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STEREOCHEMISTRY OF THE ADDITION OF CYCLOHEPTATRIENYLIDENE (?) TO ELECTRON DEFICIENT DOUBLE BONDS (1)

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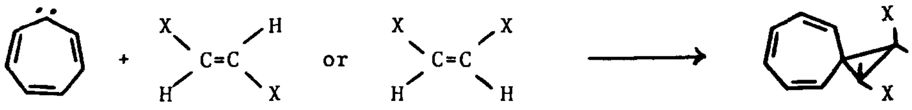
The addition of cycloheptatrienylidene (from the thermal decomposition of the sodium salt of tropone tosylhydrazone in diglyme) to either dimethylmaleate or dimethylfumarate has been reported (3) to give only one of the possible spirononatrienes (the trans isomer). From this observation a two step addition mechanism was suggested although possible isomerization of products was acknowledged.



X = CO_2CH_3

At this time we would like to report an independent investigation of the stereochemistry of the addition of photolytically produced cycloheptatrienylidene to an electron deficient double bond. Our results lead us to the conclusion that the addition is, at least under our conditions and within experimental error, completely stereospecific.

Photolysis of the sodium salt of tropone tosylhydrazone in the presence of dimethylfumarate (4) gives the same spirononatriene as that reported by Mukai. Photolysis of this salt in the presence of dimethylmaleate was also found to give the same trans isomer. However, under our reaction conditions it was found that some isomerization of dimethylmaleate to dimethylfumarate occurs. Since it has been reported in other systems that cycloadditions to dimethylfumarate occur substantially faster than to dimethylmaleate,[†] (5,6) it was realized that our "apparent" non-specific addition might arise from a combination of isomerization and rate differences rather than a two step addition.

Acknowledging the inevitable possibility that electron deficient alkenes may undergo some isomerization under the basic conditions (sodium salt of the tosylhydrazone) of this reaction, an attempt was made to find a pair of electron deficient alkenes that would undergo more nearly comparable addition rates. Fumaronitrile and maleinitrile have been reported to undergo cycloaddition reactions at nearly comparable rates. (5,7) The photo-induced decomposition of the sodium salt of tropone tosylhydrazone (in THF) in the presence of each of these dinitriles was therefore studied. In each case, reaction proceeded smoothly to give the spirononatriene of retained stereochemistry as the obvious predominant product.[‡] The stereochemistry of the addition to the nitriles in THF was studied very carefully[§] and it was found that if extreme precautions were taken to exclude all excess base, the degree of isomerization of one nitrile to the other could be held to a few percent. The results of reactions run under these conditions are shown in the Table. Taking into consideration the relative rates of addition to the *cis* and *trans* isomers and the amount of isomerization that occurred, it must be concluded that within experimental error the addition in THF is completely stereospecific. This observation obviously mitigates against a two step addition reaction under the photolysis conditions (in THF) at room temperature.

[†] The reason for this difference in rate has been explored and Huisgen (6) has proposed a most reasonable explanation involving steric inhibition of resonance as well as crowding effects in the transition state.

[‡] The relative rates of addition to fumaronitrile and maleinitrile were determined by competition experiments to be 1:1. The rate of addition to dimethylfumarate relative to fumaronitrile was 1:2. The rate of addition to dimethylmaleate (using a 10:1 molar ratio of ester to nitrile) relative to fumaronitrile was 0.007. From these numbers the rate of reaction with dimethylfumarate can be calculated to be about 175 times faster than reaction with dimethylmaleate. This may run as low as 80 if a suspicious new peak in the nmr in the presence of the *cis* diester actually arises from the *cis* spirononatriene. Attempts to isolate this product have failed.

[§] When a Hanovia immersion lamp with Pyrex filters was used, substantial photoisomerization of products occurred. This isomerization was avoided by carrying out the experiments in a Rayonet type RS preparative photochemical reactor using 3500 Å lamps.

TABLE I. Stereochemistry of additions to fumaronitrile and maleinitrile.

Solvent	Olefin	% Olefin Isomerization[a]	% trans-isomer[b]	% cis-isomer[b]
THF	trans[c]	< 1.0	> 98	< 2[d]
THF	cis[c]	5.6	2	98
CH_2Br_2	trans	3.6	> 98	< 2[d]
CH_2Br_2	cis	3.7	< 6[e]	> 94

a) Determined by v.p.c. b) Determined by nmr; no isomerization of the spirononatriene occurred under these conditions. c) 0.8 mole %. d) None detectable. e) Maximum value. See text.

The multiplicity of the ground state of this aromatic carbene is of much interest. The most widely used chemical test for the multiplicity of a carbene is the often applied Skell (8) test involving the stereochemistry of addition to double bonds. Although our observation of stereospecific addition most certainly means that reaction has occurred with the singlet state, unfortunately, it does not guarantee that this is the ground state, since intersystem crossing may be slower than reaction with the alkene. There have been at least two experimental methods used to promote intersystem crossing of carbenes and nitrenes. In one, the reaction is conducted in low concentrations of substrate in the presence of an inert solvent. (9) The basic idea is to give the carbene an opportunity to find its ground state before it reacts with the substrate. With carbenes of known triplet ground states, this method has been found to be effective with some carbenes but not with others. The reaction reported above in tetrahydrofuran was carried out at substrate concentrations of less than 1 mole %.

A second method that has been used to promote intersystem crossing takes advantage of spin orbit coupling with heavy atoms (for example, Br) in the solvent. (10) When our addition was carried out in methylene bromide, complications arose - apparently from reaction of the tosylhydrazone salt with methylene bromide. As a result, the yields of spirononatriene were low and the accuracy of the nmr method that was used to determine the stereospecificity of the reactions was seriously reduced. Nonetheless, even under these unfavorable conditions, reaction with fumaronitrile in methylene bromide gave (insofar as our experimental methods would detect) exclusively the trans isomer (although 3.7%

isomerization to maleinitrile occurred) and with the cis dinitrile gave greater than 94%[†] of the cis-isomer (once again with 3.7% isomerization of the starting olefin).

Stereospecific addition to the dinitrile in the presence of very low concentrations of substrate in THF and (probable) stereospecific addition in a heavy atom solvent both point to a singlet ground state for cycloheptatrienylidene. This is supported by the fact that, to date, no free radical products have been detected[‡] in the reactions in tetrahydrofuran or methylene bromide. However, it must be recognized that unless it can either be established that these reaction conditions universally promote intersystem crossing of carbenes to their ground states or factors influencing the rate of intersystem crossing can be better defined, evidence of this type can be taken as indirect at best.

References

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2. a) Alfred P. Sloan Fellow 1963-67; b) University of Florida Ford Fellow; c) Gulf Oil Fellow 1966-67.
3. T. Mukai, T. Nakazawa, and K. Isobe, *Tet. Let.*, 565 (1968).
4. W. M. Jones and C. Lawrence Ennis, *J. Am. Chem. Soc.*, 89, 3069 (1967); W. M. Jones and C. Lawrence Ennis, paper submitted to *J. Am. Chem. Soc.*, for publication.
5. L. Horner and E. Lingnan, *Ann.*, 591, 21 (1955).
6. R. Huisgen, *Angew. Chem. internat. Edit.* 2, 565 (1963).
7. J. Sauer, H. Wiest, and A. Mieleit, *Z. Naturforsch*, 17b, 203 (1962); J. Sauer, D. Lang, and H. Wiest, *ibid.*, 17b, 206 (1962).
8. P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, 78, 5430 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, 78, 4496 (1956).
9. M. Jones, Jr. and Kenneth R. Rettig, *J. Am. Chem. Soc.*, 87, 4013 (1965); M. Jones, *Tet. Let.*, 183 (1967).
10. A. G. Anastassiou, *J. Am. Chem. Soc.*, 89, 3184 (1967).

[†] An apparent impurity absorbs in the same region as the trans-spirononatriene which, when coupled with the low yields, allows the experimental error to become so large that the integrated peak area of 6% cannot be taken as significant.

[‡] Trace amounts, at most, of any products other than those described in this note were observed in the nmr of crude reaction mixtures.