

tive contribution canceled by symmetry, are at the low end of the range, as might be expected. We conclude that the effect of charge on "W-plan" splittings is reasonably close to that on β -hydrogen splittings.

The vinyl hydrogen splittings do not show ratios nearly as close. The value of $a(\text{H}_v)$ for **6a** is greater than for **5a**, but this order is reversed in the semifurquinones. The $a(\text{H}_v)$ ratios are 4.5 for **6**, but only 2.5 for **5**. It is possible that the difference in hybridization at nitrogen, reflected in the differing $a(\text{N})$ values, is responsible for this difference in $a(\text{H}_v)$ although whether nitrogen is more sensitive than carbon to such effects is not known. In both cases, however, the $a(\text{H}_v)$ ratio is at least as sensitive to charge as are β splittings. The importance of homoconjugative interactions as a spin delocalization mechanism for **5** and **6** is still largely open.^{2,3} We have recently questioned the reliability of the technique of probing for π spin density in the vinyl group (as required for homoconjugation to be important) by methyl substitution.¹⁴ Our results here seem consistent with a homoconjugative contribution to $a(\text{H}_v)$, since such a contribution should be relatively more important for cationic than anionic systems.

(14) S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **92**, 6212 (1970).

We do not doubt that there is also an important contribution due to spin polarization, and separation of these factors is not yet possible.

Experimental Section

Materials. The dimethylhydrazine precursors to **1a-4a** were prepared by literature procedures.^{10b} Mass spectral analysis of *exo*-5,6-dideuterio-2,3-diaza-2,3-dicarboethoxynorbornane, prepared by the method of Roth and Martin,¹¹ and its LAH reduction product showed that our material was approximately 84% d_2 , 13% d_1 , and 3% d_0 .

Esr spectra were determined by intramuros electrolytic oxidation in a platinum gauge electrode in a flat quartz cell in the cavity of a Varian E-3. Acetonitrile (stored over Linde 3A Molecular Sieve and distilled from calcium hydride) which was 0.05 *M* in sodium perchlorate was used as supporting electrolyte. The hydrazine cations were quite stable enough for esr work under these conditions, and persisted for hours if current was passed continuously. Splitting constants due to the alkyl portion of the molecule were determined by examination of the outer group of lines. All spectra were synthesized by computer as a check on the splitting constants so derived. The values of $a(\text{N})$ and $a(\text{Me})$ are probably not better than $\pm 2\%$ (0.3 G), for they depend on the accuracy of the "Field-dial" and line widths in excess of 250 mG were observed.

Acknowledgment. We wish to thank the National Science Foundation for generous support of this work and Robert Keppel for preparation of the precursors to **2a** and **5a**.

Chemical and Spectroscopic Studies of the Decomposition of Bicyclic Azo Compounds Derived from Isopyrazoles

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Contribution from the Union Carbide Research Institute, Tarrytown, New York 10591. Received April 10, 1970

Abstract: The reaction of isopyrazoles (IX) with 4-phenyl-1,2,4-triazoline-3,5-dione (X) affords the adducts XI in high yield. The decomposition of these azo compounds (XI) was studied; loss of nitrogen occurs both photochemically and thermally to afford 1,3 diradicals (XII) which either disproportionate intramolecularly (to XIX) or close to form the bicyclo[2.1.0]pentane derivatives (XXI). If the irradiation of XI is carried out in matrices at $T < 77^\circ\text{K}$, triplet signals which are consistent with the 1,3-diradical XII are obtained. The stability of the signals indicates that the triplet is the lowest state for this diradical. The reactions of bicyclo[2.1.0]pentane derivatives (XXI) were also studied; they reflect the extremely weak central bond (D 2–20 kcal).

The characterization of 1,3 diradicals is a subject of great current interest. These species are believed to be intermediates in the synthesis of several important classes of small ring compounds: cyclopropanes from pyrazolines,^{1a} cyclobutanones,^{1b} lactones,^{1c} or olefins and carbenes,^{1d} cyclopropenes from pyrazolenines,² or butenolides,^{1c} and bicyclo[2.1.0]pentanes from diazanorbornenes.³ In addition, their involvement is strongly implied in the *cis-trans* isomerization of cyclopropanes^{4a} and of bicyclopentanes.^{4b}

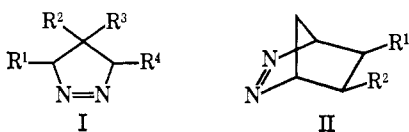
* To whom correspondence should be addressed at the Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, 72, Canada.

- (1) (a) R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Amer. Chem. Soc.*, **87**, 3023 (1965); (b) T. H. McGee, *J. Phys. Chem.*, **72**, 1621 (1968); (c) I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969).
 (2) G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968); R. Anet and F. A. L. Anet, *ibid.*, **86**, 525 (1964).
 (3) (a) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957); (b) C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

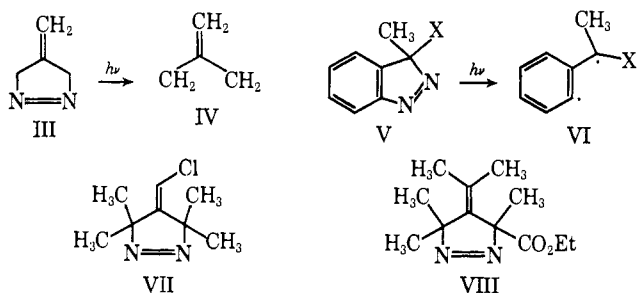
Most attempts to probe for the existence and properties of 1,3 diradicals have utilized cyclic azo compounds as precursors. Crawford and coworkers^{1a,5} have demonstrated that both C–N bonds break in the rate-determining step of the thermal decomposition of 1-pyrazolines (I), as is the case with acyclic azo compounds,⁶ and that a nitrogen-free diradical intermediate is formed. This has been supported for 2,3-diazabicyclo[2.2.1]hept-2-enes (II) by Allred's group,⁷ although

- (4) (a) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934); P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968); (b) J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962).
 (5) (a) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (b) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967); (c) Basil H. Al-Sader and R. J. Crawford, *ibid.*, **46**, 3301 (1968).
 (6) S. Seltzer, *J. Amer. Chem. Soc.*, **85**, 14 (1963); S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965); and S. Seltzer and S. G. Mylonakis, *ibid.*, **89**, 6584 (1967).
 (7) E. Allred and R. L. Smith, *ibid.*, **89**, 7133 (1967); **91**, 6766 (1969).

Roth and Martin⁸ have suggested a stepwise decomposition.



The nature of the lowest state of the 1,3 diradicals generated in the decompositions of I and II and in the thermolysis and photolysis of other precursors is not known, and could be singlet, triplet, or a pair of doublets. Calculations have indicated both a singlet⁹ and a triplet¹⁰ lowest state for trimethylene itself, and the introduction of substituents must effect the degeneracy of the highest occupied orbitals. Attempts to observe directly the 1,3 diradicals have, however, been unsuccessful^{11,12} except in the special cases of IV¹³ and VI;¹⁴ these were shown to have triplet ground states by observation of characteristic triplet esr spectra upon ir-



radiation of matrices (77°K) of the azo compounds III and V, respectively. On the other hand, irradiation of substituted 4-methylene-1-pyrazolines, such as VII and VIII, under identical conditions does not produce triplet esr signals.¹⁵

Since direct observation of 1,3-diradical intermediates has not been possible in most cases of interest, attempts have been made to define their multiplicity by comparison of the thermal, photochemical, and sensitized photochemical behavior of various cyclic azo precursors.¹⁶ Thermal decomposition of appropriately labeled 1-pyrazolines (I) has been shown to proceed stereoselectively with a preference for conrotation,⁵ while diazabicyclo[2.2.1] compounds afford bicyclo[2.1.0]pentanes with an inverted configuration.^{7,8} Recent studies of the direct and photosensitized irradiations of II ($R^1 = \text{OCH}_3$, $R^2 = \text{H}$)⁷ of VII^{15a} and of VIII^{15b} have strongly indicated the involvement of singlet and triplet 1,3 diradicals, respectively, although unambiguous assignments could not be made for the lowest state.

(8) (a) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); (b) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).

(9) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); *Chem. Commun.*, 240 (1969).

(10) H. E. Simmons, private communication.

(11) C. G. Overberger and J. P. Anselme, *J. Amer. Chem. Soc.*, **86**, 658 (1964).

(12) W. R. Roth, private communication.

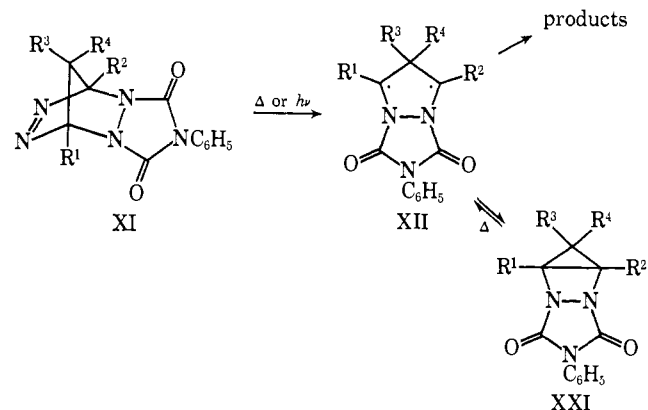
(13) (a) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966); (b) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967); (c) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

(14) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, **89**, 3367 (1967).

(15) (a) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966); *J. Chem. Soc. B*, 1271 (1968); (b) T. Sanjiki, H. Kato, and M. Ohta, *Chem. Commun.*, 496 (1968).

(16) A. B. Evin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968).

The reaction of isopyrazoles (IX) with 4-phenyl-1,2,4-triazoline-3,5-dione (X), which we previously communicated in preliminary form,¹⁶ affords the novel azo compounds (XI). The unique substitution patterns present in XI provide a rare opportunity to study both the chemistry and spectroscopy of a series of 1,3 diradicals. We have generated the diradical intermediates XII from several directions and have defined the lowest energy state of these species.



Results

Preparation and Properties of the Diels–Alder Adducts. In the extensive literature on the Diels–Alder reaction there are only a few examples of cycloadditions with azadienes as the 4e components.¹⁷ Among these, the only well-investigated systems are oxazoles¹⁸ and 1,4-disubstituted tetrazines¹⁹ which, although aromatic molecules, react with electron-deficient and electron-rich olefins, respectively. Recently, acyclic 1,2-diazadienes have also been reported to react as 4e components in the Diels–Alder cycloaddition.²⁰

Our examination of 4,4-disubstituted isopyrazoles (rearrangement to the pyrazole occurs unless blocked by 4,4-disubstitution) indicates that these 2,3-diazadienes react only with the most potent dienophiles; no cycloaddition occurred with maleic anhydride, hexafluoro-2-butyne, tetracyanoethylene,²¹ or diethyl azodicarboxylate. Electron-rich dienophiles were similarly unreactive. With 4-substituted 1,2,4-triazoline-3,5-diones (X),²² however, reaction was rapid (1–5 min) at 25° and afforded the cycloaddition products XI in >90% yield. Diels–Alder adducts were also obtained with 4,4-dialkylpyrazoline-3,5-diones.²³ Attempts to utilize less stable azo diketones such as phthalazine-1,4-dione²⁴ were unsuccessful; apparently the rate of decomposition of the azo compound exceeds the

(17) The subject has been recently reviewed in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 182.

(18) G. Ya Kondrat'yeva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 484 (1959).

(19) R. A. Carboni and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81**, 4342 (1959); J. Sauer and D. Lang, *Angew. Chem.*, **76**, 603 (1964).

(20) K. N. Zelenin and Z. M. Matveeva, *Zh. Org. Khim.*, **4**, 532 (1967).

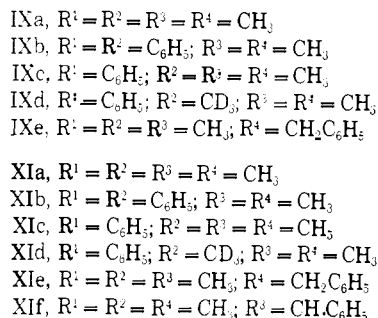
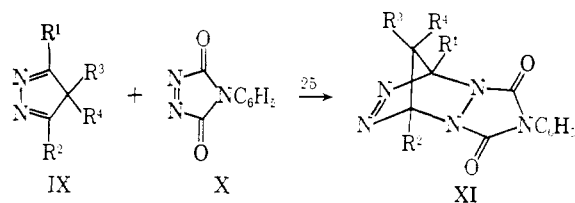
(21) Small amounts of adducts may have formed with TCNE (4 days at 45°), but the reaction mixtures were extremely complex.

(22) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967), and earlier publications by this group.

(23) A. B. Evin, A. Y. Lam, J. J. Maher, and J. J. Blyskal, *Tetrahedron Lett.*, 4497 (1969). This dienophile has also been described recently by other groups: B. T. Gillis and R. A. Izydore, *J. Org. Chem.*, **34**, 3181 (1969); H. Stetter and P. Woernle, *Justus Liebigs Ann. Chem.*, **724**, 150 (1969).

(24) R. A. Clement, *J. Org. Chem.*, **27**, 1115 (1962).

rate of cycloaddition in these cases. Isopyrazoles, thus, do not provide a general route to diazanorbornenes but the cycloadducts, XIa-f, that can be synthesized in this way have proved to be extremely interesting.



The Diels-Alder adducts, XIa-f, are crystalline, readily isolable compounds. They are light sensitive, but can be stored for many months in the dark at room temperature. The physical and spectroscopic data for XIa-f are summarized in Table IV in the Experimental Section.

The ultraviolet spectra of these compounds contain a long-wavelength absorption maximum which is assigned to the n, π^* transition of the azo linkage; it occurs between 390 and 400 nm ($\epsilon \sim 500$) with no distinct vibrational structure. This transition is shifted to the red when compared to the parent azo compound, 2,3-diazabicyclo[2.2.1]hept-2-ene (II, R¹ = R² = H) which has a maximum at 340 nm (ϵ 420);²⁵ however, there is no evidence for transannular interaction between the hydrazine and azo groups.

In the infrared spectra of XIa-f there are very weak absorption bands in the region 1630-1575 cm⁻¹ which may be due to the -N=N- stretching frequency. No assignment could be made, however, as is not unexpected for symmetrical azo compounds such as XI.²⁶

The nuclear magnetic resonance (nmr) spectra provide a striking example of magnetic shielding by the azo linkage.²⁷ The methyl group situated *syn* to the azo linkage XIa-e appears at δ 0.33-0.6 in most solvents. The assignment is readily made by a comparison of the nmr spectra of XIa-f with those of the symmetrical structures XXIIIa-e. The *syn*-methyl absorption in XIa-e is about 0.8 ppm to higher field than the *anti*-methyl group and 0.3 ppm higher than the 7-*syn*-methyls in norbornene derivatives.²⁸ The 7-*syn* hydrogen in II (R¹ = R² = H)²⁹ and the two *syn*-hydrogens in 7-spirocyclopropyl-2,3-diazabicyclo[2.2.1]hept-

(25) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

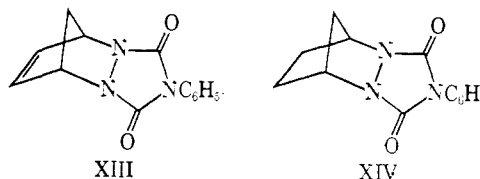
(26) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London, 1969, p 271-272.

(27) The anisotropy of the azo linkage has been previously remarked upon: J. J. Uebel and J. C. Martin, *J. Amer. Chem. Soc.*, **86**, 4618 (1964); R. J. Crawford, A. Mishra, and R. J. Dummel, *ibid.*, **88**, 3959 (1966).

(28) V. F. Bystrov, A. U. Stepanyants, and V. A. Mironov, *J. Gen. Chem. USSR*, **34**, 4099 (1964).

2-ene²⁸ are, on the other hand, not significantly shielded. These protons are considerably farther away from the azo linkage than are the *syn*-methyls in XIa-f.

The stereochemistry of the 1,2,4-triazolidine-3,5-dione (urazole) moiety in XI was of considerable concern to us. Although the use of 4-substituted 1,2,4-triazoline-3,5-diones (X) as Diels-Alder dienophiles has become widespread, there has been little commentary on the stereochemistry of the adducts.²⁹ The question was raised by Gillis and Hagarty³⁰ in regard to their study of XIII, but they decided that the urazole was endo simply by analogy to the adduct of cyclopentadiene and maleic anhydride. Cookson and



coworkers established that XIV was identical with material prepared from 2,3-dicarboethoxy-2,3-diazabicyclo[2.2.1]heptane by a multistep route but made no comment on the stereochemistry of XIV.²²

The nmr spectra of XIa-d have two absorptions due to methyl groups on the methylene bridge while XIe and XIIf have but one (Table IV). These spectra, moreover, are unchanged over the temperature range +60 to -60°. Analogously, the spectra of XXIIIa-c indicate that the two methyl groups on the bridge are magnetically equivalent. These observations are consistent with either a rigid urazole moiety, where the hydrazine nitrogens are planar or pyramidal, or with one that is rapidly flipping even at -60°. Variable temperature nmr studies of XI and XXIII do little to differentiate these possibilities since the *exo* and *endo* conformations for these molecules are expected to have significantly different energies³¹ and the less stable *exo* isomer is unlikely to be evident in the nmr spectrum. In order to shed further light on this question, variable-temperature nmr studies of XV,²² XVI, and XVII,³² were carried out. In these compounds if the urazole moiety is nonplanar, the two nonplanar conformations are identical.

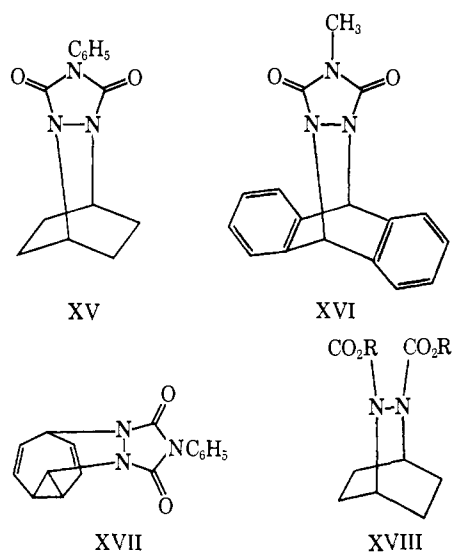
The nmr spectrum of XV has an A₂B₂ pattern for the eight bridge hydrogens which is invariant over the temperature range -85 to +40°. Analogously, the aryl hydrogens of XVI appear as a single A₂B₂ pattern at +40° and are unchanged at -50°. The olefinic absorptions of XVII show symmetrical features even at -90°. The symmetry of the nmr spectra of XV-XVII indicates that the hydrazine nitrogens in the urazole ring do not have rigid, pyramidal structures, and this

(29) The lack of concern is especially surprising in light of the considerable interest in conformational studies of N,N-disubstituted piperazines and bridged derivatives of this system: for a summary of work in this area, see J. M. Lehn and J. Wagner, *Tetrahedron*, **25**, 677 (1969).

(30) B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, **32**, 330 (1967).

(31) The *exo* conformation should be significantly destabilized by interactions between the urazole ring and the methyl group *syn* to it on the bridging methylene. Studies of the adducts of 5- and 5,5-dimethylcyclopentadienes with maleic anhydride provide no examples of compounds in which the anhydride is *exo* and the bridging methyl *syn*: ref 28 and C. F. Wilcox, Jr., and M. Mesirov, *J. Org. Chem.*, **25**, 1841 (1960).

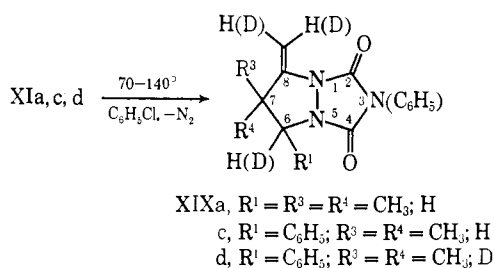
(32) A. B. Evin, R. D. Miller, and G. R. Evaneaga, *Tetrahedron Lett.*, 5963 (1968).



must be the case for XI, XXI, and XXIII, as well. The absence of temperature dependence in the spectra of XV–XVII also argues against inverting pyramidal conformations for the hydrazine nitrogens since such inversion processes should be slow on an nmr time scale at the lowest temperatures studied. In related but less constrained analogs of XIV–XVI, such as XVIII, all inversion processes had ceased by -50° .²⁹ Rapid inversion around pyramidal nitrogens would be even less likely for XI than for XV and XVI due to the additional strain³³ and the substantial steric hindrance to such flipping. The hydrazine nitrogens in the urazole ring of XI, XXI, and XXIII must therefore be planar or very close to planar.³⁴

Reactions of the Diels–Alder Adducts, XIa–f

Thermolysis. Thermal decomposition of XIa, c, and d in solution affords XIXa, c, and d, respectively, in yields of 60–80%. All spectral and analytical data are in agreement with the assigned structure (see Table IV). The nmr is an unambiguous analytical technique



in these cases because the spectra of the 1,3,5-triazabicyclo[3.3.0]octa-2,4-diones (XIX) are extremely characteristic; the olefinic hydrogens have widely different chemical shifts ($\Delta \sim 60$ Hz), and the methyl groups R³ and R⁴ are separated by 2–5 Hz.

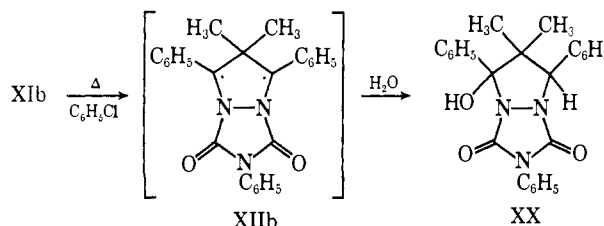
The results obtained with partially deuterated XI d (80% on the basis of nmr measurements) are especially

(33) II and XXVII should be significantly more strained than norbornene itself due to interactions of the methyl groups, compression due to shortened N–N linkages, and the additional rigidity resulting from the third ring (and fourth in XXIII). Norbornene has ~ 25 kcal of strain energy: P. von R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

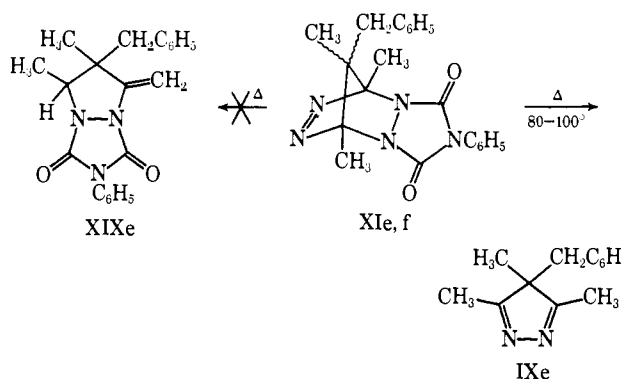
(34) Acyclic diacyl hydrazines have been shown by X-ray studies to be transoid and planar: R. Shintani, *Acta Crystallogr.*, **13**, 609 (1960). It is uncertain, however, whether this result pertains to our system because of the presence of the cisoid conformation, the imide nitrogen and ring strain.

interesting. Nearly all of the deuterium is retained in the thermal product XIXd and, in addition, a marked preference for hydrogen migration is observed: $k_H/k_D \cong 2$. The mechanistic implications of this are discussed below.

Thermal decomposition of XIb afforded a complex reaction mixture which appeared from tlc to contain at least five components. Only one of these, XX, could be positively identified; it is formally the product of reaction of the bicyclo[2.1.0]pentane derivative with adventitious moisture either during the reaction or the work-up.



The thermal decomposition of XIe and f follows a different pathway. In this case, the major product is the isopyrazole IXe that formally arises from a retro Diels–Alder reaction. This is surprising since loss of nitrogen would appear to be energetically more favorable and does, in fact, occur photochemically. No other products were isolated; however, it was established by nmr spectroscopy that less than 5% of the starting material could have gone over to the radical disproportionation product XIXe. The bicyclic olefin, XIXe, which was prepared by a different route (thermolysis of the photoproduct XXIe), is stable under the conditions used for thermal decomposition of XIe. Careful

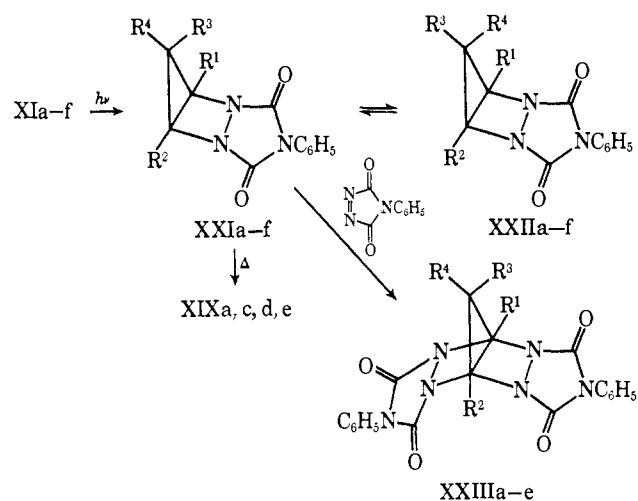


analysis of the reaction mixtures from the thermal decomposition of XIa–d reveals that minor amounts ($< 10\%$) of isopyrazoles were formed.

The rates of the thermal decompositions of XIa–c were evaluated using nmr spectroscopy as an analytical tool. The results obtained (see Table III) were insufficiently precise to derive activation energies; however, it was apparent that the decomposition followed first-order kinetics and that the relative rates are XIb $>$ XIc $>$ XIa. Since the entropy terms are expected to be similar for these molecules, the rates suggest that both C–N bonds are breaking in the transition state for thermal decomposition of XIa–d.

Photochemical Decomposition of XIa–f. Irradiation of XIa–f in solution at or below 25° results in the formation of the corresponding 1,5,7-triazatricyclo[3.1.0.0^{2,4}]octanes (XXI) in good yield. Isolation of the

photoproducts was possible in the cases of XXIa ($R^1 = R^2 = R^3 = R^4 = \text{CH}_3$) and XXIe ($R^1 = R^2 = R^3 = R^4 = \text{CH}_2\text{C}_6\text{H}_5$), although extreme care was necessary due to the instability of these compounds in the atmosphere. All analytical data agree with the structural assignments (see Experimental Section, Table IV).



$R^1 = R^2 = R^3 = R^4 = \text{CH}_3$; $R^4 = \text{CH}_2\text{C}_6\text{H}_5$, although extreme care was necessary due to the instability of these compounds in the atmosphere. All analytical data agree with the structural assignments (see Experimental Section, Table IV).

The photoproducts XXIb,c,d, and f were too unstable for isolation and were identified by nmr spectroscopy at low temperature and by trapping with 4-phenyl-1,2,4-triazoline-3,5-dione (X). Reaction between XXIa-e and X affords the symmetrical products XXIIIa-e, respectively, in good yields. The temperature at which the reaction occurs is dependent on the groups R^1 and R^2 ; with XXIb ($R^1 = R^2 = \text{C}_6\text{H}_5$) reaction is rapid at -50° while with XXIa ($R^1 = R^2 = \text{CH}_3$), several hours are required for completion of reaction at 25° . The addition of electron-deficient olefins³⁵ and azo compounds^{3b} across the central bond of bicyclo[2.1.0]pentanes has been previously reported.

Examination of the nmr spectra of XXIa-d and XXIf reveals temperature-dependent phenomena which are reversible for XXIa-d and irreversible for XXIf; they appear to be the result of inversion around the $R^1\text{C}-\text{CR}^2$ bond which effects the isomerization of XXI \rightleftharpoons XXII. The phenomenon is observed at a characteristic temperature for each photoproduct (see Table II), and the relative rates are in the same order as those for reaction with X. A detailed discussion of this behavior appears below. At temperatures somewhat higher than those required for the inversion XXI \rightleftharpoons XXII, isomerization of XXIa-e to XIXa-e, respectively, occurs: these olefins are also observed in thermal fragmentation of the Diels-Alder adducts.²⁶

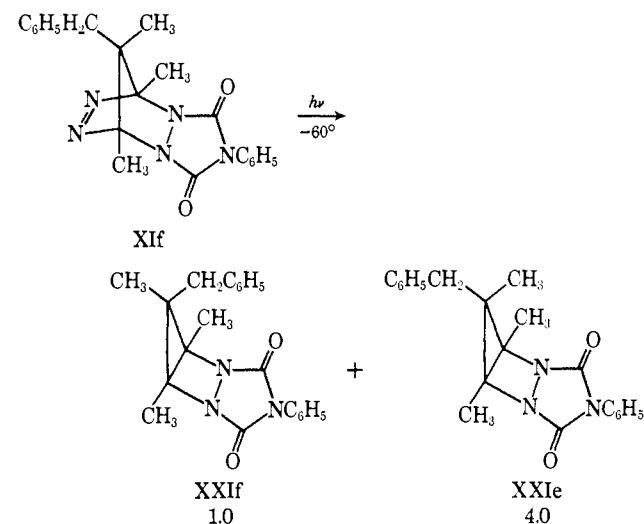
Information on the mechanism of nitrogen evolution from XI and on the stereochemistry of ring closure to XXI comes from an analysis of the photolytic decomposition of XIe and f. Irradiation of XIe at -60° in DMF-*d*₇ or pyridine-chlorobenzene (1:1)³⁷ affords a single product, XXIe, on the basis of nmr spectral examination of the crude reaction mixture. This product is thermally stable at 39° and is isolable. Under identi-

(35) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969), and previous papers by these authors.

(36) An exception to this is thermolysis of the adducts XIe and f which results in retro Diels-Alder reaction. Warming a solution of XXIb affords a complex mixture similar to that obtained from heating XIb.

(37) Insolubility in more traditional solvents necessitated the use of these exotic media for irradiations of XIe and XIc.

cal conditions, XIc gives primarily the same product, XXIc; however, about 20% of the other isomer, XXIc', is also formed. The mixture of XXIc and XXIc' obtained by irradiation of XIc is stable at -40° , but above that temperature XXIc' isomerizes to XXIc. The exact position of the equilibrium XXIc \rightleftharpoons XXIc' at 39° is not known: however, our nmr studies indicate the mixture contains >95% of XXIc (no XXIc' was observed).



The assignment of structures XXIc and XXIc' is based in part on nmr spectroscopy, since the substituent on the methylene bridge that is oriented toward the urazole is expected to be deshielded;³⁸ XXIc has absorptions (pyridine) at δ 2.76 ($\text{CH}_2\text{C}_6\text{H}_5$) and 1.29 (bridge, CH_3), whereas in XXIc' the resonances (pyridine) are at 3.23 ($\text{CH}_2\text{C}_6\text{H}_5$) and 0.87 (bridge, CH_3). More definitive, however, is the thermal behavior of XXIc and XXIc'. Models indicate that the isomer with the benzyl group cis to the urazole ring is substantially the more hindered of the two and should be less stable. Equilibration of the two isomers should thus afford a mixture in which the more stable isomer predominates. The observed conversion of XXIc' to XXIc at $T > -40^\circ$ confirms the structural assignments.

The photochemistry of XIc in DMF-*d*₇ matrices at 77 and 4°K has also been studied. The matrices contained about 10% (wt) of XIc. Examination of the nmr spectra (-60°) of irradiated samples which had never been allowed to warm up beyond -60° revealed that at least 90% of XIc was converted to XXIc'. The irradiation of XIc is, thus, more stereoselective (with inversion) in the matrix than in solution.

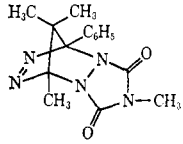
Spectroscopic Studies of the Diradical Intermediate (XII). Irradiation of XIa-e in various matrices followed by examination by esr spectroscopy indicates that triplet species are produced.³⁹ The spectrum consists of four lines assignable to the parallel and perpendicular signals of randomly oriented triplet species with an axially symmetrical spin-spin term, and a fifth line at half-field due to the $\Delta M = 2$ transition.⁴⁰

(38) Nuclear magnetization transfer experiments with XXIa indicate that the group that is shifted to higher field relaxes the fastest. The methyl group oriented toward the urazole is expected to have the shorter relaxation time by virtue of its proximity to other C-H bonds.

(39) The results were previously communicated in preliminary form: D. R. Arnold, A. B. Evin, and P. Kasai, *J. Amer. Chem. Soc.*, **91**, 784 (1969).

(40) For a discussion of diradical esr spectra see: P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, London, 1967, pp 401-413.

Table I. Results of ESR Studies of XIb Irradiated in Inert Matrices

Compd	Temp of irradiation and spectrum, °K	<i>g</i>	Zero-field parameters, <i>D</i> (cm ⁻¹)	<i>E</i>	Average separation between unpaired electrons, Å
XIa	4	2.000 ± 0.002	0.068 ± 0.002	0.0030 ± 0.0005	3.4
XIb	77	2.000 ± 0.002	0.048 ± 0.002	<0.0010 ± 0.0005	3.8
XIc	77	2.000 ± 0.002	0.055 ± 0.002	0.0020 ± 0.0005	3.6
XId	77	2.000 ± 0.002	0.055 ± 0.002	0.0020 ± 0.0005	3.6
XIe	4	2.000 ± 0.002	0.048 ± 0.002	<0.001 ± 0.0005	3.8
	77	2.000 ± 0.002	0.055 ± 0.002	0.0020 ± 0.0005	3.6
XXVI	77	No signal			

The triplet signals from irradiated matrices of XIb-d are stable for many hours at 77°K but disappear upon annealing at 190°K. No signals are observed for XIa and XIe at 77°K; however, triplet spectra can be obtained at 4°K and are stable at that temperature.

The spectra are consistent with an assignment of structure XIIa-e for the triplet diradicals (see Table I). Calculation of the average electron separation, assuming point dipoles, affords values whose magnitude and variations are reasonable for diradicals XIIa-e. Increasing delocalization into the phenyl rings accounts for the greater distance between the electrons: XIIa < XIIc < XIIf. The line width of the absorption increases with the increasing number of hydrogens capable of hyperconjugation: XIIa > XIIc > XIId > XIIf.

Isomerization of XXI. The observation of reversible temperature dependence in the nmr spectra of XXIa-d led us into a detailed study of their isomerizations as well as those of XXIe and f. Thermal isomerization of bicyclo[2.1.0]pentane and its simple derivatives have been examined in some detail and formulated as inversions around the central bond by way of a 1,3 diradical.^{4b}

The nmr spectra of XXIa,c, and d at -60° in various solvents all contain sharp, methyl singlets at high field. When a solution of XXIc in (CD₃)₂CO is warmed to +30°, the singlets for the R³ and R⁴ methyl groups broaden markedly while R² remains sharp. At 36° the peaks are very broad, and new absorptions due to XIXc appear. Cooling the solution back to 0° affords the original, sharp, methyl signals plus those from a small amount of XIXc. The same phenomenon is observed with XXIa, however, at temperatures approximately 40° higher. In the spectrum of XXIb, the signals of the methyl groups R³ and R⁴ appear to be broad even at -60° suggesting that exchange is rapid on an nmr time scale even at this temperature; problems with solubility prevent the examination of XXIb's spectrum at still lower temperatures.

The nmr spectra of XXIa and XXIc indicate that R³ and R⁴ are exchanging in a process that does not effect R². Further evidence that R³ and R⁴ are exchanging, and a quantitative estimate of the rate of this exchange was obtained by the technique of magnetization transfer

developed by Hoffman.^{41,42} The results of these experiments are recorded in Table II.

In the case of XXIIf (XXIe does not have a temperature-dependent nmr spectrum) the exchange of the R³ and R⁴ groups could be followed conveniently by nmr spectroscopy. The shifts of the methyl and benzyl groups in XXIIf and in XXIe are strongly dependent on their relationship to the urazole ring, and the isomerization was monitored by scanning those signals.

The relative rates of exchange of the R³ and R⁴ groups are XXIb > XXIc > XXIa. The data in Table II compare the rate of isomerization of XXIa,c, and e to that of other bicyclo[2.1.0] derivatives reported to date.

Our data on the isomerization XXI ⇌ XXII are interpreted in terms of opening of the R¹C-CR² bond with formation of the diradical which can close to either XXI or XXII. This is considered in more detail in the Discussion.

At a temperature somewhat above that required for the isomerization (XXI ⇌ XXII) of a given photoproduct, disproportionation to the isomeric olefin XIX occurs. As is the case for isomerization, the temperature at which this occurs is highly dependent on the substituents R¹ and R² on XXI. With methyl groups in these positions (XXIa, XXIe) the reaction is complete in 1 hr at 90°, whereas with a methyl and a phenyl group on the bridgehead, reaction is rapid at 45° and proceeds at a significant rate even at 25°. In the case of XXIa,c,d, and e the transformation is extremely clean; only minor amounts of side products are formed. Upon warming XXIb, which cannot form an intramolecular disproportionation product, a complex mixture is obtained which includes XX.

Discussion


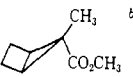
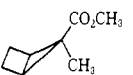
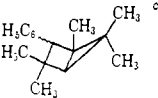


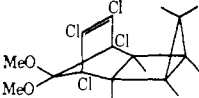
Preparation and Properties of the Diels-Alder Adducts. The reaction of isopyrazoles with 4-phenyl-1,2,4-triazoline-3,5-diones appears to be a straightforward example of a 4 + 2 cycloaddition. Experimental verification of the concertedness⁴³ of the reaction

(41) S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).

(42) S. Forsén and R. A. Hoffman, *ibid.*, **40**, 1189 (1964).

(43) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1967); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

Table II. Inversion of Bicyclo[2.1.0]pentane Derivatives

Compd	Equilibration rate (T, °C)	E_a (kcal) for equilibrium	Destruction of [2.1.0] system, deg
XXIa	0.3 (28)		~80
XXIc	0.5 (-8)		45
	4×10^{-4} (204)	38.9	~300
	5.2×10^{-4} (150)	35.8 ± 2.2	~300
	6.3×10^{-3} (150)	32.9 ± 1.4	
	No equilibration		250
	$\sim 9.6 \times 10^{-6}$ (100) $t_{1/2} = 20$ hr		
			160
	$t_{1/2} = 10$ hr (40)		

^a Reference 4b. ^b M. J. Jorgenson, T. J. Clark, and J. Corn, *J. Amer. Chem. Soc.*, **90**, 7020 (1968). ^c H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5970 (1967). ^d S. Moon and C. R. Ganz, *Tetrahedron Lett.*, 6275 (1968). ^e J. C. Hinshaw and E. L. Allred, *Chem. Commun.*, 72 (1969). ^f K. MacKenzie, W. P. Lay, J. R. Telford, and in part D. L. Williams-Smith, *ibid.*, 761 (1969).

between electron-deficient azo compounds and dienes has not been made here or in the literature; however, the similarity of solvent^{44a} and substituent effects^{44b} and of the activation parameters^{44a} to those observed with olefinic dienophiles makes this a reasonable assumption. The inability to obtain cycloadducts of isopyrazoles with dienophiles other than the cyclic azo diketones may simply reflect the remarkable reactivity of X and of the pyrazoline-3,5-diones; however, the possibility of specific interactions (e.g., charge transfer) between IX and X has not been eliminated.⁴⁵

The geometry of the Diels-Alder adducts XIa-f is worthy of comment. Our variable-temperature nmr studies considered together with data in the literature on analogous systems indicate that bonding around the hydrazine nitrogens in XI (and also in XXI and XXIII) is planar or close to planar. One factor in determining the geometry of the urazole ring may be the contribution of charged, dipolar resonance structures which are formally 6π electron systems.⁴⁶

Thermolysis. The formation of 1,3,5-triazabicyclo-[3.3.0]octa-2,4-diones (XIX) in good yield by the thermal decomposition of XIa, c, and d is best explained by decomposition of the diradical. Support for this mechanism comes from the experiments with XI and XIId. The appearance of deuterium at the *tert*-benzylic position in XIXd establishes the 8-methyl group as the

source of this deuterium (protium). The fact that a primary alkyl hydrogen (deuterium) has been abstracted by a *tert*-benzylic radical indicates that the hydrogen must have been activated by an adjacent unpaired spin, as in XII. It also rules out any intermolecular, radical-chain mechanism. The facile 1,4-hydrogen migration observed in these 1,3 diradicals is unusual, although there is an analogy in the work of Frey.⁴⁷

The observation of a deuterium isotope effect is also noteworthy. The presence in XIId of a complex mixture of d_0 , d_1 , d_2 , and d_3 prevents a quantitative assessment of the relative rates of hydrogen and deuterium transfer; however, the difference is clearly too large to be due to a secondary isotope effect. The demonstration of an energy barrier between the diradical and the olefin is a further indication that the diradical is an intermediate in the thermolysis of XI and not a transition state.

The thermal decomposition of XIb also appears to involve loss of nitrogen and formation of the 1,3-diradical XIIb. In this case, however, there is no possibility for intramolecular disproportionation, and a complex series of reactions occurs instead. Of the many products indicated by tlc, only the alcohol XX was isolable; the presence of insoluble products containing only methyl and aryl hydrogens suggests that some dimerization may have occurred, but isolation of dimers was not accomplished.

The behavior of XIe and XIIf was somewhat surprising to us. We had anticipated that they would decompose thermally in a manner identical with that

(44) (a) A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953); (b) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967).

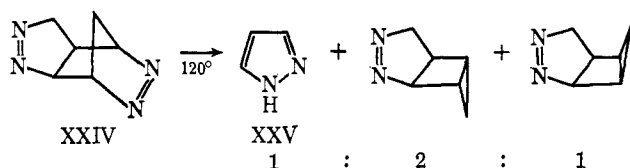
(45) Attempts to generate and carry out $4 + 2$ cycloadditions with less highly substituted isopyrazoles were unsuccessful: G. Gubelt and J. Warkentin, *Chem. Ber.*, **102**, 2481 (1969).

(46) We acknowledge the comments of a referee for our communication (ref 16) in focusing our attention on this point.

(47) H. M. Frey, *J. Amer. Chem. Soc.*, **82**, 5947 (1960).

of XIa-c. Apparently steric interactions in both XIe and XI f are sufficiently important to make the retro Diels-Alder pathway more favorable than nitrogen elimination. The difference between the thermal and photochemical behavior of XIe and XI f (they both lose nitrogen exclusively on photolysis) is explained by the orbital symmetry rules;⁴³ the retro Diels-Alder reaction is expected to be a 4 + 2 concerted electrocyclic reaction⁴⁴ which is allowed thermally but forbidden photochemically. Although nitrogen elimination from XI and formation of XXI could also be a concerted reaction, the demonstration here and elsewhere^{5,7} of the intermediacy of a 1,3 diradical rules this out.

An analogy for the retro Diels-Alder reaction observed with XIe and XI f is found in recently published work by Hinshaw and Allred on the tricyclic azo compound XXIV.⁴⁵ In that study, both nitrogen elimination and the retro Diels-Alder reaction are observed, although the isopyrazole isomerizes to the pyrazole XXV.



Photolyses. The observation of triplet spectra from the irradiation of XIb-d which are stable for many hours at 77°K indicates that the lowest state for the diradicals XIIb-d is the triplet. Our spectral results do not define the geometry of these triplet diradicals; however, they are expected to be planar to permit delocalization of the unpaired electrons into the phenyl ring(s), and onto the nitrogens of the urazole. No evidence for triplet diradicals can be obtained from irradiation of XIa or e at 77°K, but, at 4°K stable triplet spectra assignable to XIIa and e are observed. Again, this stability indicates that the triplet is the lowest state. One must be more equivocal about the geometry of these diradicals, since in the absence of a phenyl substituent bonding around the radical site may be either planar or pyramidal.⁴³

Our results taken together with those on compounds III,¹³ V,¹⁴ VII,¹⁵ and VIII¹⁵ demonstrate that the multiplicity of the ground state for 1,3 diradicals may be either singlet or triplet depending on the many factors which can effect the degeneracy of the highest occupied orbitals. It is possible, at this time, to make an *a priori* prediction of lowest state multiplicity only in special cases.⁵⁰ It seems likely that there may be examples where the energy of the two states is sufficiently close and the barrier to intersystem crossing sufficiently low that mixtures of singlet and triplet may occur.

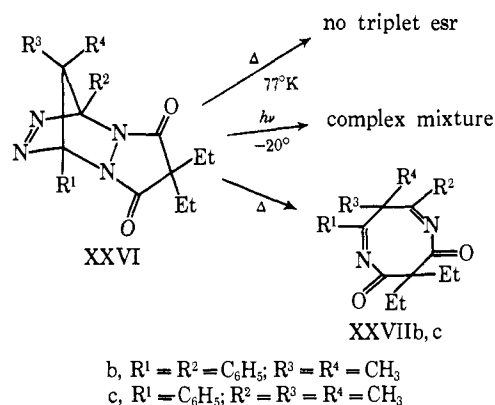
It is apparent from the reported spectroscopic studies of 1,3 diradicals¹³⁻¹⁵ that the lack of a triplet esr signal may indicate a ground-state singlet. On the other hand, lack of a triplet signal does not rule out a

(48) See Table II, footnote e.

(49) Several examples of nonplanar alkyl radicals have been reported in the literature. A relevant one is the 2,4,6-trimethyltrioxanyl radical: A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 1353 (1969).

(50) Trimethylenemethane (IV) is one such case. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 43.

triplet ground state for the diradical. Our results suggest that even if the ground state of the diradical is triplet there must be no low-energy decomposition pathway, and there must be substituents capable of delocalizing the unpaired electrons for the triplet species to be sufficiently long lived for observation. A case in point is the failure to observe an esr signal from XIa and e under conditions (77°K) where the triplets XXIb-d are stable; this must reflect the ability of the phenyl groups to delocalize the unpaired electrons and, thus, decrease the rate of closure of the diradical. Also of interest in this regard are our studies of XXVIb and XXVIc, analogs of XIb and XIc prepared from isopyrazoles, IXa and IXc, and 4,4-diethylpyrazoline-3,5-dione.²³ Irradiation of matrices containing XXVIb or XXVIc at 77°K does not afford observable (by esr) concentrations of triplet species. An explanation for this is suggested by the thermal behavior of XXVIb and XXVIc. Opening of the N-N bond with formation of XXVII is the major pathway here, although it has not been observed for XIa-f either thermally or photochemically. The lack of triplet signal from XXVI, can, therefore, be attributed to decomposition of the diradical to XXVII by N-N bond breaking. The



apparent difference in the strength of the N-N bonds in XII and in the intermediate from XXVI is attributed to contributions from dipolar resonance structures in the case of XII; these would be expected to both strengthen the N-N bond and to stabilize the diradical by delocalization of the unpaired electrons.

Although our spectroscopic studies establish that XIIa-f are ground-state triplets, most of the matrix and solution photochemistry that we observe is best attributed to transient singlet diradicals which close faster than they undergo intersystem crossing. The photolyses of XI f at 77 and 4°K are especially relevant. We interpret the observation that irradiation of XI f affords matrices containing almost exclusively the unstable, photoproduct XXI f as indicative of closure *via* a singlet diradical. The triplet is long lived at 4°K and, although its geometry is not known, stereospecific closure to the thermodynamically unfavorable isomer XXI f is unlikely. Since virtually none of the stable isomer XXI e is formed, one concludes that product formation occurs primarily by way of singlet diradicals. The increase in stereoselectivity (inversion) observed on going from the solution to the matrix is best explained by closure of the singlet diradical prior to diffusion of the nitrogen molecule. Under these

circumstances bonding on the same side as the nitrogen is inhibited by electron-electron repulsions.

It was hoped that sensitizer studies in solution would establish whether the triplet diradical arises from the singlet (in competition with closure to XXI^f) or by loss of singlet nitrogen from triplet XI^f. These studies were not possible due to the low solubility of XI^f at the temperatures required to prevent interconversion of XXI^e \rightleftharpoons XXI^f.

The selectivity for inversion (>95%) that we observe in our matrix irradiations of XXI^f contrasts with results obtained by Allred and Smith^{7b} and by Roth;⁸ their reaction conditions were quite different, however. Allred reports that irradiation of neat, crystalline II ($R^1 = \textit{endo-OCH}_3$, $R^2 = \text{H}$) at -70° affords 2-methoxybicyclo[2.1.0]pentane with more retention of configuration than upon irradiation of neat glasses (-70°) or solutions (25°). These observations are attributed to the direct formation of inverted pyramidal diradicals upon decomposition of II due to a recoil mechanism; these species can close prior to equilibrating and account for net inversion in solution. The increasing rigidity of the matrix in going from solution to glass to solid is thought to restrict the recoil and thus favor closure with retention. Our data on XII^f are obviously not correlated by this explanation.

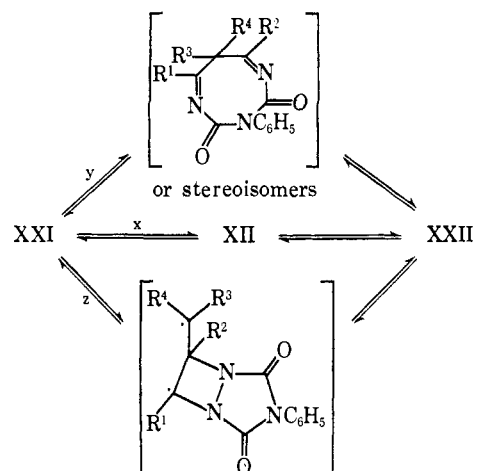
Our results on the stereochemistry of the conversion XI to XXI are, on the other hand, in good agreement with previously reported studies of the decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene (II) derivatives. We observe that XI^e and XI^f are photolyzed in solution with about 15% net inversion of configuration. The selectivity is similar in both its direction and magnitude to that observed by Allred in thermal and photochemical decompositions of II ($R^1 = \textit{endo-OCH}_3$, $R^2 = \text{H}$) and by Roth in the thermolysis of II. The explanation offered for our matrix photochemical studies extends to our solution results; the decrease in stereoselectivity (inversion) observed in solution is expected from the higher temperature and greater mobility of the media. All product formation presumably occurs *via* singlet diradicals for which under these conditions $k_{\text{closure}} > k_{\text{intersystem crossing}}$.

Our results have little bearing on the problem of the stereospecific closure of acyclic 1,3 diradicals which has been characterized as predominantly conrotatory.⁵

The formation of XXI by photolytic elimination of nitrogen from the Diels-Alder adducts, XI, is in accord with the extensive work on cyclic azo compounds in the previous literature. The properties of the photoproducts themselves are, however, somewhat novel. They are significantly more reactive toward nucleophiles and in cycloadditions than any of the bicyclo[2.1.0]pentanes reported to date. We attribute the instability of XXI^{a-f} to ring strain and to substitution capable of stabilizing the diradical.

Isomerization. The isomerization XXI \rightleftharpoons XXII, which involves exchange of the R^3 and R^4 groups, could occur by one of three pathways.

Results with simple bicyclo[2.1.0]pentane have been interpreted in terms of mechanism x which involves a 1,3-diradical intermediate. In those cases, sequence y is unlikely since it would involve the orbital symmetry forbidden thermal 2 + 2 intramolecular cycloaddition of divinylmethane;⁴³ pathway z is generally not con-



sidered. We also prefer mechanism x for the isomerization of XXI \rightleftharpoons XXII. The two major considerations are the effect of the substituents R^1 and R^2 on the rate of exchange of R^3 and R^4 , XXI^b \gg XXI^c \gg XXI^a, and the formation of the disproportionation product from XXI^c and XXI^a at temperatures only slightly higher than those required for the isomerization. The second point is a cogent one since the disproportionation product XIX must be formed by way of the diradical intermediate XII; this fits nicely if the isomerization XXI \rightleftharpoons XXII occurs only by mechanism x but requires complex assumptions about simultaneous reactions if y or z is involved. Further arguments against mechanism y are the inability to observe the intermediate eight-membered ring which should be isolable (see XXVII) and the inability to explain the large influence of R^1 and R^2 on the rate. Mechanism z would contradict the vast literature that attests to the weakest bond in bicyclo[2.1.0]pentane derivatives being the central bond.^{51,52}

Consideration of the data in Table II indicates that XXI^a and c isomerize at a much lower temperature than do any of the known carbocyclic systems. It is reasonable on the basis of the above discussion to conclude that the mechanism of the isomerization of XXI and carbocyclic systems is the same. The difference in the rates must be due to the relative destabilization of the ground state of XXI by compression due to the short N-N bond and the third ring and by steric interactions between the substituent R^3 and the urazole ring; these probably result in a strain energy for XXI well beyond the 54 kcal of bicyclo[2.1.0]pentane.^{4c} Stabilization of the diradical intermediate, XII, by delocalization of the unpaired electrons into R^1 and R^2 and to some extent by the involvement of the nitrogens of the urazole ring is certainly important, as well.

The 1,7-bond strength in XXI^{a-c} has been estimated using data obtained by Chesick and by Turner,^{4b,53} and confirms a very low dissociation energy

(51) K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1967).

(52) Pathway z could be rigorously differentiated in principle from x or y by observation of the isomerization XXI \rightleftharpoons XXII for a derivative in which R^1 and R^2 were nonequivalent and the *dl* isomers could be distinguished; e.g., by nmr magnetization transfer experiments in an optically active solvent. An equivalent experiment would be to attach a group such as ethyl or isopropyl at R^1 and/or R^2 and observe whether the molecular asymmetry was averaged.

(53) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

for it. The energy of dissociation of the central bond in bicyclopentane itself is about 27.5 kcal. Assuming a value for the resonance energy of a benzyl radical of 12 kcal⁵⁴ and the effect of a methyl group to be about 3 kcal,⁵⁵ one arrives at values of 22, 13, and 4 kcal for this bond in XXIa,b, and c, respectively. The actual values are probably even lower than these due to the presence of the α -nitrogen atoms.

The isomerization of XXI to XIX and of XXI to XXII have the 1,3-diradical XII as a common intermediate. The higher temperatures required for the disproportionation, XXI \rightarrow XIX, and the isotope effect observed in the thermal decomposition of XIId to XIXd indicate an energy of activation for this reaction. Chesick has reported that the E_{act} for the isomerization of 2-methylbicyclopentane to cyclopentene is 7 kcal higher than for the isomerization of *cis*-2-methylbicyclopentane to the *trans* isomer. In our case, an energy difference greater than 7 kcal may be expected since a 1,4 shift of hydrogen rather than a 1,2 shift is required for disproportionation.

Conclusions

The photochemical and thermal reactions of XI and the isomerizations of XXI are all consistent with the intermediacy of 1,3-diradical intermediates. The observation of triplet esr signals from the irradiation of matrices containing XIa-e indicates that the lowest state of the diradicals is the triplet. The multiplicity of the diradicals in the thermal and photochemical reactions in solutions cannot be unambiguously assigned. We believe, however, that the stereoselective closure observed in the irradiation of XIe and XI f involves singlet species which close faster than they undergo intersystem crossing. Similarly, the thermal decomposition of XI and the isomerizations of XXI must involve singlet 1,3 diradicals.

Experimental Section

General. Melting points were corrected. Elemental analyses were carried out by Union Carbide European Research Associates, Brussels, Belgium, or Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were taken with a Varian A-60 and absorptions are given in parts per million downfield from TMS (δ). Studies of the isomerization of XXI were carried out by Dr. E. B. Whipple of UCRI using a Varian HR 60. Mass spectral analyses were performed either by I. Ladd, UCRI, B. Wilkes, Union Carbide, South Charleston, W. Va., or Morgan Schaffer, Montreal, Canada. All reactions were carried out in a nitrogen atmosphere. The esr studies were carried out by Dr. P. Kasai at UCRI.

Preparation of 4,4-Disubstituted Isopyrazoles, IX. The isopyrazoles used in this study were prepared in two steps from the appropriate 1,3-dione. The sodium enolate of the ketone was first dialkylated in DMSO⁵⁶ and the dialkylated dione was then condensed with $N_2H_4 \cdot H_2O$ in hot benzene with azeotropic removal of the water.⁵⁷ In the case of 1-phenyl-1,3-butanedione, which was typical, a slurry of 25 g (0.154 mol) of the dione, 200 ml of DMSO (MCB anhydrous), and 6.86 g (0.35 mol) of sodium hydride (mineral oil dispersion) was prepared in a three-necked flask equipped with an efficient overhead stirring apparatus. To this was added 28.1 g (0.2 mol) of methyl iodide during a 25-min period. After stirring for an additional 30 min, 6.86 g of sodium hydride was added, followed by 28.1 g of methyl iodide 20 min later. After stirring for 1 hr the reaction mixture was still basic; an additional 28.1 g of methyl iodide was added and the reaction mixture stirred

overnight. In the morning a precipitate was present; addition of ether caused additional precipitation. Filtration, removal of the DMSO by an aqueous extraction, drying (Na_2SO_4), and concentration of the ether solution afforded a golden liquid. Distillation gave a forerun, bp 57-67° (4 mm), and a main fraction, bp 68° (4 mm), which was identified as 1-phenyl-2,2-dimethylbutane-1,3-dione (see Table IV). The yield was 18.45 g (63%). A portion of this material (16.8 g, 0.88 mol) was heated with excess hydrazine hydrate (0.88 mol) in 55 ml of benzene for about 2 hr. A Dean-Stark trap was then added and water was removed azeotropically. The reaction mixture was concentrated on a rotary evaporator affording a cloudy oil which crystallized on cooling, mp 92-94°. One recrystallization from benzene-hexane gave 9.3 g (55%) of analytically pure material, mp 94-94.5°, which was identified as 3-phenyl-4,4,5-trimethylisopyrazole, IXc. The yields of isopyrazole were generally 30-40% based on the starting 1,3-dione.

A solution of 0.5 g (2.7 mmol) of 3-phenyl-4,5,5-trimethylisopyrazole (IXc) and 0.1 g of sodium hydroxide in 40 ml of a 1:1 mixture of D_2O and acetonitrile were heated at 45° for 36 hr. Evaporation of the reaction mixture to dryness *in vacuo* and removal of the inorganic salts with D_2O left an oil. This was dissolved in chloroform, dried, concentrated, and heated with hexane until crystallization commenced. The yield was 0.3 g (60%). The nmr spectrum ($CDCl_3$) of the product had a broad absorption at δ 2.3 in addition to a singlet at δ 1.39 and aryl absorptions; the relative areas of the absorptions at δ 2.3 and 1.39 were 0.9 and 3.0 indicating that the isopyrazole ring was intact but that 2.1 D were present at the 5 position, IXd. The extent of exchange was corroborated by mass spectral analysis (70 eV). Heating for longer periods afforded >97% trideuterated material.

Reaction of Isopyrazoles (IX) with 4-Phenyl-1,2,4-triazoline-3,5-dione (X). Reactions between the isopyrazoles (IX) and 4-phenyl-1,2,4-triazoline-3,5-dione (X) were carried out in benzene or acetone at room temperature. The disappearance of the red color of the dienophile was rapid under these conditions; however it was slow at -78°.

A solution of 2.48 g (0.01 mol) of 3,5-diphenyl-4,4-dimethylisopyrazole in 15 ml of benzene was added dropwise to a slurry of 1.75 g (0.01 mol) of 4-phenyl-1,2,4-triazoline-3,5-dione (X) in 50 ml of benzene. Within 5 min the red color of the azo compound disappeared, and a yellow precipitate formed. Filtration afforded 3.5 g, mp 115° dec. Concentration and addition of hexane resulted in the precipitation of an additional 0.5 g (overall yield 94%). Recrystallization from methylene chloride-hexane afforded 3.8 g of yellow crystals, mp 118° dec. The product was identified as 1,4,7-triphenyl-10,10-dimethyl-2,4,6,8,9-pentazatricyclo-[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (XIb). Care must be taken during the work-up to avoid heating solutions above 50°. Once pure, the material can be stored for months in the dark at 0°. The other Diels-Alder adducts XIa, c, d, e, and f were obtained in comparable yields; they are stable and may be stored at room temperature in the dark.

Reaction of 0.6 g (30 mmol) of 4-benzyl-3,4,5-trimethylisopyrazole with 0.525 g (30 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in benzene gave 1.05 g of light yellow crystals. Examination of the crude product by nmr spectroscopy ($CDCl_3$) revealed two high-field methyl signals at δ 0.65 and 1.30, among other absorptions. The intensities of the two high-field signals were the same indicating that the XIe and XI f were present in 1:1 ratio. Fractional crystallization from warm benzene afforded the isomer with a signal at δ 1.30 in 48.5% yield, mp 120.5-123°; this was assigned structure XI f. Removal of the benzene and trituration of the oily residue with methanol afforded upon cooling 0.172 g (15.3%) of the other isomer, mp 152-153°, which was assigned structure XIe.

Table III. The Rate of Thermal Decomposition of the Azo Compounds

Compd	Rate of decomposition, 10 ⁻⁴ sec ⁻¹	Temp, °C
IIa	4.7	99.5
IIa	1.6	91.5
IIa	0.6	84.0
IIc	13.0	84.5
IIc	8.1	79.5
IIc	5.9	76.5
IIc	2.6	72.5
IIb	9.8 ^a	67.0

^a Average of two runs at this temperature.

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Table IV. Analytical Data

Compd	Mp, °C	Nmr, δ^a	Uv, λ_{max} , and ir, γ	Mass spectrum ^b	Anal.								
					Calcd				Found				
					C	H	N	O	C	H	N	O	
CH ₃ C(=O)- CCH ₃ (CH ₂ Ph)- C(=O)CH ₃	155 (17 mm) (bp) n^{23D} 1.5134	1.22 (s, 3 H) ^c 1.98 (s, 6 H) 3.16 (s, 2 H) 7.16 (m, 5 H)				76.45	7.89			76.22	7.95		
IXa	44	1.16 (s, 6 H) 2.15 (s, 6 H)											<i>j</i>
IXb	127-128	1.18 (s, 6 H) 7.43-8.3 (m, 10 H)	315 nm (ϵ 19,900) ^d			82.22	6.50	11.08		82.25	6.56	11.08	
IXc	94-95	1.42 (s, 6 H) 2.24 (s, 3 H) 7.3-7.6 (m, 5 H)				77.38	7.58			77.39	7.43		
IXd	93	1.39 (s, 6 H) 7.35-8.17 (m, 5 H)											
IXe	92.5-94	1.24 (s, 6 H) 2.15 (s, 3 H) 2.97 (s, 2 H) 6.82-7.57 (m, 5 H)				77.96	8.05			77.66	8.00		
XIa	148-149	0.53 (s, 3 H) 1.07 (s, 3 H) 2.18 (s, 6 H) 7.4 (m, 5 H)	397 nm (ϵ 542) ^d	<i>m/e</i> 299 (0) 271 (4) 256 (100)		60.18	5.73	23.40		60.40	5.83	22.95	
XIb	123	0.33 (s, 3 H) 1.18 (s, 3 H) 7.1-8.1 (m, 10 H)	400 nm (ϵ 562) ^e	<i>m/e</i> 423 (0) 395 (1) 119 (100) 105 (90) 77 (32)		70.90	5.00	16.54		71.48	5.16	16.65	
XIc	141-141.5	0.49 (s, 3 H) 1.18 (s, 3 H) 2.23 (s, 3 H) 7.3-8 (m, 10 H)	396 nm (ϵ 537) ^e	<i>m/e</i> 361 (0) 333 (3) 307 (23) 119 (55) 105 (100)		65.96	5.53	19.82	8.85	66.47	5.30	19.38	8.68
XId	139-140	0.48 (s, 3 H) 1.18 (s, 3 H) 7.3-8 (m, 10 H)											
XIe	152-153	1.27 (s, 3 H) 2.09 (s, 3 H) 2.28 (s, 2 H) 6.99-7.56 (m, 10 H)	399 nm (ϵ 604) ^f	<i>m/e</i> 347 (4) 256 (93) 137 (100) 91 (62)		67.19	5.63			67.20	5.86		
XIf	120.5-123	0.65 (s, 3 H) 2.07 (s, 6 H) 2.92 (s, 2 H) 7.94-7.54 (m, 10 H)	396 nm (ϵ 457) ^f	<i>m/e</i> 375 (0) 347 (3) 256 (100) 137 (73) 91 (34)		67.19	5.63			67.64	5.76		
XIXa	110-112	1.18 (s, 3 H) 1.24 (s, 3 H) 1.39 (d, <i>J</i> = 6.5 Hz, 3 H) 3.76 (d, <i>J</i> = 6.5 Hz, 1 H) 4.50 (d, <i>J</i> = 1.9 Hz, 1 H) 5.34 (d, <i>J</i> = 1.9 Hz, 1 H) 7.2-7.7 (m, 5 H)	1655 cm ⁻¹ ^f	<i>m/e</i> 271 (100; pp) 81 (71)		66.39	6.33	15.49	11.79	66.11	6.38	15.44	12.28
XIXc	140-142	0.91 (s, 3 H) 1.38 (s, 3 H) 4.59 (d, <i>J</i> = 2 Hz, 1 H) 4.77 (s, CH ₂ C ₆ H ₅ , 2 H) 5.48 (d, <i>J</i> = 2 Hz, 1 H) 7.2-7.9 (m, 10 H)	1650 cm ⁻¹ ^f			72.05	5.74	12.61		72.18	5.79	12.40	
XIXe	169.5-172	0.84 (s, 3 H) 1.45 (d, <i>J</i> = 7 Hz, 3 H) 2.45 (s, 2 H) 3.61 (d, <i>J</i> = 2 Hz, 1 H) 5.43 (d, <i>J</i> = 2 Hz, 1 H)	1655 cm ⁻¹ ^f			72.60	6.09	12.10		72.46	6.21	12.10	

Table IV (Continued)

Compd	Mp, °C	Nmr, δ^a	Uv, λ_{max} , and ir, γ	Mass spectrum ^b	Anal.							
					Calcd				Found			
					C	H	N	O	C	H	N	O
XXb	230-231	0.45 (s, 3 H) 0.17 (s, 3 H) 5.20 (s, 1 H) 7.2-7.9 (m, 15 H)	3560 cm^{-1} ^c 3250 cm^{-1}	<i>m/e</i> 413 (10; pp) 266 (100) 147 (54)	72.62	5.60	10.16	11.61	72.10	5.82	9.97	11.55
XXIa	102-104 dec	1.01 (s, 3 H) 1.43 (s, 3 H) 1.66 (s, 6 H) 7.25-7.65 (m, 5 H)		<i>m/e</i> 271 (38; pp) 119 (36) 96 (19) 91 (27) 82 (15) 81 (100)	66.11	6.38	15.44		66.10	6.50	15.46	
XXIc		0.88 (s, 3 H) 1.64 (s, 3 H) 1.78 (s, 3 H) 7.35-7.65 (m, 10 H)										
XXId		0.88 (s, 3 H) 1.64 (s, 3 H) 7.35-7.65 (m, 10 H)										
XXIe	129-130	0.87 (s, 3 H) 1.63 (s, 3 H) 3.23 (s, 2 H) 7.17-7.67 (m, 10 H)		<i>m/e</i> 347 (1; pp) 257 (16) 256 (27) 137 (100) 119 (25) 91 (64) 42 (12)	72.60	6.09	12.10		71.58	5.92	11.90	
XXIf		1.29 (s, 3 H) ^h 1.78 (s, 3 H) 2.76 (s, 2 H) 7.2-7.7 (m, 10 H)										
XXIIIa	257.5-259	1.17 (s, 6 H) 2.20 (s, 6 H) 7.45 (m, 10 H)			61.87	4.97	18.83	12.28	61.95	4.76	18.75	14.85
XXIIIb	332 dec	1.19 (s, 6 H) 7.25-8.1 (m, 15 H)		<i>m/e</i> 570 (23; pp) 380 (100) 261 (28) 119 (15) 91 (9) 77 (13)					<i>l</i>			
XXIIIc	211-213	1.28 (s, 6 H) 2.37 (s, 3 H) 7.25-7.8 (m, 10 H)		<i>m/e</i> 508 (52; pp) 318 (100) 199 (25) 145 (15) 119 (15)	66.13	4.76	16.53	12.59	66.0	4.8	16.9	12.10
XXIIIe	194-194.5	1.17 (s, 3 H) 2.12 (s, 6 H) 3.02 (s, 2 H) 7.26-7.64 (m, 10 H)		<i>m/e</i> 522 (15; pp) 345 (33) 257 (78) 177 (20) 137 (51) 119 (31) 91 (100) 77 (23)	66.65	5.02	16.08		66.49	4.98	16.27	

^a In CDCl_3 with TMS as an internal standard unless otherwise indicated. ^b At 70 eV. ^c Neat. ^d Hexane. ^e Acetonitrile. ^f Chloroform. ^g KBr. ^h DMF-*d*. ⁱ It was not possible to obtain satisfactory elementary analyses for XXIIIb probably due to the difficulty of achieving complete combustion. ^j Reference 57.

Variable-Temperature Nmr Studies of XV, XVI, and XVII. 4-Phenyl-2,4,6-triazatricyclo[5.2.2.0^{2,5}]undeca-3,5-dione, mp 210.5-212.5°, was prepared from reaction of 1,3-cyclohexadiene with 4-phenyl-1,2,4-triazoline-3,5-dione as previously described by Cookson, *et al.*,¹³ and hydrogenation of the adduct (EtOAc; Adams catalysts; 1 atm). All analytical data agree with the assigned structure. The nmr spectrum (CDCl_3) contained an A_2B_2 pattern centered at δ 2.01 (8 H), and absorptions at 4.57 (m, 2CHN) and 7.4-7.7 (m, 5 ArH). Variable-temperature nmr studies were carried out with a Varian HR-60 over the temperature range +40 to -60° (CDCl_3) and +40 to -85° (CD_2Cl_2). The A_2B_2 pattern at δ 2.0 showed no temperature dependence. *Anal.* Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$ (mol wt 257.2): C, 65.35; H, 5.88; N, 16.33. Found (mol wt 272 in THF): C, 64.80; H, 5.95; N, 16.64.

The reaction of 4-methyl-1,2,4-triazoline-3,5-dione (X) and anthracene was carried out in benzene using an excess of the dienophile. The reaction was complete in 3 hr at 25°. A portion of the adduct crystallized directly from the reaction mixture and the remainder was precipitated by addition of hexane. One recrystallization from chloroform hexane gave analytically pure material, mp 233-235°. The product was identified as 8,9,10,11-dibenzo-4-methyl-2,4,5-triazatricyclo[5.2.2.0^{2,5}]undeca-8,10-diene-3,5-dione by elemental and spectral analyses. The nmr spectrum (CDCl_3) had δ 2.83 (s, *N-CH*), 6.23 (s, 2CH), and an A_2B_2 pattern centered at δ 7.35 (5 H). The nmr signal of XVI in CDCl_3 at δ 7.35 was examined over the temperature range +40 to -50°. The A_2B_2 pattern was unchanged over this range. *Anal.* Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_2$ (mol wt 291.3): C, 70.09; H, 4.50; N, 14.43; O, 10.99.

Found (mol wt 300 in THF): C, 69.72; H, 4.50; N, 14.41; O, 11.14.

The nmr spectrum (CD_2Cl_2) of X^{32} at room temperature consists of resonances at δ 4.39 (m, 4 H), 4.91 (m, 2H), and 6.11 (m, 2 H) in addition to the aryl hydrogens at δ 7.5. The spectrum does show temperature-dependent features due to the occurrence of Cope rearrangements which exchange cyclopropyl and olefinic hydrogens. Even at -90° , however, the two hydrogens that remain olefinic throughout (δ 6.11) are equivalent indicating that the compound has a plane of symmetry.

Thermal Decomposition of the Diels-Alder Adducts (XI). The rates of the decomposition of XIa-c were examined by nmr spectroscopy in pyridine using either durene or anisole as internal standards. The singlet resonances of the methyl groups in azo compounds and the reference were monitored using both peak heights and area integrals. Plots of $\log C$ vs. time afforded straight lines indicating that the decompositions followed first-order kinetics; rates are shown in Table III.

In preparative runs the decompositions were carried out in chlorobenzene. Gas evolution was monitored through a bubbler. In the case of XIa, which was characteristic, 0.109 g of the adduct was dissolved in 1.5 ml of chlorobenzene and the solution heated rapidly. Gas evolution was complete by the time the mixture reached 130° (about 10 min). Removal of the solvent *in vacuo* and examination of the crude reaction mixture by nmr spectroscopy and tlc (silica gel; chloroform-methanol, 9:1) indicated the presence of a single product. The reaction mixture was worked up by column chromatography on Florisil (hexane-chloroform eluent). Sublimation of the residue (100° (0.01 mm)) afforded 0.068 g of colorless crystals, mp $110-112^\circ$. All of the analytical data are in agreement with the structure XIXa. Catalytic hydrogenation of 0.031 g of XIXa over Adams catalyst in ethyl acetate (1 atm H_2) gave a quantitative yield of dihydro product which was purified by two sublimations, mp $140-146.5^\circ$ (isomers). The hydrogenation product was assigned the structure 3-phenyl-6,7,7,8-tetramethyl-1,2,4-triazabicyclo[3.3.0]octa-2,4-dione on the basis of spectral and analytical analyses: 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, $J = 6.8$ Hz; 6 H), 3.63 (d, $J = 6.8$ Hz; 2 CHN), and 7.25-7.7 (m, 5 H). *Anal.* Calcd for $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_2$: C, 65.91; H, 7.06; N, 15.33; O, 11.71. Found: C, 65.91; H, 6.99; N, 15.55; O, 11.97.

Decomposition of XIc under analogous conditions afforded a 70% yield of a compound identified by spectral and elemental analyses as XIXc.

In the thermolysis of XI d (containing 2.1 D on the average) the product was not chromatographed but crystallized directly. The nmr spectrum (CDCl_3) of the product had absorption at δ 5.48 (d, $J = 2.5$ Hz; 0.26 H); 4.77 (s, 0.47 H), and 4.59 (d, $J = 2.5$ Hz, 0.26 H) for the benzylic and two methylene hydrogens. The product contains an average of 2.0 D. Neglecting complications due to the distribution of D in the starting material, the isotope effect is 2.0 ± 0.3 .

Decomposition of XIb afforded a complex mixture which was shown by tlc (silica gel; chloroform-methanol, 9:1) and nmr spectroscopy to contain at least four components. Column chromatography on Florisil (chloroform-hexane) effected partial separation of the mixture. Fractional crystallization of later fractions afforded colorless crystals, mp $230-231^\circ$, which were assigned structure XX on the basis of spectral and elemental analyses (see Table IV). None of the other products could be isolated. Analysis of the crude mixture by nmr (CDCl_3) and tlc established that the isopyrazole IXb was not present in significant amounts.

Thermolysis of either XIe or XI f in chlorobenzene or pyridine afforded closely similar product mixtures. A solution of 0.202 g of XIe was heated in 10 ml of chlorobenzene for 30 min. Removal of the solvent *in vacuo* gave an oil and some solids. Examination of these by tlc indicated the presence of one major (~80%) and two minor components. The major component was separated by column chromatography (Florisil; chloroform-methanol, 19:1) and identified as 4-benzyl-3,4,5-trimethylisopyrazole (IXe) by comparison of ir and nmr spectra with an authentic sample and by a mixture melting point determination. The isolated yield was 75 mg (70%).

Irradiation of Matrices Containing XI at Low Temperature. Samples of XIa-e (0.1 M) dissolved in fluorolube, pyridine, acetonitrile, or chlorobenzene were transferred by syringe to 2-mm quartz tubes which were then sealed off. The tubes were placed in a specially designed quartz dewar and irradiated for several minutes with a 450-W Hanovia medium-pressure mercury

arc through a Corning 7-54 filter. The dewar and sample were then placed in the esr cavity. In the case of XIb, c, and d spectrum characteristic of the triplet diradicals, XIIb, c, and d, respectively, were observed (see Table I), in addition to a strong central signal due to other carbon free radical species.⁵⁸ The esr studies of 1-phenyl-2,7,10,10-tetramethyl-2,4,6,8,9-tetraazatricyclo-dec-8-ene-3,5-dione⁵⁹ and of XXVI were conducted in the same way. The esr spectra of XIb, c, and d were unchanged over a 6-hr period at 77°K . Warming to 100° (annealing) resulted in complete disappearance of the esr spectra.

Samples of XIa and XIe were also irradiated under the conditions described above but did not yield observable concentrations of triplet diradicals. Irradiation of XIa and XIe at 4°K using a specially constructed, transparent helium dewar mounted in a liquid nitrogen dewar did, however, afford triplet spectra assignable to XIIa and XIIe, respectively (Table I). The esr spectra were unchanged during a 3-hr period at 4°K .

An nmr tube containing 0.040 g of XI f in 300 μl of DMF-*d*₇ was sealed under nitrogen, placed in a transparent Pyrex dewar, and cooled to 77°K with liquid nitrogen. The sample was irradiated with a 450-W Hanovia medium-pressure mercury lamp which was maintained a few inches from the dewar. The sample was periodically rotated to maximize exposure, and at 30-min intervals was removed and annealed at -60 to -70° . After 4 hr of irradiation the nmr spectrum (at -60°) contained absorptions due to starting material (65% had survived) but had new bands at δ 1.42 (s), 1.84 (s), and 2.8 (s) due to XXIf and at δ 0.90 (s), 1.69 (s), and 3.22 due to XXIe. The area ratio of the peaks at δ 1.84 and 1.69 was 10:1. Upon warming to 0° , resonances due to XXIf disappeared and those due to XXIe increased in intensity.

A medium-wall nmr tube containing 0.020 g of XI f in 300 μl of DMF-*d*₇ was evacuated (freeze-thaw), sealed, and irradiated at 4°K for 1.5 hr using the apparatus described above. Examination of the sample by nmr spectroscopy at -60° indicated that all of the starting material had been consumed and that XXIf and XXIe had been formed in a ratio of greater than 19:1.

Irradiation of XIa-f in Solution. A solution of 0.540 g (1.8 mmol) of XIa in 50 ml of benzene (freshly distilled from LAH) in a Pyrex flask was irradiated at 10° using a 450-W Hanovia medium-pressure lamp. The evolution of nitrogen was complete in 25 min. Removal of most of the solvent *in vacuo*, addition of dry hexane, and cooling resulted in crystallization. Two crops of off-white crystals were obtained by filtration in a glove bag 0.260 g (53%), mp $90-100^\circ$. Two recrystallizations from benzene-hexane afforded colorless crystals, mp $102-104^\circ$. All manipulations were carried out in an atmosphere of dry nitrogen since the product decomposed rapidly in the atmosphere. The photoproduct was assigned the structure 1,7,8,8-tetramethyl-2,4,6-triazatricyclo[5.1.0]octa-3,5-dione (XXIa) on the basis of spectral and elemental analyses. Examination of the photolysis mixtures by nmr spectroscopy did not reveal the presence of any other products. A solution of 0.055 g (0.18 mmol) of XXIa in 20 ml of benzene was treated at 25° with 0.030 g (0.2 mmol) of 4-phenyl-1,2,4-triazoline 3,5-dione (X); the red color of the solution faded slowly and was gone after 20 hr. Removal of the solvent *in vacuo* and trituration with ether afforded 0.149 g of a product which was homogeneous by tlc (silica gel; chloroform-methanol, 9:1). Recrystallization from chloroform-benzene afforded colorless crystals, mp $257.5-259^\circ$, which were characterized as the 1:1 adduct, XXIIIa, by spectral and elemental analyses.

The irradiation of XIb was carried out at -60° in a DMF- $(\text{CD}_3)_2\text{CO}$ mixture. Analysis of the irradiated solutions by nmr spectroscopy at -60° indicated the starting material had been completely consumed but showed only broad absorption in the high-field region. No attempt was made to isolate the photoproduct (XXIb). Addition of 0.035 g (0.23 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione (X) to a solution of 0.080 g (0.19 mmol) of XIb in 2 ml of a 1:1 mixture of acetone (dried over MgSO_4) and DMF (dried over Linde molecular sieves) that had been irradiated for 1 hr at -60° led to rapid decolorization (1 hr) of the solution. The temperature was kept below -50° until the solution was colorless. Removal of the solvents *in vacuo* and recrystallization from methylene chloride-benzene afforded 0.075 g (70%) of off-white crystals; examination of the crude reaction mixture by tlc revealed

(58) A strong central signal was also observed by Dowd in spectra obtained by irradiation of 3-methylenepyrzoline (see ref 13).

(59) Prepared from 3-phenyl-4,4,5-trimethylisopyrazole and 4-methyl-1,2,4-triazoline-3,5-dione. All analytical data were in accord with this structure.

only traces of other products. One recrystallization gave 0.059 (55%) of colorless material, mp 332° dec. Spectral and analytical data were in agreement with the structure XXIIIb.

Irradiation of solutions of XIc in $(\text{CD}_3)_2\text{CO}$ at temperatures below -20° resulted in the rapid evolution of nitrogen and formation of a single photoproduct, on the basis of low-temperature nmr studies. Similar results were obtained when chlorobenzene, fluorobenzene, pyridine, or acetonitrile were utilized as the solvent. No attempt was made to isolate XXIc since the compound appeared from the nmr studies to have limited stability at $T > 25^\circ$. A solution of 1.0 g (4 mmol) of XIc in 100 ml of chlorobenzene (distilled from CaH_2) was irradiated for 1 hr at -25° and then treated in a dropwise fashion with 4-phenyl-1,2,4-triazoline-3,5-dione (X) until the red color of the azo compound persisted. About 3 mmol of the azo compound reacted within 20 min at -25° . Removal of the solvent and crystallization of the nonvolatile residue afforded 0.97 g (65%) of crystalline material, mp 200–205°. One recrystallization from chloroform–hexane afforded analytically pure material, mp 211–213°, which was assigned structure XXIc.

Irradiation of solutions of XIe under conditions similar to those utilized for XIc afforded a single photoproduct XXId in high yield. The nmr spectrum was identical with that of XXIc except for the absence of absorption at δ 1.78.

A solution of 0.019 g of XIe in 200 μl of DMF- d_7 in a Pyrex nmr tube was irradiated at -60° . The reaction mixture was examined by nmr spectroscopy at -60° and found to contain only three high-field absorptions, at δ 0.90, 1.69, and 3.22; the spectrum was unchanged on warming to 39° . Removal of the solvent *in vacuo* with care taken to exclude moisture and air, addition of acetone, and concentration led to formation of off-white crystals. Recrystallization from acetone afforded crystalline material, mp 129°. Analytical data indicate the structure XXIe for the photoproduct. A solution of 0.080 g (0.22 mmol) of XIe in 1 ml of acetone (dried over molecular sieves) was irradiated for 30 min at 10° and then treated with 0.040 g (0.22 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione, X. Decolorization was slow at 10° but complete within several hours at 25° . Removal of the solvent *in vacuo* afforded an amorphous solid which was crystallized from methanol. Recrystallized material, 0.065 g (54%), had mp 194° and was identified as XXIIIe.

A solution of 0.019 g of XIe in 200 μl of DMF- d_7 in a Pyrex nmr tube was irradiated for 45 min at -60° . Examination of the nmr spectrum of the irradiated solution at -60° revealed the absence of starting material and the presence of 1:4 mixture of XXIf and XXIe (see discussion of irradiations in matrices above). Attempts to isolate or derivatize XXIf were unsuccessful due to its thermal instability.

Isomerization of XXI. The rate of isomerization, XXIa \rightleftharpoons XXIa, was determined by the technique of magnetization transfer in the manner described by Fung.⁶⁰ The results appear in Table II. A solution of 0.050 g of recrystallized XXIa in 200 μl of chlorobenzene in an nmr tube was heated at 120° and kept at that temperature for 20 min. Examination of the sample's nmr spectrum revealed none of the absorptions of the starting material; all of the bands that were present could be assigned to XIXa (see Table IV). The nmr spectrum and tlc (silica gel; chloroform–methanol, 9:1) indicated the presence of only minor amounts of products other than XIXa.

A solution of 0.020 g of XIb in 250 μl of DMF- d_7 in an nmr tube was irradiated at -60° for 3 hr. The nmr spectrum of the solution at -60° showed only broad absorption in the high-field region. Attempts to observe the spectrum at $T < -60^\circ$ were thwarted by the inhomogeneity of the samples. Analysis of the reaction mixture at 25° by nmr (CDCl_3) and tlc (silica gel) indicated a complex mixture of products similar to that obtained from the thermal decomposition of XIb. Fractional crystallization of the photolysate

afforded 5 mg of crystalline material, mp 228° , which was shown by ir and a mixture melting point determination to be XXb.

An nmr tube containing 0.080 g of XXIc in 250 μl of CD_3CN sealed under nitrogen was irradiated for 40 min at -40° . The nmr spectrum of the irradiated sample in the range -20 to $+30^\circ$ consisted of sharp singlets (equal peak heights) at δ 0.91, 1.70, and 1.93, in addition to the aryl absorption. At 35° , the two highest field singlets were broadened, while the resonance at δ 1.93 remained sharp. At 45° the height of the peaks at δ 0.91 and 1.70 was substantially decreased, and absorptions due to the olefin, XIXc, were evident at δ 0.95 and 1.43. Cooling the sample to 0° caused the absorptions at δ 0.91 and 1.70 to become sharp again; absorptions at δ 0.95 and 1.43 due to XIXc were also discovered. Similar behavior was observed when acetone- d_6 was the solvent; in that case broadening of the high-field methyls was apparent at temperatures as low as 30° . The rate of the isomerization XXIc \rightleftharpoons XXIc was determined in the manner described for XXIa; the results are shown in Table II.

A solution of 0.050 g of XXIc in 250 μl of CD_2Cl_2 in an nmr tube was maintained at 25° and its nmr spectrum evaluated periodically at 20° . Absorptions due to XXIc were observed to decline slowly and new peaks assignable to XIXc emerged. Complete conversion to XIXc required about 1 day. Samples of XXIc in either CD_3CN , acetone- d_6 , or pyridine were placed in the nmr probe and slowly heated to 50° ; at that temperature conversion to XIXc was rapid (< 1 hr). In one case, the solvent was removed *in vacuo* and the product identified as XIXc by comparison of ir spectrum and mixture melting point determination.

A solution of XXIe prepared by the irradiation of 0.020 g of XIe in 250 μl of DMF- d_7 in an nmr tube at -60° was placed in the probe of an A-60 nmr and gradually warmed from -60 to $+39^\circ$. The spectrum did not change over that range of temperature. Heating a solution of 0.056 g of XXIe in 250 μl of chlorobenzene for 1 hr at 90° resulted in the complete disappearance of XXIe on the basis of nmr spectroscopy. The new absorptions which appeared in the nmr of the reaction mixture were assignable to XIXe; the widely separated doublets for the two vinylic hydrogens, which occurred at δ 3.61 and 5.43, were especially characteristic. Removal of the solvent and crystallization of the residue from chloroform–hexane afforded 0.018 g of colorless crystals, mp 168 – 171° ; these were identified as XIXe. Despite the low isolated yield, nmr and tlc indicate clean transformation of XXIe to XIXe.

The 1:4 mixture of XXIf and XXIe obtained by irradiation of 0.19 g of XIe in 250 μl of DMF- d_7 was maintained at -60° and examined periodically by nmr spectroscopy (at -60°). There was no change in the spectrum during a 7-hr period. Gradual warming of the sample in the nmr probe resulted in isomerization of XXIf \rightarrow XXIe; the isomerization was occurring at a visible rate at -32° , and at -5° the half-life of XXIf is less than 30 min.

Irradiation of a solution of 0.105 g of XIe in 0.5 ml of chlorobenzene for 1 hr followed by warming to 90° for 1 hr afforded primarily a single product, on the basis of nmr and tlc analysis of crude reaction mixtures. Removal of the solvent *in vacuo* and recrystallization of the residue from methanol afforded 0.037 g (38%) of colorless crystals, mp 169.5 – 172° . These were assigned structure XIXe on the basis of elemental and spectral analyses (see Table IV). No other products could be isolated from the reaction mixture.

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