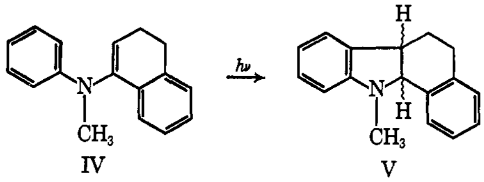
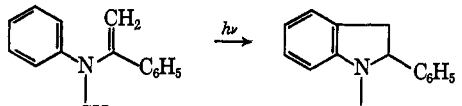
Similar irradiation of the enamine IV derived from N-methylaniline and 1-tetralone gave two isomers of V[12] in a combined isolated yield of 60%. The same two stereoisomers are obtained by reduction of the corresponding indole.



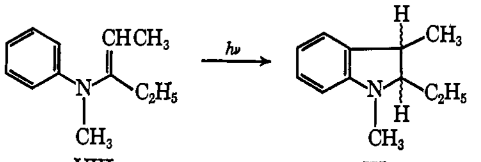
IV V

The cyclization is not limited to enamines derived from cyclic ketones. Irradiation of α-(N-methylanilino)styrene (VI) gives VII[13] in 66% isolated yield, and irradiation of a mixture of *cis* and *trans* isomers of



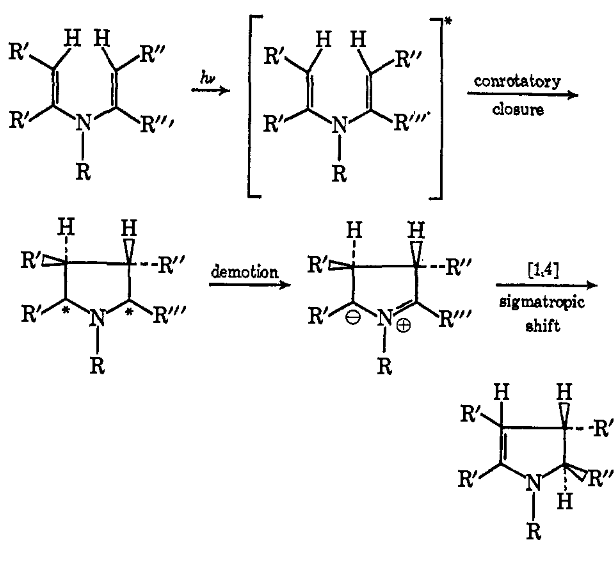
VI VII

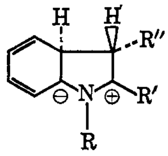
VIII gives two stereoisomers of IX (43%).[14] Reduction of 1,3-dimethyl-2-ethylindole gives the same two isomers of IX.



VIII IX

The cyclizations illustrated above may be considered as an electrocyclic reaction of divinylamines which, if it is a photochemical process, should occur in a conrotatory manner.[15-19] Election demotion should then produce a dipolar species[20] which can undergo a thermal, suprafacial [1,4] sigmatropic shift of a hydrogen atom giving the *trans*-2,3-disubstituted product.[16,21,22]





If this is the path by which the *trans* products are formed, it is not clear how the *cis* products are formed. Deuterium labeling experiments with 1-(N-methyl-2,4,6-trideuterioanilino)cyclohexene showed that at least the major portion of the hydrogen transfer is intramolecular. Satisfactory quantitative data are difficult to obtain because both starting material and product fragment even at low ionizing potential.

Irradiation of the N-aryl enamines cited above in the presence of oxygen or iodine, conditions known to favor oxidative cyclization,[1] gives small amounts of the corresponding indoles, but the 2,3-dihydroindoles are still the major products.

Acknowledgment. This research was supported by Grant G-6740 from the National Science Foundation.

---

[12] Va: mp 135–136°; mol wt 235 (mass spectrometry); aromatic protons (δ 6.1–7.2, m, 8 H), methine protons (δ 4.29, d, 1 H; δ 3.35–3.75, m, 1 H), methylene protons (δ 2.5–2.8, m, 2 H; δ 1.7–2.1, m, 2 H), N-methyl protons (δ 2.57, s, 3 H); $\lambda_{max}^{95\%\ EtOH}$ 257 (ε 9720), 302 mμ (ε 2910); 13.27, 13.50 μ; Vb: liquid; mol wt 235 (mass spectrometry); aromatic protons (δ 6.4–7.4, m, 8 H), methine proton (δ 3.52, d, 1 H), N-methyl protons (δ 2.85, s, 3 H), methylene and methine protons (δ 1.5–3.0, m, 5 H); 13.3 (sh) and 13.5 μ.

[13] VII: mp 94–95°; mol wt 209 (mass spectrometry); aromatic protons (δ 6.2–7.5, m, 9 H), methine proton (δ 4.1–4.5, q, 1 H), methylene protons (δ 2.7–3.5, m, 2 H), N-methyl protons (δ 2.57, s, 3 H); $\lambda_{max}^{95\%\ EtOH}$ 252 (ε 8960), 297 mμ (ε 2870); 13.06, 13.33, 13.47, 14.02, and 14.25 μ.

[14] IXa: liquid; mol wt 175 (mass spectrometry); aromatic protons (δ 6.2–7.1, m, 4 H), methine protons (δ 2.8–3.3, m, 2 H), N-methyl protons (δ 2.64, s, 3 H), methylene protons (δ 1.4–1.9, m, 2 H), C-methyl protons (δ 1.07, d, 3 H; δ 1.0, t, 3 H); 13.31 and 13.60 μ; IXb: liquid; mol wt 175 (mass spectrometry); aromatic protons (δ 6.2–7.0, m, 4 H), methine protons (δ 2.7–3.0, m, 2 H), N-methyl protons (δ 2.68, s, 3 H), methylene protons (δ 1.4–1.9, m, 2 H), C-methyl protons (δ 1.30, d, 3 H; δ 0.98, t, 3 H); 13.38 and 13.72 μ.

[15] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965).

[16] R. Hoffmann and R. B. Woodward, *Accounts Chem. Research*, 1, 17 (1968); R. B. Woodward, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, pp 217–249.

[17] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 87, 2045 (1965).

[18] K. Fukui, *Tetrahedron Lett.*, 2009 (1965).

[19] H. E. Zimmerman, *J. Amer. Chem. Soc.*, 88, 1564, 1566 (1966).

[20] An intermediate has been detected in the oxidative cyclization of N-substituted diphenylamines to N-substituted carbazoles which has been assigned a dipolar structure.[3a]

[21] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 2511 (1965).

[22] In the dihydroindole system the hydrogen shift could also be considered a [1,8] sigmatropic shift. The thermal reaction in this case should also be suprafacial. Antarafacial shifts are excluded by the ring system.

O. L. Chapman, G. L. Eian
Department of Chemistry
Iowa State University, Ames, Iowa 50010

Received July 15, 1968

Diels–Alder Reactions of Diazadienes and Chemistry of the Adducts

Sir:

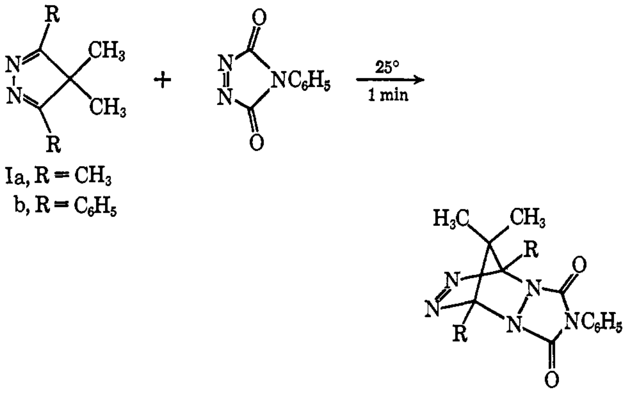
Despite the wealth of mechanistic and synthetic information on the Diels–Alder reaction, little is known about the behavior of heterodienes in this reaction. This communication describes our results with 2,3-diazadienes which are reactive four-electron components and yield interesting and otherwise inaccessible products.

Cyclic azines such as the isopyrazoles Ia and Ib[1]

---

[1] Prepared by Mrs. V. Abraitys of these laboratories by reaction of the corresponding 1,3-dione with hydrazine according to the method of I. I. Grandberg, A. P. Krasnoshchek, A. N. Kost, and G. K. Faizova, *J. Gen. Chem. USSR*, 33, 2521 (1963). The compound Ia was reported; Ib is a new composition.

react rapidly at room temperature with 4-phenyl-1,2,4-triazoline-3,5-dione[2] to give the Diels–Alder adducts, IIa and IIb, in quantitative yield.[3] The structures of



Ia, R = CH_3
b, R = C_6H_5

IIa, R = CH_3
b, R = C_6H_5

the adducts were established by ir, uv, and nmr spectroscopy and by mass spectral and elemental analyses.[4] The adduct IIa is a light yellow, crystalline compound: mp 147–149.5° dec; mass spectrum (70 eV at 50°), *m/e* 299 (0), 271 (4), 256 (100); λ_{max}^{hex} 397 mμ (ϵ 542); nmr ($CDCl_3$), δ 0.53 (s, 3 H), 1.07 (s, 3 H), 2.18 (s, 6 H), 7.4 (s, 5 H). Compound IIb is similarly light yellow crystals: mp 123° dec; $\lambda_{max}^{CH_3CN}$ 400 mμ (ϵ 562); nmr ($CDCl_3$), δ 0.33 (s, 3 H), 1.18 (s, 3 H), 7.1–8.1 (m, 15 H).[5] The 2,3,5,6-tetraazabicyclo[2.2.1] ring system present in IIa and IIb has not been previously reported.

The thermal and photochemical decompositions of IIa and IIb have been examined. The mechanism by which cyclic azo compounds decompose is a subject of intense current interest[6] and, in this case, the decomposition products are also novel.

Heating a solution of IIa in chlorobenzene at 120° for 20 min affords the olefin III in 70–80% yield. A pure sample obtained by sublimation consisted of colorless crystals: mp 110–112°; mass spectrum (70 eV), *m/e* 271 (100), 81 (71, trimethylcyclopropenium?); γ^{CHCl_3} 1655 cm^{-1} (C=CH_2); nmr ($CDCl_3$), δ 1.18 (s, 3 H), 1.24 (s, 3 H), 1.39 (d, J = 6.5 cps, 3 H), 3.75 (q, J = 6.5 cps, 1 H), 4.50 (d, J = 1.9 cps, 1 H), 5.34 (d, J = 1.9 cps, 1 H), 7.2–7.9 (m, 5 H). Additional proof of structure was obtained by catalytic hydrogenation (PtO_2; 1 atm of H_2 in benzene) to IV: mp 140–146.5° (isomers); mass spectrum (70 eV), *m/e* 273 (29), 204 (100); nmr ($CDCl_3$), δ 0.99 (s, 3 H), 1.03 (s, 3 H), 1.48 (d, J = 6.8 cps, 6 H), 3.63 (d, J = 6.8 cps, 2 H), 7.25–7.7 (5 H). Noteworthy among the analytical data for IV are the occurrence of a quartet (2 H) and a doublet (6 H) in the nmr spectrum, which confirm the symmetrical structure assigned.

Irradiation of IIa in benzene at 10° through a Pyrex filter affords a 75% yield of V.[7] The photoproduct has the same elemental analysis and molecular ion as the thermal product III, while the other spectral data support the assigned structure V: mp 102–104°; mass spectrum (70 eV), *m/e* 271 (38), 81 (100); nmr ($CDCl_3$), δ 1.01 (s, 3 H), 1.43 (s, 3 H), 1.66 (s, 3 H), 7.3–7.7 (m, 5 H). The photoproduct is stable under nitrogen for prolonged periods but decomposes in the presence of moisture and air. On heating under nitrogen at 120° for 20 min it is converted cleanly to the bicyclic olefin III.

Reaction of V with 4-phenyl-1,2,4-triazoline-3,5-dione results in the formation of the cycloaddition product VI in 70% yield. Compound VI is a colorless crystalline solid: mp 257.5–259°; nmr ($CDCl_3$), δ 1.17 (s, 6 H), 2.20 (s, 6 H), 7.3–7.5 (m, 10 H). Cycloadditions (2 + 2) of electron-deficient olefins and acetylenes with the strained central bonds of bicyclo[2.1.0] molecules have recently been reported by several authors.[6c,8] Ene-type addition which is often observed as a competing pathway is not detectable in this case.

The thermal and photochemical decompositions of IIb have also been studied; however, isolation of products has not yet been possible due to their sensitivity and to the presence of mixtures. Thermal decomposition in chlorobenzene begins at 80° in this case.

The stereochemistry of the triazoline moiety in IIa, IIb, V, and VI has been tentatively established by nmr spectroscopy. The observation of two singlets for the bridge methyls of IIa, IIb, and V and one singlet for those of VI is consistent only with the presence of a single isomer, presumably *endo*[9] in each case, or with rapid flipping of the triazoline ring. Low-temperature spectra of IIa and V show no broadening, and the spectrum of VI is unchanged over the range −57 to 130°. Allred[10a] and Anderson and Lehn[10b] have observed temperature-dependent nmr spectra for 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]hept-5-ene with a coalescence temperature of −10° and have invoked slow nitrogen inversion and hindered rotation about the N–CO_2-Me linkage, respectively, to explain their results. Anderson and Lehn's mechanism does not apply to our

---

[2] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc., C*, 1905 (1967).

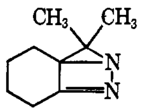
[3] A recent review reports no clear-cut examples of Diels–Alder reactions of 2,3-diazadienes: "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 182.

[4] Satisfactory elemental analyses were obtained for all new compounds.

[5] Nmr spectra of IIa and IIb contain a methyl group at unusually high field, 0.53 and 0.33 ppm, respectively. This absorption is attributed to the bridge methyl *syn* to the azo linkage. The anisotropy of the azo linkage is not well studied but work of McGreer and of Crawford supports our assignment: D. E. McGreer, N. W. Chiu, and M. G. Vinje, *Can. J. Chem.*, **43**, 1398 (1965); R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).

[6] (a) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967); (b) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (c) W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967); (d) C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *J. Am. Chem. Soc.*, **87**, 4119 (1965); (e) D. E. McGreer and W.-S. Wu, *Can. J. Chem.*, **45**, 461 (1967).

[7] Attempts to obtain diazabicyclo[2.1.0]pentanes by direct irradiation of isopyrazoles have not been successful to date: D. R. Arnold and V. Y. Abraitys, unpublished results. The diazabicyclo[2.1.0]-containing molecule, i, which is formed by low-temperature photo-



i

isomerization of the pyrazolenine is the closest analog of V: G. L. Closs and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3904 (1963).

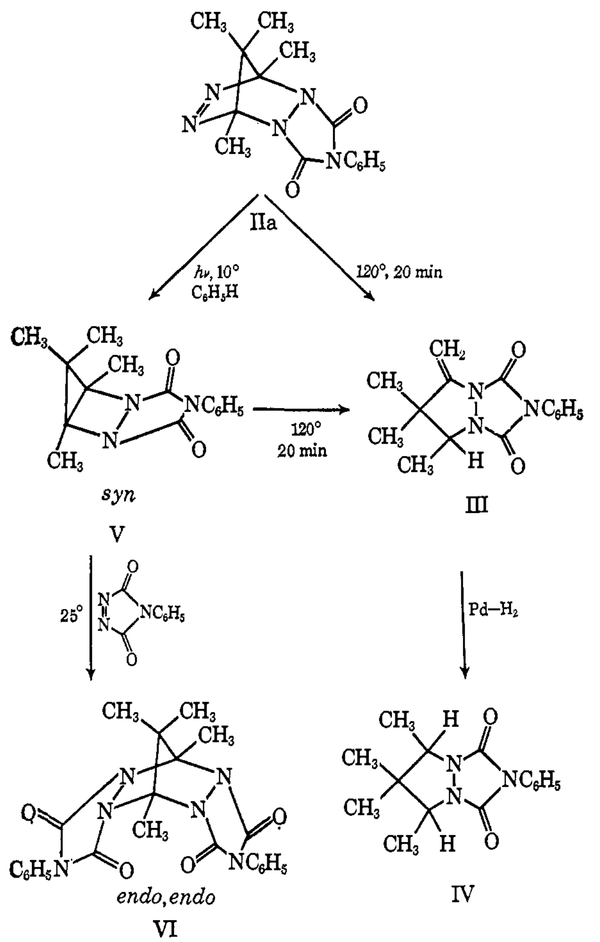
[8] (a) P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965); (b) A. Cairncross and E. P. Blanchard, Jr., *J. Am. Chem. Soc.*, **88**, 496 (1966).

[9] If a single isomer is present, it is almost certainly the *endo* adduct. Cyclopentadiene, 5-methylcyclopentadiene, and, closer to the point, 5,5-dimethylcyclopentadiene yield predominantly or exclusively the *endo* adduct with maleic anhydride and maleimides: C. F. Culberson and P. Wilder, Jr., *J. Org. Chem.*, **25**, 1358 (1960); V. A. Mironov, J. M. Fadeeva, and A. A. Arkhem, *Dokl. Akad. Nauk. SSSR*, **174**, 852 (1967).

[10] (a) E. L. Allred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Letters*, 525 (1967); (b) J. E. Anderson and J. M. Lehn, *Tetrahedron*, **24**, 123 (1968).

case, and neither simultaneous nor sequential inversions of the nitrogens in the rigid tricyclic ring systems of IIa, V, and VI are likely to be fast (on an nmr time scale) at −57°. Accordingly IIa and IIb are assigned the *endo* configuration and VI the *endo,endo* geometry. The fact that the low-field bridge methyl of IIa and the two bridge methyls of VI have virtually identical chemical shifts supports this assignment. The photoproduct V is assigned the *syn* configuration. Allred[11a] and Roth[11b] have shown that loss of nitrogen from 2,3-diazanorbornenes proceeds with inversion of the bridge. Roth has also demonstrated that carbocyclic [2.1.0] molecules react with 5-phenyl-1,2,4-triazoline-3,5-dione with inversion.[6c] These results should apply to our system yielding the geometries assigned in Scheme I.

Scheme I



The thermal isomerization of V to III must involve the dissociation of the weak central bond of V and intramolecular disproportionation of the resultant diradical. There is ample precedent for the disproportionation of 1,3 diradicals,[6b,12] although in nearly all these cases the migrating hydrogen atom comes from the 2 position. The thermal decomposition of the Diels–Alder adduct IIa to form III may involve the same diradical intermediate; it is not known, however, whether bond formation intervenes between loss of nitrogen and formation of the 1,3 diradical. A 1,3 diradical has been proposed as an intermediate in the thermal and photochemical decomposition of 2,3-diazabicyclo[2.2.1]hept-2-enes, although Roth has suggested another explanation.[6c] Our results demonstrate the plausibility of a diradical mechanism for both thermal and photochemical decomposition of IIa and IIb. In order to obtain further evidence we are examining the kinetics of the decomposition of analogs of II as well as attempting to characterize the intermediate(s) by electron spin resonance spectroscopy.

In addition to the isopyrazoles, acyclic 2,3-diazadienes react with 4-phenyl-1,2,4-triazoline-3,5-dione apparently in part by an analogous pathway. In systems examined thus far the product mixtures are complex and unstable.

A. B. Evnin, D. R. Arnold
Union Carbide Research Institute
Tarrytown, New York 10591

Received June 21, 1968

---

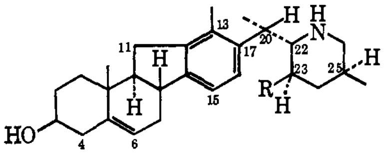
[11] (a) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967); (b) W. R. Roth and M. Martin, *Ann.*, **702**, 1 (1967).

[12] Pyrolysis of 1,4-dimethylbicyclo[2.1.0]pentane yields 1,3-dimethylcyclopentane and none of the *exo*-methylene anolog: R. Srinivasan, private communication.

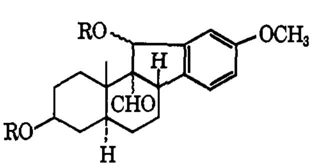
The Total Synthesis of Veratrum Alkaloids.
I. Verarine[1,2]

Sir:

The synthesis of Veratrum alkaloids is of considerable interest, since members of this class possess the C-nor-D-homo steroid skeleton, a unique system among the steroidal alkaloids. Recently[3,4] synthetic routes to the alkaloids jervine and veratramine (II) have been described, and we now wish to present a total synthesis of verarine (I)[5,6] by a novel pathway which is also potentially applicable to veratramine and jervine. In general the approach involves the conversion of optically active 3β-acetoxyetiojervan-17-one (XII) to the natural series. Since the former compound is available by degradation[7,8] of the totally synthetic sapogenin, hecogenin,[9] the present work constitutes a total synthesis of this alkaloid. In addition, we have also completed in a separate series of experiments the total synthesis of



I, R = H
II, R = OH



III, R = H
IV, R = Ac

---

(1) Total Synthesis of Steroidal Derivatives. V.

(2) Presented in part at the IUPAC International Symposium on Natural Products, London, July 1968.

(3) T. Masamune, M. Takasugi, A. Murai, and K. Kobayashi, *J. Am. Chem. Soc.*, **89**, 4521 (1967).

(4) W. S. Johnson, H. A. P. de Jongh, C. E. Coverdale, J. W. Scott, and U. Burckhardt, *ibid.*, **89**, 4523 (1967).

(5) T. Masamune, I. Yamazaki, and M. Takasugi, *Bull. Chem. Soc. Japan*, **39**, 1090 (1966).

(6) S. M. Kupchan and M. E. Suffness, *J. Am. Chem. Soc.*, **90**, 2730 (1968).

(7) H. Mitsuhashi and K. Shibata, *Tetrahedron Letters*, 2281 (1964).

(8) W. F. Johns and I. Laos, *J. Org. Chem.*, **30**, 4220 (1965).

(9) Y. Mazur, N. Danieli, and F. Sondheimer, *J. Am. Chem. Soc.*, **82**, 5889 (1960).