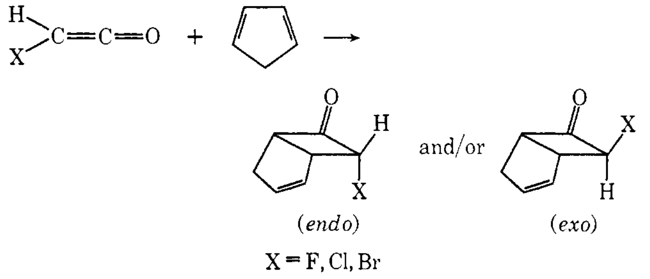
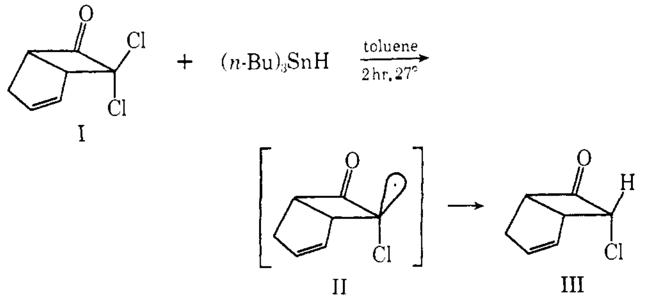


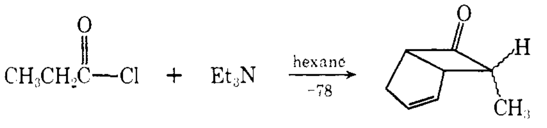
pected, but a consideration of steric factors would lead to the prediction that the *exo* isomer would predominate, particularly as the size of the substituent increases. However, vapor phase chromatography disclosed only one isomer in each of the ketene systems. In an effort to prove that the *exo* isomer was the probable isomer produced stereospecifically, the *endo*-chloro isomer III was synthesized.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one[4] (I) was preferentially reduced with tri-*n*-butyltin hydride[5] to produce only the *endo* isomer III (this was possible because I was present in slight excess). A comparison of



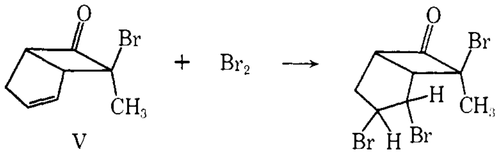
the nmr spectrum of III with the spectrum of the cycloadduct obtained by the dehydrochlorination of chloroacetyl chloride in the presence of cyclopentadiene showed the two were exactly superimposable. This result was of course very surprising. A study of the nmr spectra of the fluoro- and bromoketene cycloadducts also indicated that it was the *endo* isomer being produced.

The possibility of some peculiarity of the halogen causing the *endo* stereospecificity prompted the investigation of an aldoalkylketene system. Propionyl chloride was dehydrochlorinated in the presence of cyclopentadiene to yield the corresponding cycloadduct, IV.[6]



IV

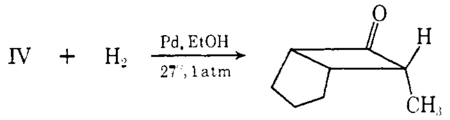
The nmr spectrum revealed the methyl resonance as a doublet centered at δ 0.99. Martin and coworkers reported that the nmr spectrum of the dimethylketene–cyclopentadiene adduct showed the methyl resonances at δ 1.28 and 0.93.[7] We have recently demonstrated in two methylhaloketene–cyclopentadiene systems that the upfield resonance was *endo*-methyl and the downfield resonance the *exo*-methyl.[8] Thus, the methyl resonance at δ 0.99 observed in this system must be due to *endo*-methyl.



$$\text{IV} + 2\text{Br}_2 \xrightarrow[0^\circ]{\text{CCl}_4} \text{VI} + \text{HBr}$$

To further demonstrate IV is the *endo* isomer, the methylketene adduct was brominated in an nmr tube and subsequently scanned. The spectrum thus obtained revealed that the product of bromination was the same as that obtained by bromination of V.[8] Compound V shows a methyl resonance at δ 1.60 which when brominated shifted to δ 1.98–1.99. The other isomer of V has a methyl resonance at δ 1.91 which when brominated shifted to δ 1.98–1.99. The methyl doublet of IV at δ 0.99 shifts to δ 1.99 upon bromination.

Furthermore, since the *endo*- and *exo*-methyl groups of IV are in different environments, hydrogenation of the residual double bond should change the environment of the *endo*-methyl and result in a shift of this doublet. This shift (~2 cps) was indeed observed upon catalytic hydrogenation, further demonstrating that IV is the *endo* isomer.



Thus, under the reaction conditions already described,[2] it appears that cycloaddition of aldoketenes, not just aldohaloketenes, with cyclopentadiene results in the stereospecific formation of the *endo* isomer. Experiments are in progress to explain this surprising phenomenon, and the results are forthcoming.

Acknowledgment. The authors express gratitude to Thomas Wardall of the Halliburton Services for assistance with the nmr determinations. Support of this investigation by the Robert A. Welch Foundation and a National Science Foundation grant (GP-7386) is gratefully acknowledged.

---

(4) (a) H. C. Stevens, D. A. Reich, D. R. Brandt, D. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965); (b) L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Lett.*, 135 (1966).

(5) Tri-*n*-butyltin hydride reductions of bicyclic halogenated compounds are known to proceed *via* free radicals; see H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968). The *exo*-chloro substituent is preferentially removed, yielding the radical II which quickly abstracts a hydrogen atom. The radical does not produce an *exo* isomer (through a planar radical intermediate or inversion of the nonplanar radical) because of torsional strain; see F. R. Jensen, L. H. Gala, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968); P. von R. Schleyer, *ibid.*, **89**, 699 (1967); **89**, 701 (1967).

(6) Compound IV has been reported by J. Jaz and E. Denis, *Bull. Soc. Chem. Belges*, **75**, 845 (1966), but no mention was made of the stereochemistry involved.

(7) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

(8) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966); W. T. Brady and B. M. Holifield, *Tetrahedron*, **23**, 4251 (1967).

William T. Brady, Edwin F. Hoff
Robert Roe, Jr., Fred H. Parry, Jr.
North Texas State University
Chemistry Department, Denton, Texas 76203

Received June 20, 1969

An Intermolecular Reaction of an Aryl Nitrene

Sir:

Although the minimal solvent effect on the first-order thermal decomposition of aryl azides[1,2] and the lack of anchimeric assistance in *meta*-substituted phenyl azide[1,2] provide a convincing kinetic argument that singlet aryl nitrenes are formed initially, no intermolecular reaction has been demonstrated to be one of a singlet aryl nitrene. Instead, aryl nitrenes appear to be related to a multitude of other reactive intermediates on singlet surfaces[3-6] which isomerize to stable compounds, or react with other species in solution. On the other hand, the participation of singlet aryl nitrene in intramolecular C–H bond insertion gains support from the formation of (−)-2-ethyl-2-methylindoline from (+)-2-azido-1-(2-methylbutyl)benzene.[7] In contrast, evidence has been accumulating that the insertion of phenylnitrene into the C–H bond of hydrocarbons is actually due to the triplet.[8]

Photolysis of *p*-methoxyphenyl azide and *p*-chlorophenyl azide in dimethylamine yields the corresponding products, 2-dimethylamino-5-methoxy-3H-azepine and 5-chloro-2-dimethylamino-3H-azepine, along with minor yields of the anilines. These results are in accord with those reported for phenyl azide in amines and liquid ammonia.[9] In contrast, a similar reaction with *p*-cyanophenyl azide gave a 70% yield of 1,1-dimethyl-2-(4-cyanophenyl)hydrazine and a 5% yield of *p*-cyanoaniline. The structural assignment of the hydrazine is in accord with its elemental analysis and its ir and nmr spectra. The nmr data are particularly significant in this respect. The spectrum has a six-proton singlet at τ 7.45 (dimethylamino) and a broad one-proton singlet at τ 5.09 (amino). The ring-proton portion consists of two two-proton doublets centered at τ 3.15 (*ortho* to the hydrazino group) and 2.60 (*ortho* to the cyano group), with a coupling constant of 8.5 Hz. The chemical shifts and coupling constant agree with those reported for *p*-dimethylaminobenzonitrile.[10]

Photolysis of *p*-cyanophenyl azide in the presence of the triplet sensitizer, xanthen-9-one, which absorbs essentially all of the light, causes reversal of product yields, 70% of *p*-cyanoaniline and 6% of hydrazine. Significantly, no loss of xanthen-9-one occurs until most of the azide is consumed. Thus, the normal reaction of xanthen-9-one, the formation of the pinacol,[11] is quenched by the azide. Xanthen-9-one has a triplet energy of 71–74 kcal/mol, depending on solvent,[12] which is comparable to sensitizers used by Lewis and Saunders[13] who report close to diffusion-controlled energy transfer to azides with sensitizers of approximately 75 kcal. Clearly, in the sensitized experiments, triplet azide is formed on energy transfer and a triplet species, presumably triplet nitrene, is mostly reduced to the amine, a result in agreement with the observation of Splitter and Calvin[3] for phenyl azide. By implication, the large yield of hydrazine in the absence of sensitizer is due to the singlet nitrene.

Interestingly, the reaction of *p*-nitrophenyl azide might be expected to be analogous to the cyano compound, but this is not the case. Photolysis of the nitro compound in dimethylamine produces *p*-nitroaniline in better than 90% yield and no other products of comparable molecular weight. This is not surprising as nitro groups are known to enhance intersystem crossing, as shown in the complete suppression of fluorescence of aromatic hydrocarbons on substitution of a nitro group, with concomitant phosphorescent quantum yield of the nitro aromatic approaching unity.[14]

The *p*-cyanophenyl nitrene must differ from other aryl nitrenes because one or both of two possible effects of the *p*-cyano group are operating. The rate of ring closure of the singlet nitrene to a 7-azabicyclo[4.1.0]hepta-2,4,6-triene may decrease and the rate of reaction of the singlet nitrene with amine may increase. The reaction of the nitrene with amine, if visualized as a simple acid–base type, should be facile. The surprising thing is that amines do not capture singlet aryl nitrenes more often.

---

(1) M. Appl and R. Huisgen, *Chem. Ber.*, **92**, 2961 (1959).

(2) P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, **84**, 480 (1962).

(3) J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1445 (1968).

(4) J. I. G. Cadogan, *Quart. Rev.* (London), **22**, 222 (1968).

(5) R. G, Sundberg, B. P. Das, and R. H. Smith, Jr., *J. Amer. Chem. Soc.*, **91**, 658 (1969).

(6) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968).

(7) G. Smolinsky and B. I. Feuer, *J. Amer. Chem. Soc.*, **86**, 3085 (1964).

(8) J. H. Hall, J. W. Hill, and J. M. Fargher, *ibid.*, **90**, 5313 (1968).

(9) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).

(10) E. Lippert and W. Luder, *Z. Phys. Chem.* (Frankfurt am Main), **33**, 60 (1962).

(11) V. Zanker and E. Ehrhardt, *Bull. Chem. Soc. Jap.*, **39**, 1694 (1966).

(12) W. G. Heckstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964); V. L. Ermolaev, *Usp. Fiz. Nauk*, **80**, 3 (1963).

(13) F. D. Lewis and W. H. Saunders, *J. Amer. Chem. Soc.*, **90**, 7033 (1968).

(14) M. Kasha, *Radiat. Res., Suppl.*, **2**, 243 (1960).

Robert A. Odum, Alan M. Aaronson
Department of Chemistry
Brooklyn College of the City University of New York
Brooklyn, New York 11210

Received April 7, 1969

Novel Photoaddition Reactions of Acyclic Olefins. Nucleophilic Photohydration

Sir:

Acyclic olefins characteristically undergo *cis–trans* isomerization as their chief reaction on photochemical activation. Cyclic olefins, which have difficulty adopting a twisted configuration, undergo a variety of reactions from their excited states, including dimerization and various addition reactions.[1] An example of the latter which has received much attention is the photosensitized addition of water and alcohols to six- and seven-membered ring olefins.[2] These reactions apparently involve photochemical carbonium ion formation. In the present communication we report efficient photoaddition reactions which, though formally analogous to the above, differ in that (a) electron-deficient acyclic olefins are photohydrated, (b) the excited state involved is a singlet, and (c) the reaction appears to be initiated by nucleophilic attack on the excited olefin.

The present photohydration appears to be fairly general for quaternary salts of pyridyl-substituted ethylenes.[3] The following are typical, well-behaved ex-

---

(1) For recent summaries see: G. J. Fonken in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 197; P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(2) (a) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969), and references therein; (b) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967); **89**, 5199 (1967); **88**, 4091 (1966).

(3) The reaction is complicated in several cases, especially for the stilbazoles, by concurrent photodimerization and isomerization.[4,5]

(4) J. L. R. Williams, J. M. Carlson, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **28**, 1317 (1963), and references therein.

(5) D. G. Whitten and M. T. McCall, *J. Amer. Chem. Soc.*, **91**, 5097 (1969).