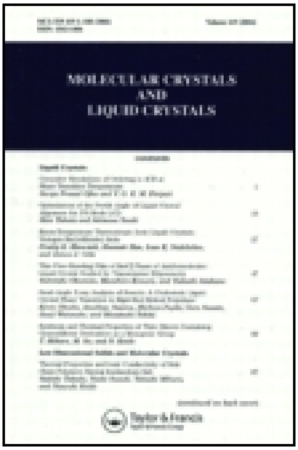

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4-Methylenecyclopentane-1,3-Diyl

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4-METHYLENECYCLOPENTANE-1,3-DIYL

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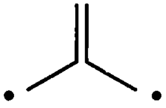
Abstract: The semilocalized diradical, 4-methylenecyclopentane-1,3-diyl, **18** has been prepared by photolysis of 2,3-diaza-5-methylenebicyclo[2.2.1]hept-2-ene (**15**). The adduct of cyclopentadiene and di-*t*-butyl azodicarboxylate was carboxylated with carbon monoxide and palladium chloride in methanol yielding the diester **8** and the chloro ester **9**. The latter was reduced with tri-*n*-butyltin hydride to the ester **10**, then with lithium borohydride to the corresponding carbinol. Formation of the mesylate was followed by potassium *tert*-butoxide promoted elimination to the exocyclic methylene derivative **13**. Trifluoracetic acid treatment removed the protecting *tert*-butyloxycarbonyl groups yielding the unstable hydrazine, which underwent spontaneous air oxidation to the desired azo compound **15.**

The diradical **18** was shown to be a ground-state triplet by Curie-Weiss Law analysis; **18** has zero field parameters D/hc=0.0591 cm^{-1} and E/hc=0.00254 cm^{-1}. The latter value was obtained from the fully deuterated diradical **18-d_8**.

The diradical **18** is converted by photolysis at 340-400 nm to the trimethylenemethane derivative, 2-methylenecyclopentane-1,3-diyl, **16**.

INTRODUCTION

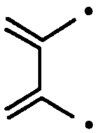
The direct experimental observation of the open-chain diradical trimethylenemethane[1,2] opened the way to a detailed examination of the



Trimethylenemethane

electronic structures and properties of a remarkable series of conjugated and unconjugated 1,3- and 1,4-diradicals using electron spin resonance spectroscopy. This powerful tool makes possible the assignment of structure and, in favorable instances, symmetry to the diradicals, as well as the establishment of the singlet or triplet character of the ground states. Trimethylenemethane is clear-cut; theory at all levels predicts a triplet ground state, and this has been confirmed by the observation of linear Curie-Weiss plots of spectral intensity versus inverse temperature for a derivative[3a] and for the parent trimethylenemethane.[3b]

With the tetramethyleneethane systems the situation is interesting and complex. Theoretical calculations[4] predict that tetramethyleneethane **1** should be a ground state singlet. Tetramethyleneethane (**1**),[5] the 2,3-dimethylenecyclohexan-1,4-diyl (**2**)[6] and the 5,5-dimethyl-2,3-dimethylenecyclopentan-1,4-diyl (**3**)[7] all yield linear Curie-Weiss plots. This set of experiments provides strong evidence that all three are ***ground state triplets*** and demonstrates that the tetramethyleneethane triplet state is not sensitive to the degree of twist about the central carbon-carbon bond.



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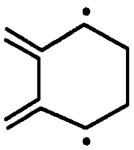

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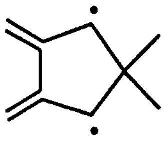

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The lack of splitting of the *xy*-line in the electron spin resonance spectrum of either the parent **1**[5] or the fully deuterated diradical **1-d$_8$** (Figure 1) suggests that the parent tetramethyleneethane **1** is twisted about the

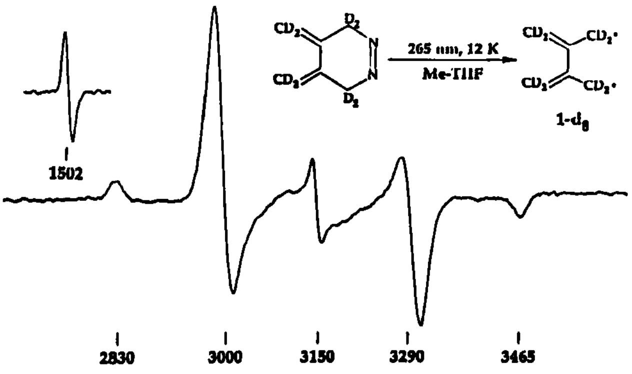
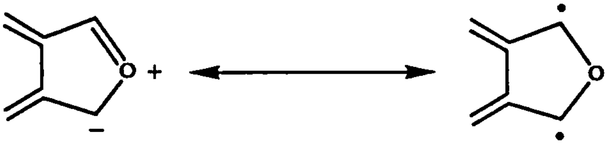


FIGURE 1. ESR spectrum of triplet tetramethyleneethane-d$_8$ (**1-d$_8$**).

central bond and probably has D_{2d} symmetry. The six-membered diradical 2,[6,8] in its most stable configuration, is twisted 25° about the central bond[9] while the five-membered diradical 3 is planar.[9] Given the variation in shape among the three diradicals, it is highly unlikely that all three diradicals are accidentally degenerate within 50 cal. Such a coincidence could also give rise to a linear Curie-Weiss plot.[10]

The heterocycle 4, and its sulfur analogue, have also been put forward

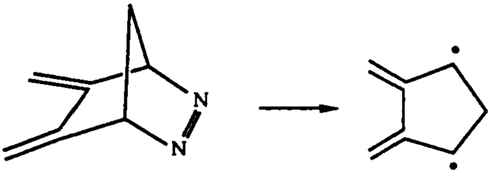


4

as tetramethyleneethane models.[11] Since 4 is a ground state singlet molecule, this has been taken as confirmation of the theoretical position[4] regarding the multiplicity of tetramethyleneethane. Implicit in this argument is the assumption that the oxygen atom causes little perturbation of the electronic structure of 4. If so, replacement of the oxygen by an atom which does not possess conjugating lone pairs should lead to an analogue with similar properties. That 3 is a ground state triplet[7] demonstrates that the assumption of a non-interacting oxygen in 4 is not well founded.

RESULTS

We have also been trying to examine this point with the synthesis of the parent five-membered diradical 5 from the azo compound 6. Although

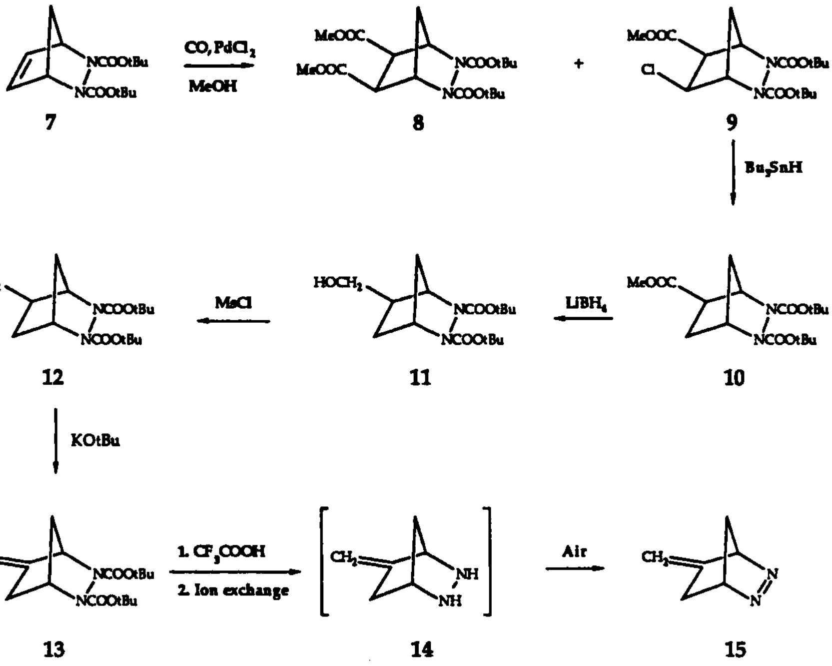


6 5

we have observed a triplet electron spin resonance spectra attributable to 5 on several occasions, the spectrum is not yet reproducible. However, research into the properties of a new 1,3-diradical may shed some light on these difficulties.

In order to prepare the azo precursor **6**, the adduct **7** of cyclopentadiene and di-*t*-butyl azodicarboxylate was carboxylated with carbon monoxide, palladium chloride and methanol.[12,13] The reaction yielded two principal products, the diester **8** and the chloroester **9** (Scheme 1). The diester **8**

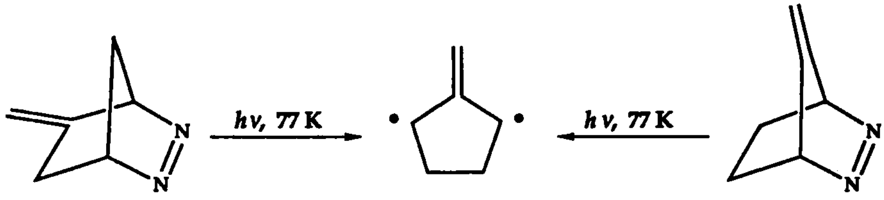
Scheme 1



was carried forward to the azo diene **6** by standard procedures.

The chloroester **9** was most interesting. We envisioned that this might be a precursor to a novel homotrimethylenemethane 1,3-diradical. Therefore, as outlined in Scheme 1, **9** was reduced with tri-*n*-butyltin hydride to the monoester **10**. Treatment of **10** with lithium borohydride yielded the carbinol **11**, which was converted to the mesylate **12** then subjected to elimination with potassium *tert*-butoxide. The resulting olefin **13** was treated with trifluoroacetic acid to remove the protecting *tert*-butyloxycarbonyl groups. The hydrazine **14**, obtained following ion exchange treatment, underwent spontaneous air oxidation to yield the desired azo compound **15**.

When **15** was irradiated at 77 K, the rearranged trimethylenemethane (D' = 285 G) **16** was observed. The latter value and the triplet esr spectrum from which it is derived are in full agreement with those obtained by Platz et al. from photolysis of 7-methylene-2,3-diazabicyclohept-2-ene **17**.[14] Photolysis of **15** in ethanol glass at 15 K yielded the esr spectrum shown in Figure 2. The most prominent part of the spectrum in Figure 2 shows the trimethylenemethane diradical **16** with D' = 285 G, but evident in the wings of the spectrum are two peaks corresponding to a diradical with a value of D' = 635 G. It seemed likely that this was the semilocalized diradical **18** (see Figure 2). Longer irradiation of the sample resulted in the slow decrease and eventual disappearance of **18**, indicating that **18** might be photochemically labile. Exploring other matrices, we discovered that photolysis of **15** in chloroform, isopentane or methylcyclohexane matrices yielded the new



15 **16** **17**

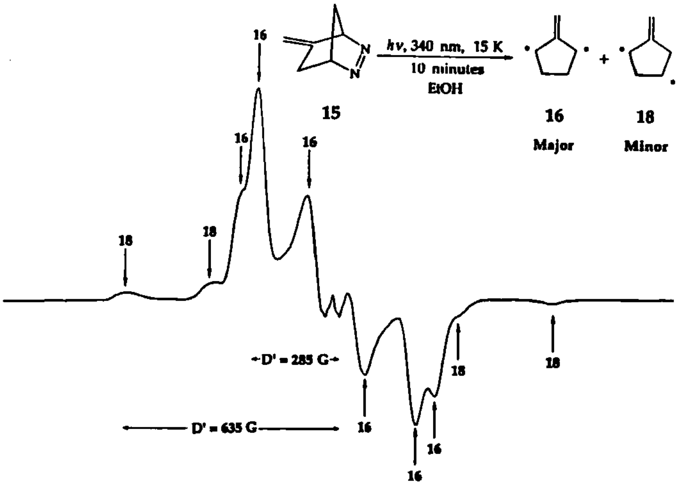
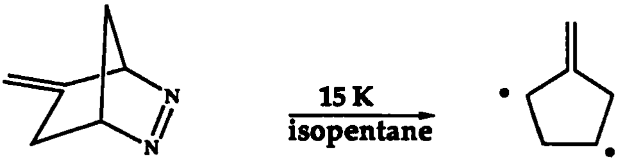


FIGURE 2. ESR spectrum from photolysis of **15** at 15 K in ethanol.

semilocalized diradical **18** with little contamination by **16**.



15 **18**

The esr spectrum of **18** in a methylcyclohexane matrix is shown in Figure 3.

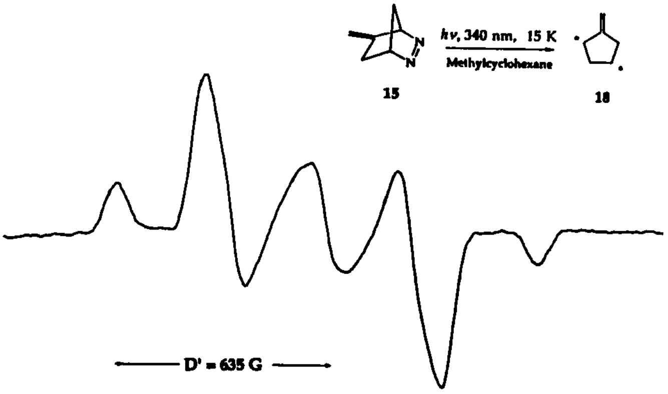


FIGURE 3. ESR spectrum of 4-methylenecyclopentane-1,3-diyl (**18**).

When a dilute sample of **15** (1 mg/0.3 mL) in isopentane was irradiated, for one minute, the esr spectrum resembled that obtained from the ethanol sample shown in Figure 2. Thus, absorption of light by the azo compound **15** at 340 nm serves as a filter for the diradical **18**, slowing conversion to the trimethylenemethane **16**. Accordingly, concentrated solutions of **15** yield satisfactory preparations of **18**, although solutions in ethanol must be extremely concentrated to give good results.

From this point it was a short step to exploring the photochemistry of the semilocalized diradical **18**. When **18** was irradiated at 340 nm, the trimethylenemethane diradical **16** increased in intensity at the expense of the semilocalized diradical **18**. However, at this wave length one cannot rule out the direct photochemical conversion of the azo precursor **15** to the trimethyleneethane **16**, bypassing **18**. When the irradiation wavelength was changed to 400 nm, where the azo compound is not photoactive, the semilocalized diradical 18 is smoothly converted to the trimethylenemethane 16 (Figure 4). This observation implicates the allyl radical as the chromophore in the phototransposition.

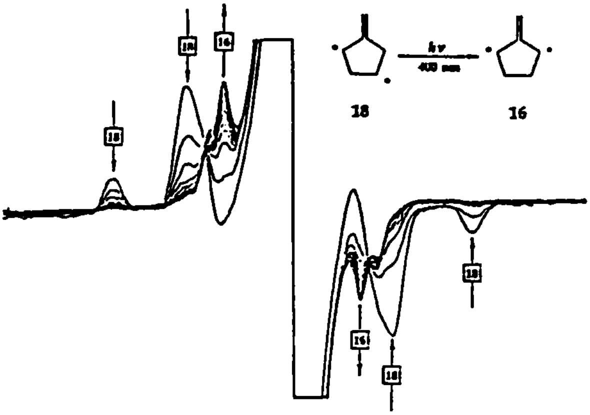


FIGURE 4. Phototransformation of 18 to 16.

This photochemical transformation (18 ⟶ 16) appears to involve a 1,2-hydrogen shift to a radical center. In order to explore the question whether tunneling plays a role in the rearrangement, we prepared the fully deuterated semilocalized diradical 18-d_8. The synthesis of Scheme 1 was followed using cyclopentadiene-d_6 as a starting material and carrying out the reduction to the carbinol 10 using $LiBD_4$. The electron spin resonance spectrum of 18-d_8 is shown in Figure 5. Because of the smaller deuterium hyperfine coupling the lines are narrowed, permitting observation of the splitting between the *x*- and *y*-lines and the assignment of an E value to 18. Accordingly, the zero field parameters for 18 are: D = 0.0591 and

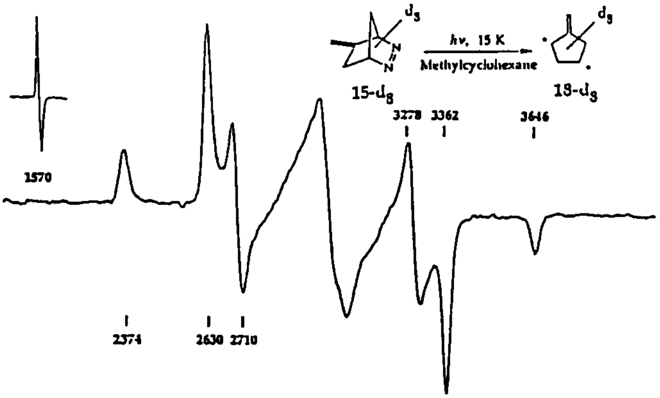


FIGURE 5. ESR spectrum of 4-methylenecyclopentane-1,3-diyl-d_8 (18-d_8).

$E = 0.00254\ cm^{-1}$. The magnitude of the D value is in excellent accord with expectation; it lies approximately halfway between the fully delocalized trimethylenemethane ($D = 0.025\ cm^{-1}$)[1,14] and the fully localized cyclopentan-1,3-diyl ($D = 0.084\ cm^{-1}$) of Buchwalter and Closs.[15]

A Curie-Weiss plot of spectral intensity of the deuterated analogue **18-d_8** versus inverse temperature gives the straight line plot shown in Figure 6.

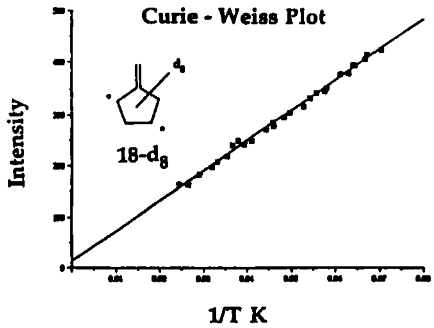
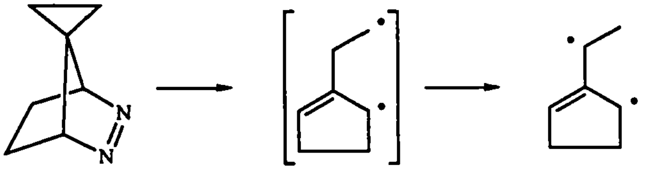


FIGURE 6. Curie-Weiss plot of spectral intensity versus inverse temperature for 18-d_8.

Accordingly, **18** is most probably a ground state triplet.

The photochemical behavior of **18-d_8** was the same as that of **18**. Thus, photolysis of **18-d_8** led readily to **16-d_8** with no obvious slowing of the change as a consequence of deuteration.

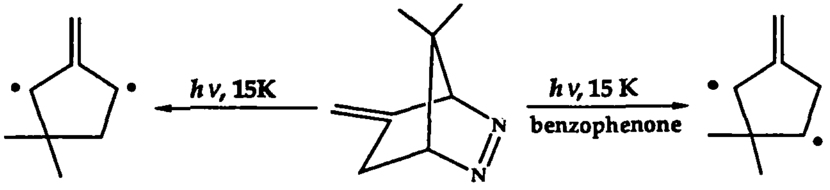
A recent very interesting elucidation of the mechanism of the rearrangement of the azo compound **19** to the trimethylenemethane **21**



19 **20** **21**

postulated a tunneling reaction in the final hydrogen shift of the semi-localized 1,4-diradical **20**.[16] However, this reaction also showed little influence of deuteration. Accordingly, we suggest that a photochemical reaction might also be important here.

The dimethyl analogue **22** of the azo compound **15**, when photolyzed under oxygen, yielded little or no peroxide product.[17] It was concluded that



23 **22** **24**

the diradical formed from photolytic nitrogen extrusion was probably not a triplet state molecule, otherwise, it would have been trapped by oxygen.[17]

We find that the dimethyl substituted azo compound **22** is somewhat different from the parent **15** in its behavior. Direct photolysis of **22** in methylcyclohexane or isopentane at 15 K (Figure 7), under a variety of

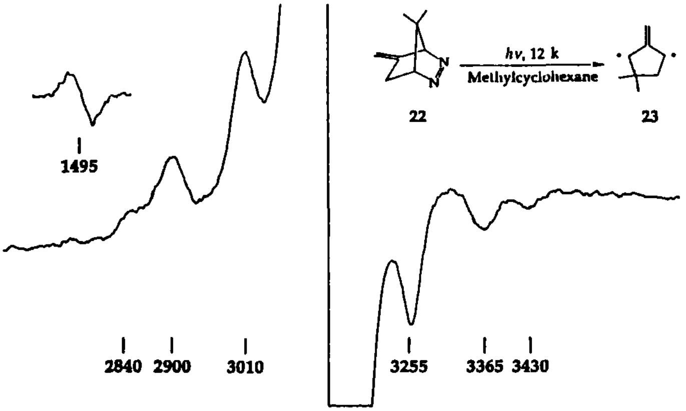


FIGURE 7. ESR spectrum of the trimethylenemethane **23**.

conditions involving changes in solvent and concentration, yielded only the trimethylenemethane diradical **23** (D = 0.0276 cm^{-1}, E = 0.0103 cm^{-1}).

The question is whether the diradical **24** is less stable than its non-methylated counterpart **18** or whether the photochemistry of the two azo precursors is different. We were able to obtain a very weak spectrum of **24** using benzophenone as a sensitizer (Figure 8). As a result of our experience with **18**, we now know where to look for the semilocalized diradical and we ***tentatively*** identify the lines at 2310, 2650, 3320 and 3650 G in Figure 8 with the diradical **24** (D' ≅ 0.065 cm^{-1}). We find that **24** shows the same sensitivity to in the 350-400 nm range as did **18** and that **24** is thermally stable up to about 30 K. Since **18** was stable up to 40 K, we feel that the two radicals are not greatly different in their thermal behavior and that the differing ease of formation of **18** and **24** is due to factors, yet to be elucidated, in the preceding photochemical steps.

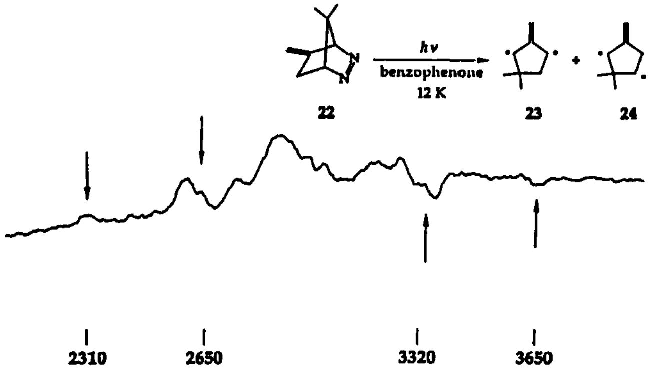
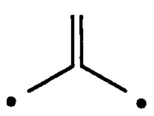


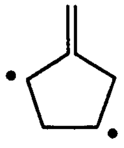
FIGURE 8. ESR spectrum following benzophenone sensitized photolysis of **22**.

SUMMARY

We have discovered a new semilocalized 1,3-diradical which bridges the gap between trimethylenemethane[1,2,14] and the localized diradical **25** of Buchwalter and Closs[15].



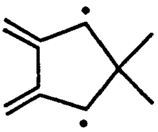
Trimethylenemethane



18

25

The discovery of the sensitivity of **18** to light may aid in understanding why the dimethyl substituted diradical **3** of Roth[7] is readily



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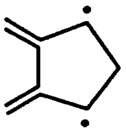

5

prepared, while our attempts to prepare the dihydrogen analogue **5** have encountered difficulty. The latter could be quite sensitive to photorearrangement while its precursor azo compound **6** is being irradiated. The lessons learned in understanding the chemical and photochemical properties of **18** are now being applied in continuing attempts to prepare **5**.

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