$\Delta G^{\ddagger}$ might be caused by the amide-shift reagent association. But at least part of it should come from the temperature-dependent entropy term in $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. The $\Delta S^{\ddagger}$ for the amides is about -5 eu,[10] enough to increase $\Delta G^{\ddagger}$ with T_c by nearly the amount observed. The dependence of T_c and $\Delta G^{\ddagger}$ upon resonance frequency as well as upon r and the nature of the shift reagent are being investigated to separate the two contributions. Such approaches could be helpful in obtaining accurate measurement of $\Delta S^{\ddagger}$.

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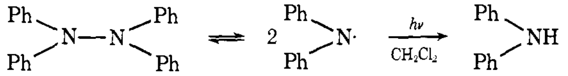
Photochemistry of Organic Cation Radicals. The Photo Benzidine Rearrangement of Tetraphenylhydrazine Cation Radical

Sir:

Aromatic cation radicals generally have absorption maxima in the visible at wavelengths of >500 nm while their parent bases absorb in the uv, usually at <290 nm. The energy of absorption corresponds to <57 and >100 kcal/mol, respectively. This suggests that it may be possible to carry out photochemical transformations in organic cation radicals using low-energy visible light in cases where the precursor undergoes fragmentation by the more energetic uv radiation. We now report an example illustrating this principle, that of the photobenzidine rearrangement of the tetraphenylhydrazine cation radical. There have been a number of recent papers[1-5] concerning the photolytic reactions of organic cations but there do not appear to be any reports of photolytic reactions of cation radicals.

Tetraphenylhydrazine (1) absorbs in the uv at 295 nm. Upon photolysis, the N–N bond undergoes cleavage producing diphenylamino radicals (2).[6] We have observed that photolysis of 1 in dichloromethane is accompanied by the formation of diphenylamine 3. The reaction is inefficient, probably due to the recombination of 2, but goes in high yield. No benzidine rearrangement product could be detected.



1 2 3

Results of quite a different nature are obtained by photolysis of the tetraphenylhydrazine cation radical (4, λ_{max} 465 nm) in either quartz or Pyrex vessels. The reaction results in the equimolar formation of tetraphenylhydrazine (1) and the oxidized form of *N,N'*-diphenylbenzidine (6).

The cation radical (4) fluoroborate was prepared by quantitative coulometric oxidation of 1 in dichloromethane. In the dark, 4 is stable in dichloromethane but when exposed to light, the violet solution of 4 first turns deep blue and then bright green. When a uv cuvette containing a 10^{-4} *M* solution of 4 was placed in front of a desk lamp (100 W), a new absorption band appeared at 580 nm while the band at 465 nm due to 4 was quickly obscured by a new broad band (λ_{max} 460 nm).[7] Both new absorption bands continued to grow for about 2 hr and then the 580-nm band began diminishing while the broad band continued to grow. The 580-nm band was shown to be due to the dication (6)[8] which was prepared independently by anodic oxidation of *N,N'*-diphenylbenzidine in dichloromethane. The new broad band at 460 nm was shown to be due to the monoprotonated quinone imine (8) by incremental addition of trifluoroacetic acid (TFA) to a dichloromethane solution of the quinone imine (λ_{max} 435 nm) and by addition of triethylamine to a solution of the dication (6) in dichloromethane. Both the 435-nm band due to the quinone imine and the 460-nm band due to 8 disappeared on addition of sufficient amounts of TFA to the dichloromethane solutions which was accompanied by the formation of 6 (λ_{max} 580 nm).

The yield of 1 was determined directly on the photolysis solution by the magnitude of the absorption band at 295 nm and the yield of 9 (λ_{max} 330 nm) was determined by the magnitude of absorption at 350 nm after treatment of the photolysis solution with triethylamine. Yields were found to be 70 (1) and 67% (9) based on the stoichiometry of Scheme I. For purposes of isolation, the fluoroborate salt of 4 (from 72 mg of 1 in 1 l. of dichloromethane) was subjected to irradiation through Pyrex using a medium-pressure mercury lamp for 20 min. Evaporation of the solvent followed by basic work-up and recrystallization from dichloromethane gave 1 (15 mg,[9] mp 144–147°, lit.[10] 149°, λ_{max} 295 nm) and 9 (12 mg,[9] mp 239–242,° lit.[11] 240–242°, λ_{max} 330 nm), the H nmr and ir spectra of which were identical with those of the authentic compounds.

The nature of the reduction of 7 on treatment with base is unknown. We have been able to reproduce this reaction with a variety of bases including 2,6-lutidine, triethylamine, sodium methoxide in methanol, and aqueous sodium hydroxide. However, in no case have we been able to find the species which has undergone oxidation.

The initial rearrangement product, presumably the cation radical of *N,N'*-diphenylbenzidine (5), was not detected. This is not surprising since electron transfer with 4 would be expected to be a rapid reaction. An alternative is that 5 disproportionates to the dication (6) and the benzidine (9) and 9 is then oxidized to 6 by the tetraphenylhydrazine cation radical (4). The latter is feasible since cyclic voltammetry of 9 in dichloro-

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(1) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, **90**, 1372 (1968).

(2) R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968).

(3) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).

(4) E. E. van Tamelen, R. H. Greeley, and H. Schumacher, *ibid.*, **93**, 6151 (1971).

(5) E. van Tamelen and T. M. Cole, *ibid.*, **93**, 6158 (1971).

(6) F. A. Neugebauer and S. Bamberger, *Angew. Chem.*, **83**, 47 (1971).

(7) No change was observed in the spectrum of a control solution contained in a uv cuvette wrapped in aluminum foil and placed in front of the lamp during the photolysis experiment.

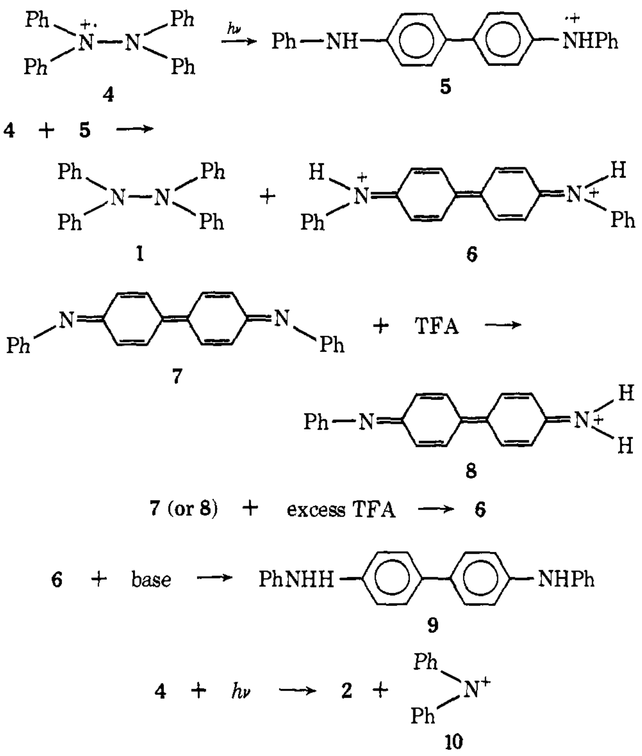
(8) G. Cauquis, J. Cognard, and D. Serve, *Tetrahedron Lett.*, 4645 (1971).

(9) Unavoidable losses were encountered during separation of the products from the large excess of supporting electrolyte used in the preparation of 4.

(10) S. Gambarjan, *Ber.*, **42**, 4011 (1909).

(11) G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, **28**, 3275 (1963).

Scheme I



methane shows a reversible two electron oxidation indicating that **5** is more easily oxidized than **9** and thus disproportionation is to be expected.

It seems reasonable to suggest that excitation of **4** results in a unimolecular rearrangement to **5**. If the first step were fragmentation to **2** and **10** some reduction of **2** to **3** would be expected. Furthermore, formation of **10**, a high-energy species, should be unfavorable.

The work reported here on the photo reactions of **4** and **1** illustrates the differences in photo reactions of cation radicals and their precursors and thus opens a new area of photochemistry to study. Our recent report[12] of the synthesis of cation radical salts by electrolysis in trifluoroacetic acid provides a route to a variety of new cation radicals, the photochemistry of which is now being investigated.

[12] O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).

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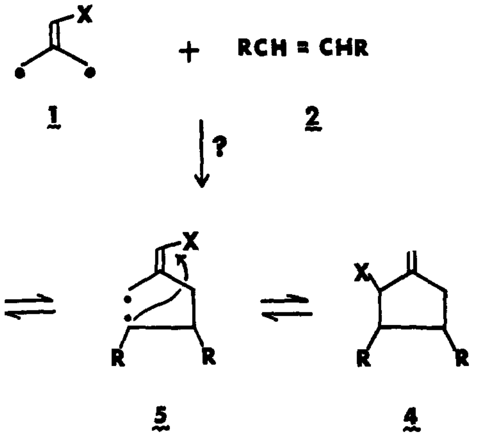
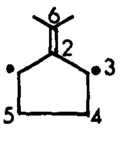
Direct Formation of Methylenecyclopentanes by Cycloaddition of a Trimethylenemethane to Olefins[1]

Sir:

Among several reasons for mechanistic interest in the cycloadditions of trimethylenemethanes and olefins (*e.g.*, **1** + **2** → **3** + **4**) is the speculation that the properties of the hypothetical intermediate **5** in the cycloaddition might serve as a model for the behavior to be expected of similar "diradical" species generated in a nonconcerted 1,3-sigmatropic rearrangement (*e.g.*, **3** → **5** → **4**). Moreover, the cycloadditions are of potential importance in synthesis as a direct route to methylenecyclopentanes.



Although there are scattered reports of formal cycloadditions of trimethylenemethane itself (TMM, **1**, X = H) to olefins, the yields usually are low.[2] One reason for this is the frequent occurrence of an intramolecular side reaction, the formal ring closure of TMM to methylenecyclopropane.[3] One might hope to suppress the ring closure by the imposition of a strain barrier, for example, by incorporation of the TMM system in a relatively small ring, thus giving the intermolecular cycloaddition a better opportunity to occur. We now report that the cyclic TMM, 2-isopropylidenecyclopentane-1,3-diyl (**6**),[4] which would give the highly strained hydrocarbon **7** upon cyclization,[5] does indeed give high yields of cycloadducts with many olefins.



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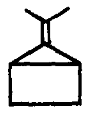

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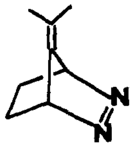

8

The cycloadditions are carried out by the slow thermal (40–60°) decomposition of the azo compound **8**[4] in a large excess (neat liquid or concentrated solution) of the olefinic acceptor. These conditions almost completely suppress the formation of the four character-

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[1] This work was supported in part by the National Science Foundation (GP11017X), the National Institute of General Medical Sciences (GM16962), and the Hoffmann-LaRoche Foundation.

[2] (a) Photolysis of 3-methylenecyclobutanone in 1,3-butadiene gives 35% of 1-methylene-3-vinylcyclopentane: P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5726 (1970). (b) Photolysis of TMM–Fe(CO)$_3$ in cyclopentene gives a 5% yield of 3-methylenebicyclo[3.3.0]octane, and in cyclopentadiene it gives 23% of 3-methylenebicyclo[3.2.1]oct-6-ene: A. C. Day and J. T. Powell, *Chem. Commun.*, 1027 (1968). (c) The action of potassium vapor on a mixture of 3-iodo-2-iodomethylpropene and diiodotetramethylcyclobutene gives a 7% yield of 3-methylene-1,5,6,7-tetramethylbicyclo-[3.2.0]hept-6-ene [R. G. Doerr and P. S. Skell, *J. Amer. Chem. Soc.*, **89**, 3062 (1967)], although no methylenecyclopentane is formed in the reaction of 3-iodo-2-iodomethylpropene, potassium, and ethylene: P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967). (d) Oxidation of TMM–Fe(CO)$_3$ with Ce(IV) ion in the presence of tetracyanoethylene gives a 4% yield of 4-methylene-1,1,2,2-tetracyanocyclopentane: J. S. Ward and R. Pettit, *Chem. Commun.*, 1419 (1970).

[3] R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, **88**, 2589 (1966); J. J. Gajewski, A. Yeshurun, and E. J. Bair, *ibid.*, **94**, 2138 (1972).

[4] J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *ibid.*, **93**, 1544 (1971).

[5] Previous studies[4] already have shown that **7** reverts readily to **6**.