

THE ELECTRONIC EXCITED STATES OF SMALL RING COMPOUNDS: HETEROBICYCLOPENTANES

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ABSTRACT

Intermediates (trimethylenes) formed upon bond cleavage of three-membered rings are usually too unstable for direct characterization. They may, however, be stabilized by substitution and by incorporation into a cyclic system where the ring closed form is strained and conrotatory closure of the trimethylene is inhibited. These principles have been applied to two heterobicyclo[2.1.0]pentane systems.

The trimethylene intermediates resulting from irradiation of substituted 2,4,6,8,9-pentazatricyclo[5.2.0^{2,6}]dec-8-ene-3,5-diones (X a-d) are triplets (XI) and are stable at low temperature. Some reactions of the ring closed form (XII) demonstrate that the central bond is weak. Ring inversion of (XII) occurs at low temperature.

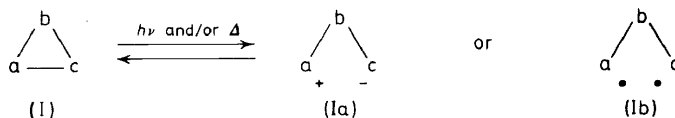
Derivatives of 5-oxabicyclo[2.1.0]pentane (XIII) are thermo- and photochromic (direct and sensitized irradiation), the result of cleavage of the central bond. The carbonyl ylide (XIV) formed is relatively stable and reverts back to the oxide with a half-life equal to 8 minutes in benzene solution at 22°. Dipolarophiles react readily with the carbonyl ylide to give cycloaddition products.

The trimethylene singlet and triplet are related to the corresponding three-membered ring by heterolytic and homolytic bond cleavage†. Consider the general case with combinations and permutations of carbon and heteroatoms¹. Many of the possible trimethylene singlets are stable, particularly if atom *b* bears an unshared pair of electrons and is thus capable of delocalizing the positive charge. When this is the case, irradiation of the trimethylene singlet frequently leads to formation of the three-membered ring².

Few examples of triplet trimethylenes have been characterized; however, they have frequently been proposed as intermediates in photochemical and thermal reactions of three-membered rings³.

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† The term trimethylene is used here in a generic sense. There are two classes of trimethylene: (1) a singlet species where the two electrons interact with one another and have the opposite spin (e.g. a 1,3-dipole); (2) a triplet species where the two electrons interact and have the same spin. When the two electrons are only three atoms apart it is unlikely that the interaction between the two can be negligible so that the quantization of each is independent of the other (i.e. a biradical).



The object of this programme was to study the interconversion of the trimethylene singlet and triplet and the three-membered ring. An understanding of these processes would be useful not only in regard to these species, but could have implications in the more general intersystem crossing and internal conversion processes between the electronic excited states and ground state of other types of molecules as well.

Our approach has been to choose systems (cyclopropane and oxirane) where the three-membered ring is usually the stable form and then stabilize the trimethylene relative to the ring closed form through substitution and relief of strain. Such a trimethylene should be stable enough to be detected and characterized.

BICYCLO[2.1.0]PENTANE

Photo-⁴ and thermal⁵ *cis*⇌*trans* isomerization of substituted cyclopropanes is believed to involve an intermediate trimethylene. The activation energy of the thermal process depends strongly on the substitution. A few examples are given in Table 1.

Table 1. The thermal *cis* ⇌ *trans* isomerization of some substituted cyclopropanes

Cyclopropane	Activation energy (kcal/mole)	Reference
<i>trans</i> -dideutero	64.2	6
<i>cis</i> -dimethyl	59.4	7
<i>cis</i> -diphenyl	33.5	8
2-methylbicyclo[2.1.0]pentane	38.9	9

A secondary radical is more stable than a primary radical and a benzylic radical is still more stable; thus, the decreased activation energy of the isomerization reaction can be attributed to stabilization of the transition state through substitution. Competing with this isomerization reaction is 1,2-hydrogen migration which must be prevented if a stable trimethylene is desired.

Further stabilization of the trimethylene (relative to the three-membered ring) can be achieved by choosing a system where the ring closed molecule is strained and this strain is largely relieved upon bond cleavage. Bicyclo[2.1.0]pentane is the system of choice since bicyclo[1.1.0]butane, although more highly strained, cleaves in a concerted fashion to the 1,3-diene, leaving the central bond intact^{*10}.

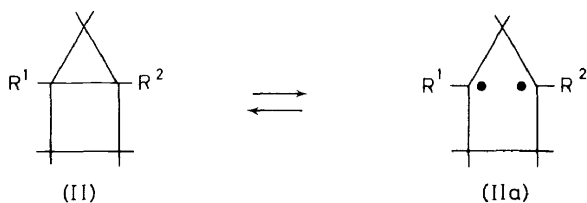
The strain energy of bicyclo[2.1.0]pentane has been calculated to be 53.6 kcal/mol¹¹. This strain should largely be relieved upon cleavage of the

* The central bond of bicyclo[1.1.0]butane does cleave when diphenyl substituted [R. B. Woodward and D. L. Dalrymple, *J. Am. Chem. Soc.* **91**, 4612 (1969)].

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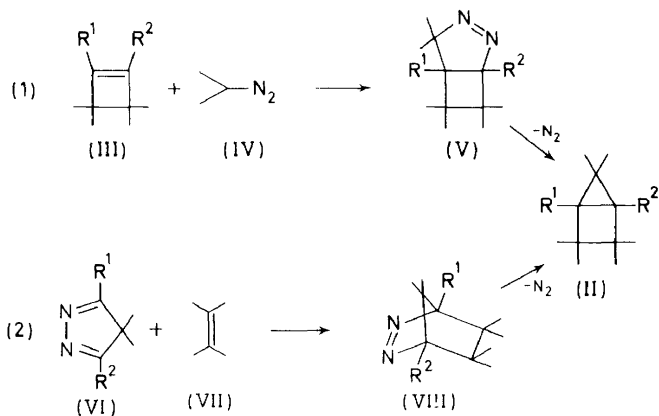
central bond. Comparison of the rate of isomerization of the bicyclo[2.1.0]pentane with that of analogous *cis*-dimethylcyclopropane reflects this influence. It should be pointed out that bond cleavage of cyclopropane can be a concerted conrotatory process^{1,2}. Bicyclo[2.1.0]pentane is prevented from undergoing this mode of reaction; thus, to the extent that a concerted pathway is followed for the opening of cyclopropane, the actual influence of the strain energy may be even larger.

If the influence of substituents and strain are additive, the 1,3-diradical (IIa) with $R^1 = R^2 = C_6H_5$ will be relatively close in energy to the ring closed form (*ca.* + 8.2 kcal/mole*).



A synthetic approach was required which would provide the bicyclo[2.1.0]pentane (II) with a variety of substituents (most interesting when R^1 and $R^2 = C_6H_5$) and also yield a bicyclopentane without the possibility of competing hydrogen migration. Two approaches have been considered (Scheme I).

Scheme I. Synthetic approaches to bicyclo[2.1.0]pentane

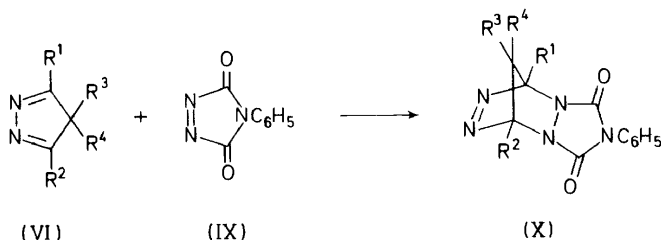


Starting with the appropriately substituted cyclobutene (III) and adding the *gem*-dimethyl group would yield (II). The desired 1,2-diphenyltetramethylcyclobutene is readily available from the photocycloaddition of diphenylacetylene to tetramethylethylene¹³. Attempts to add 2-diazopropane¹⁴ (IV) to this cyclobutene have thus far failed. Other methods for introducing the *gem*-dimethyl group will be attempted.

* This estimate is based on the assumption that diphenyl substitution will have the same influence on the bicyclo[2.1.0]pentane as it has on cyclopropane.

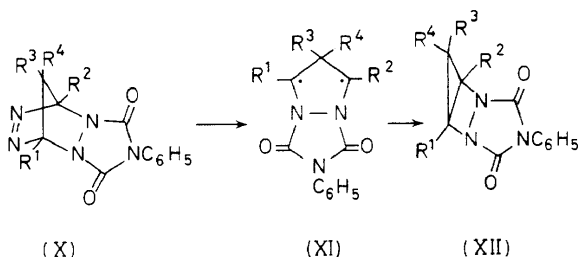
The second approach utilizes isopyrazoles (VI) as cyclic dienes in the Diels–Alder reaction to give the 2,3-diazobicyclo[2.2.1]hept-2-ene derivative (VIII). Decomposition of the parent member in this series, is known to yield bicyclo[2.1.0]pentane⁹, and a variety of derivatives would be available since isopyrazoles are readily prepared. Furthermore, this route is attractive because the intermediate in the decomposition of the azocompound (VIII) may be the desired trimethylene.

Unfortunately this Diels–Alder reaction proceeds only with the most powerful of dienophiles. Treatment of the isopyrazoles (VI) (a–d) with 4-phenyl-1,2,4-triazoline-3,5-dione (IX) does, however, give the adducts (X) (a–e) in good yield. The synthesis and properties of these adducts are reported elsewhere¹⁵; only those properties pertinent to the present discussion of trimethylene will be summarized here. It must also be kept in mind that in the discussion that follows the influence of the urazole is uncertain; further attempts to prepare (II) are being made.



- (a) $R^1 = R^2 = R^3 = R^4 = \text{CH}_3$
 (b) $R^1 = R^2 = \text{C}_6\text{H}_5$; $R^3 = R^4 = \text{CH}_3$
 (c) $R^1 = \text{C}_6\text{H}_5$; $R^2 = R^3 = R^4 = \text{CH}_3$
 (d) $R^1 = R^2 = R^3 = \text{CH}_3$; $R^4 = \text{CH}_2\text{C}_6\text{H}_5$
 (e) $R^1 = R^2 = R^4 = \text{CH}_3$; $R^3 = \text{CH}_2\text{C}_6\text{H}_5$

Photochemical decomposition of the azocompounds (X) (b and c) at 77 K, and of (X) (a and d) at 4 K leads to a triplet species as evidenced by the characteristic e.s.r. spectrum attributed to the perpendicular and parallel signals and absorption at half-field strength for the $\Delta M = \pm 2$ transition. The zero-field splitting parameters are in accord with structures (XI) (a–d)¹⁶.



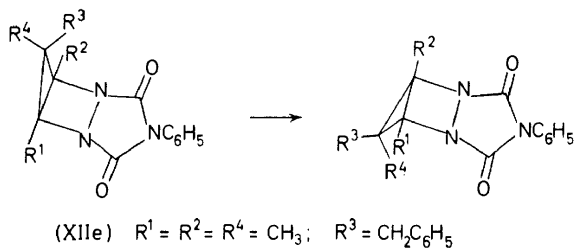
The triplet species are stable at low temperature indicating that the triplet state is either the lower energy state, or is close enough in energy to the singlet trimethylene that a significant population of triplet exists in thermal equilibrium with the singlet at these low temperatures¹⁷. No signal

was observed from (XII) (a-d) under these conditions and the signals due to (XI) disappeared irreversibly upon warming the sample. These results imply that there is an activation energy for the formation of the central bond from the triplet (XI); however, it is difficult to rule out a geometrical restraint for reaction imposed by the rigid medium.

The observation and characterization of these triplet species was one objective of this work. Definition of the role of these species during the reactions of the azocompound (X) and the ring closed form (XII) is more difficult. If the photodecomposition of (X)(e) is carried out at low temperatures 4–77°K (the triplet signal was not observed at 77°K), the tricyclic system (XII) (e) initially obtained has the *inverted* structure. That is, starting with the benzyl substituent over the azo linkage, the decomposition product has the benzyl group *endo*-cyclic. Since there seems little reason to suspect the triplet species (XI) other than flat (or nearly flat and flipping at the radical positions), this result implies that (XI) is not involved along the major pathway to the inverted product (XII).

The inverted structure may arise from decomposition of the singlet azocompound with bond formation occurring before the nitrogen can diffuse away. The triplet species would then derive either from those molecules of azocompound which have undergone intersystem crossing before decomposition or through intersystem crossing of the singlet species before bond formation. Experimental difficulties (i.e. solubility, low temperature, n.m.r. detection) have prevented sensitizer studies which would distinguish between these possibilities.

The isomer with the benzyl group *endo* is more hindered than the *exo* isomer and in fact isomerizes at -5° to the *exo*-isomer which is then stable at room temperature and can easily be isolated.



The other derivatives of (XII) also invert around the central bond at a temperature dependent upon the bridge-head substituents (i.e. rate of inversion for diphenyl > phenyl, methyl > dimethyl). It seems unlikely that the triplet is an intermediate in this inversion process since no e.s.r. signal is observed under these condition. The low temperature at which these inversions take place attests to the validity of the original hypothesis that the central bond is weakened by substituents capable of stabilizing the trimethylene and by strain in the ring closed molecule.

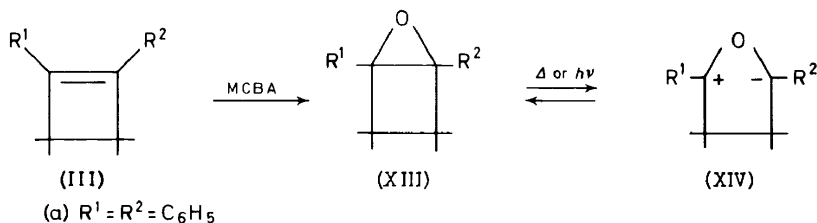
5-OXABICYCLO[2.1.0]PENTANE

The same type of substituent and strain effects can be expected with the oxirane system. To the extent that the strain energy of a bicyclic system can

be estimated by adding the strain energy of the component rings, bicyclo[2.1.0]pentane and 5-oxabicyclo[2.1.0]pentane have essentially the same strain energy, i.e. 53.5 kcal/mole and 53.3 kcal/mole respectively^{11,18}.

Cleavage of the central bond of 5-oxabicyclo[2.1.0]pentane, however, results in formation of a species where the central atom (b in the generalized picture above) bears a pair of non-bonding electrons. Thus, the singlet trimethylene form is further stabilized by delocalization of the positive charge on to oxygen giving a carbonyl ylide structure. The decrease in energy that results from delocalizing only one electron in the triplet trimethylene form is not as great.

The same two synthetic approaches considered above for the cyclopropane series were applied to this system. In this case, however, 2,5-diphenyl-1,3,4-oxadiazole was unreactive in the Diels-Alder reaction even with the triazolinonide (IX). On the other hand, the oxidation of 1,2-diphenyl-tetramethylcyclobutene (III) (a) with *m*-chloroperbenzoic acid occurs readily to give the 5-oxabicyclo[2.1.0]pentane (XIII) (a) system¹⁹.



This molecule (XIII) (a) is photo- and thermo-chromic, the result of heterolytic cleavage of the central bond and formation of the singlet 2-oxa-trimethylene (carbonyl ylide) (XIV) (a). This carbonyl ylide is relatively stable and reacts with a first order rate constant ($t_{1/2} = 8$ min at 22 °C, benzene) presumably to give back the starting oxide. In contrast the analogous acyclic carbonyl ylides from monocyclic oxiranes are stable only at low temperatures²⁰. Here again the closure of a carbonyl ylide can be a concerted conrotatory thermal process²¹ which is prohibited when a *trans*-fused bicyclo[2.1.0]pentane results. Thus, the closure of the acyclic and cyclic carbonyl ylides may involve different mechanisms.

Before assigning the carbonyl ylide structure to the coloured species we looked to see if we could detect an e.s.r. signal from the coloured solution. A freshly prepared and degassed solution of the 5-oxabicyclo[2.1.0]pentane was cooled to 77 K and irradiated (2537 Å) until highly coloured. A weak e.s.r. signal was observed for a free radical (~ 3250 G) but no signal for a triplet. When this sample was allowed to warm to room temperature, the colour disappeared, and the e.s.r. signal became more intense. The rate of formation of the radical is approximately the same as the rate of disappearance of the coloured species. This was shown by irradiation of the solution at room temperature until the sample was highly coloured and then following the increase of the e.s.r. signal as the colour disappeared. These results show that the coloured species does not have a detectable e.s.r. signal but decomposes, in part, to give a stable radical of unknown structure. The hyperfine splitting pattern for the radical is dependent upon the solvent and upon substitution

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in the phenyl rings. The salient features of these spectra are summarized in Table 2. In none of these cases have we seen evidence for a triplet species.

Table 2. The carbonyl ylide reacts to give a free radical

	$t_{1/2} = 8 \text{ min} \quad (R^1 = R^2 = \text{C}_6\text{H}_5)$ $\xrightarrow[22^\circ]{\text{C}_6\text{H}_6}$	
<u>Derivative(solvent)</u>	<u>e.s.r. spectrum</u>	
Unsubstituted(C_6H_6 or C_6D_6)		
(decalin)		
(diglyme)		
4,4'-dibromo (C_6H_6)		

In an attempt to prepare the triplet, the photosensitized reaction of the 5-oxabicyclo[2.1.0]pentane has been studied. Irradiation, through a Pyrex filter, of a solution of (XIII)(a) with xanthone(triplet energy = 74.2 kcal/mole) or acetophenone (73.6 kcal/mole) present as sensitizers led to formation of the colour characteristic of (XIV). This was the case even at 4 K (acetophenone solution). There was no signal for a triplet species in the e.s.r. spectrum of an acetophenone sensitized irradiation at 77 K: a short-lived triplet could, however, have gone undetected. These results leave unanswered the question as to where along the reaction coordinate the intersystem crossing process occurs. It seems probable that the triplet species is formed initially and that intersystem crossing to the carbonyl ylide is fast even at 4 K.

CONCLUSIONS

Trimethylene singlets and triplets which are usually too unstable to be detected can be made more stable, relative to the three-membered ring, through substitution and relief of strain in the ring closed form. Thus the lifetimes of these species are extended so that they may be characterized by conventional spectroscopic methods.

ACKNOWLEDGEMENT

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