revealed it to be a two-component mixture of carbomethoxy adducts (ratio 2:1). The mixture was separated by fractional crystallization from 95% ethanol and the major component, mp 196–197°, was assigned as (3*R**,5*S**,6*R**,7*R**,7a*R**)-dimethyl-5,6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**14**): ir (KBr) 5.80, 6.90, 7.00, 7.25, 8.52, 8.98, 9.70, 10.68, 10.93, 12.97, 13.00, 14.35, and 14.50 $\mu$; uv (95% ethanol) 247 nm ($\epsilon$ 16,100); nmr ($CDCl_3$, 100 MHz) $\tau$ 7.04 (3 H, s), 6.40 (3 H, s), 6.20 (m, 2 H), 5.24 (d, 1 H, $J$ = 10.0 Hz), 4.60 (dd, 1 H, $J$ = 9.0 and 5.0 Hz), 4.34 (d, 1 H, $J$ = 5.0 Hz), 2.1–3.4 (m, 15 H); mass spectrum $m/e$ 454 ($M^+$), 452, 351, 310, 309, 292, 233, 230, 206, and 193 (base).

*Anal.* Calcd for $C_{28}H_{26}O_4N_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.97; H, 5.90; N, 6.16.

The minor component from the second peak in the chromatogram was recrystallized from cyclohexane, mp 137–139°, and was assigned as (3*R**,5*R**,6*S**,7*S**,7a*S**)-dimethyl-5,6,7,7a-tetrahydro-1,3,5-triphenyl-3*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**15**): ir (KBr) 5.80, 6.17, 6.90, 7.92, 8.15, 8.38, 8.52, 9.72, 13.12, and 14.36 $\mu$; uv (95% ethanol) 247 nm ($\epsilon$ 15,800); nmr ($CDCl_3$, 100 MHz) $\tau$ 7.00 (s, 3 H), 6.86 (s, 3 H), 6.30 (m, 2 H), 5.14 (d, 1 H, $J$ = 7.0 Hz), 4.42 (dd, 1 H, $J$ = 8.0 and 4.0 Hz), 4.10 (d, 1 H, $J$ = 4.0 Hz), 2.0–3.1 (m, 15 H): mass spectrum $m/e$ 454 ($M^+$), 452, 393, 311, 310 (base), 309, 293, 233, 206, 193, and 174.

The third and smallest peak isolated from the liquid–liquid chromatogram contained 20 mg (2%) of a solid whose nmr spectrum showed it to be a mixture of oxidation products. These products were identical with those obtained from the palladium/charcoal oxidation of the dimethyl fumarate adducts (see below).

When the irradiation of *endo*-diazabicyclic aziridine **1** (1.89 g) and 140 mg of dimethyl fumarate was carried out in 300 ml of benzene for 3.5 hr, the same four adducts were isolated from the liquid–liquid partition chromatogram. There were no detectable quantities (*i.e.*, less than 3%) of any other isomers present in the chromatogram.

**Base-Catalyzed Epimerization of the Dimethyl Maleate and Dimethyl Fumarate Adducts.**—A representative example consists of stirring a solution containing 60 mg of the adducts with 25 mg of sodium methoxide in 25 ml of methanol at 55° for 4.5 hr. The mixture was diluted with 1.0 ml of water and the solvent was removed under reduced pressure. The residue was taken up in chloroform, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a residue which was examined by nmr spectroscopy. In this way the following results were obtained.

| Starting isomer | Epimerized product | Starting isomer | Epimerized product |
|---|---|---|---|
| **9** | **14** | **10** | **12** |
| **13** | **9** and **14** | **11** | **12** |
| **14** | **9** | **15** | **12** |

**Oxidation of the Dimethyl Maleate and Fumarate Adducts.**—A solution containing 150 mg of the dimethyl maleate adduct **11** and excess palladium on charcoal was refluxed in 25 ml of benzene for 24 hr. Filtration of the catalyst followed by removal of the solvent under reduced pressure gave 142 mg (95%) of a white solid whose nmr spectrum indicated it to be a two-component mixture (ratio 4:1). The major product was purified by fractional crystallization from 95% ethanol, mp 193–195°, and was assigned as (5*R**,6*R**,7*S**)-dimethyl-5,6,7-trihydro-1,3,5-triphenylpyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**16**): ir (KBr) 5.85, 7.00, 7.56, 8.02, 8.25, 8.38, 9.58, 9.75, 13.05, 13.90, 14.25, and 14.60 $\mu$; uv (95% ethanol) 274 nm ($\epsilon$ 21,700); nmr ($CDCl_3$, 100 MHz) $\tau$ 6.30 (6 H, s), 6.00 (t, 1 H, $J$ = 8.0 Hz), 5.28 (d, 1 H, $J$ = 8.0 Hz), 3.88 (d, 1 H, $J$ = 8.0 Hz), 2.0–3.2 (m, 15 H); mass spectrum $m/e$ 452 ($M^+$), 394, 393 (base), and 230.

*Anal.* Calcd for $C_{28}H_{24}O_4N_2$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.23; H, 5.34; N, 6.17.

The minor isomer obtained from the mixture was recrystallized from 95% ethanol, mp 181–183°, and was assigned as (5*R**,6*S**,-7*S**)-dimethyl-5,6,7-trihydro-1,3,5-triphenylpyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**17**): ir (KBr) 5.85, 6.90, 7.00, 7.88, 8.05, 8.27, 9.28, 9.85, 12.85, 14.10, and 14.45 $\mu$; uv (95% ethanol) 274 nm ($\epsilon$ 21,500); nmr ($CDCl_3$, 100 MHz) $\tau$ 6.54 (s, 3 H), 6.26 (s, 3 H), 5.88 (t, 1 H, $J$ = 3.0 Hz), 5.36 (d, 1 H, $J$ = 3.0 Hz), 4.00 (d, 1 H, $J$ = 3.0 Hz), 1.9–3.0 (m, 15 H); mass spectrum $m/e$ 452 ($M^+$ and base), 393, 333, 231, 230, and 77.

*Anal.* Calcd for $C_{28}H_{24}O_4N_2$: C, 74.32; H, 5.35; N, 6.19. Found: C, 73.92; H, 5.43; N, 6.18.

The dimethyl fumarate adduct **14** was also oxidized by a similar procedure. A solution containing 150 mg of the dimethyl fumarate adduct **14** and excess palladium on charcoal in 25 ml of benzene was heated at reflux for 60 hr. Filtration of the catalyst and removal of the solvent under reduced pressure gave 132 mg (89%) of a white solid whose nmr spectrum revealed it to be a mixture of two oxidation products (ratio 5:1). The major component was shown to be isomer **17** while the minor component was identified as **16**.

**Registry No.**—**6**, 36476-66-1; **7**, 36476-67-2; **9**, 36476-68-3; **10**, 36476-69-4; **11**, 36476-70-7; **12**, 36476-71-8; **13**, 36476-72-9; **14**, 36476-73-0; **15**, 36476-74-1; **16**, 36476-75-2; **17**, 36476-76-3; 2,3,5-triphenylpyrazine, 36476-77-4.

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