

# 2,2-DIMETHYLISOINDENE AND 5,5-DIMETHYLBENZOBICYCLO [2.1.0] PENT-2-ENE

William R. Dolbier, Jr.\*, Kazumasa Matsui\*\*

Josef Michl\*\*\* and David V. Horák\*\*\*

## ABSTRACT

2,2-Dimethylisoindene, 1, has been generated from an azoxy precursor, 2, (a) in an EPA matrix at 77°K by photolysis, and (b) in solution at 25°C through deoxygenation by Si<sub>2</sub>Cl<sub>6</sub>. The UV and NMR absorption spectra and the fluorescence emission spectrum of 2 have been determined. Isoindene 2 was found to undergo quantitative photochemical conversion to 5,5-dimethylbenzobicyclo [2. 1. 0] pent-2-ene, 7. Moreover, 3 was found to quantitatively reconvert to 2 thermally at room temperature. Other reactions of 1 and 2 are also discussed.

Sir :

While ortho-xylene<sup>1)</sup> and various ortho-xylene derivatives<sup>2)</sup> have been generated, isolated and characterized spectroscopically, isoindenes

---

\*Department of chemistry, University of Florida, Gainesville, Florida 32611 U. S. A.

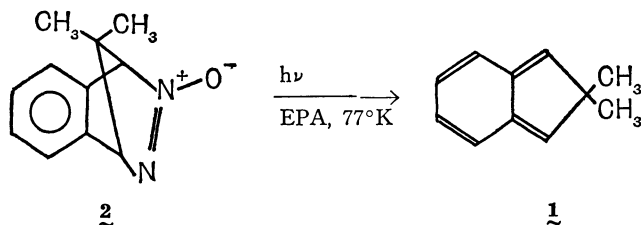
\*\*Chemistry laboratory, Konan Women's College, Morikita Cho, Higashinada-Ku, Kobe City 658, JAPAN.

\*\*\*Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 U. S. A.

236 2,2-DIMETHYLISOINDENE AND 5,5-DIMETHYLBENZOBICYCLO  
[2.1.0] PENT-2-ENE

have heretofore eluded isolation, although they have been demonstrated to exist as transient intermediates under various reactive conditions.<sup>3)</sup>

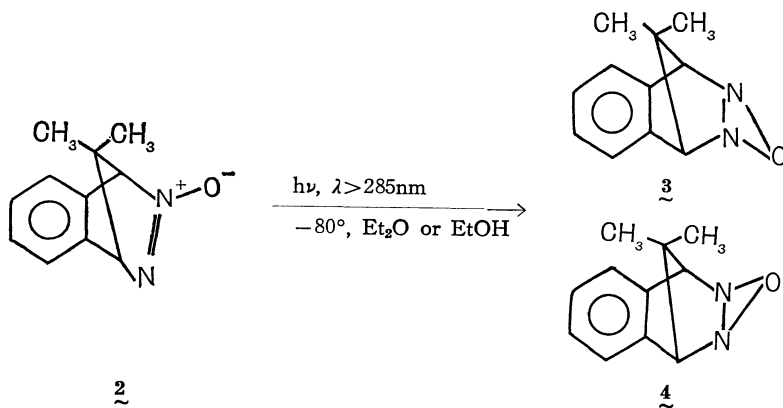
We have found that 2,2-dimethyl-2H-indene (2,2-dimethylisoidene), 1, may be generated and isolated in an EPA glass matrix at 77°K by irradiation of azoxy compound 2<sup>3b)</sup> (high pressure mercury lamp and  $\lambda > 285$  nm filter, or lowpressure mercury lamp). 1 exhibited a structured absorption band ( $\lambda_{\text{max}} = 405\text{nm}$ ) and a similarly structured light blue fluorescence ( $\lambda_{\text{max}} = 467\text{nm}$ ) in a good



mirror-image relationship. Both were quite similar to the spectra reported for alkyl substituted orthoxylylenes<sup>2a)</sup> as well as for orthoxylylene itself, but were red-shifted by about  $2000\text{cm}^{-1}$ , presumably due to cyclic hyperconjugation. The shape of the emission curve of 1 is independent of excitation wavelength and the excitation spectrum follows the shape of the absorption band. The onsets of absorption and emission almost coincide, and the 0-0 bands are clearly discernible as relatively intense peaks ( $\lambda_{\text{max}}(\text{A}) = 432$  nm and  $\lambda_{\text{max}}(\text{E}) = 439$  nm).<sup>1,2)</sup> As in the case of other reported spectra of o-xylylenes, the calculated (PPP) first transition is allowed and occurs near the observed position, and a very weak transition into a predominantly doubly excited state at somewhat higher energies is apparently buried under the first band.

While 1 was found to be stable indefinitely at room temperature in EPA solution, it was produced only in very small quantities upon irradiation ( $\lambda > 285\text{nm}$ ) of 2 at 25° or even at  $-80^\circ\text{C}$ . At the latter

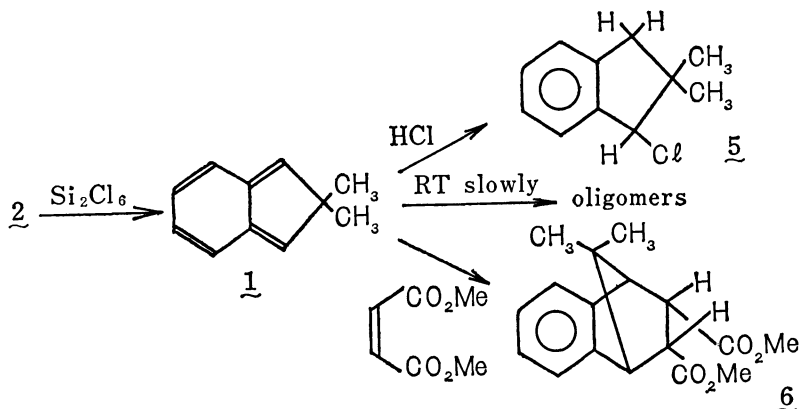
temperature there was a smooth conversion to species containing the benzene chromophore and isomeric with 2, stable for days at  $-80^{\circ}\text{C}$  but reconverting to 2 in several hours upon warming to  $-20^{\circ}\text{C}$ . NMR ( $\text{CD}_3\text{OD}$ ) showed that two photoisomers were



formed in a ratio of about 2.5:1. Both contribute to a narrow multiplet at  $\delta$  7.38 (4H); the major isomer also has singlets at  $\delta$  4.64 (2H), 1.50 (3H), and 0.57 (3H), the minor isomer also has singlets at  $\delta$  4.81 (2H), 1.44 (3H), and 0.60 (3H). Thus, the probable solution photoproducts are *endo* and *exo* oxadiaziridines, 3 and 4. Greene and Hecht have previously demonstrated the ability of azoxy compounds to cyclize in this manner.<sup>4)</sup>

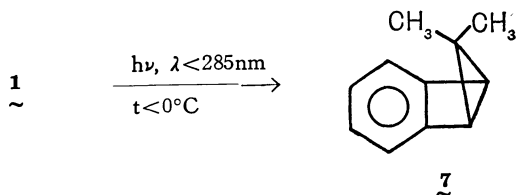
In view of the apparent ability of the gem dimethyl substituents to stabilize the isoindene toward oligomerization, we attempted to generate 1 at room temperature by an alternative method. Thus, it was found that 2 underwent deoxygenation by  $\text{Si}_2\text{Cl}_6$ <sup>5)</sup> followed by loss of  $\text{N}_2$  from the probable transient azocompound to produce 1.

The NMR spectrum of the bright yellow solution (100 MHz) showed a singlet at  $\delta$  1.16 (6H) and vinylic multiplets at  $\delta$  6.08 (4H) and  $\delta$  6.55 (2H). This is the first reported NMR spectrum for an ortho-xylylene derivative,<sup>6)</sup> although NMR spectra have been obtained for paraxylylene,<sup>7)</sup> isoindole,<sup>8)</sup> isobenzofuran and for 1,2-(2,3-naphtho)-



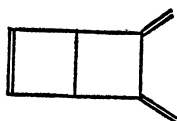
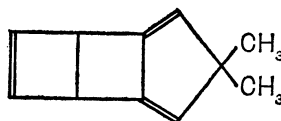
<sup>9)</sup> o-carborane. The reported chemical shift for ring protons of paraxylene ( $\delta$  6.49) is indicative of a similar lack of aromaticity in ortho and para xylene-type molecules. The yellow color of the isoindene was rapidly discharged when the solution was treated with either  $\text{HCl}$  or dimethyl maleate with products **5** and **6** being formed, isolated and characterized by comparison with authentic samples.

When a fluid isoindene solution in various solvents was irradiated at  $0^\circ\text{C}$  or below, it rapidly lost its color. When warmed to room temperature, the color soon reappeared. An NMR analysis of this photolytic-thermal interconversion in  $\text{Si}_2\text{Cl}_6$  showed that 5,5-dimethylbenzobicyclo [2.1.0] pent-2-ene was the photoproduct.



**7** gave an NMR with singlets at  $\delta$  0.94 (3H), 1.06 (3H), and 2.54 (2H) and a pair of symmetrical multiplets at  $\delta$  6.62 (2H) and 6.82 (2H). The singlet bridgehead proton absorption ( $\delta$  2.54) was at almost the exact chemical shift which would be predicted for this

molecule considering the chemical shifts of the benzylic protons of benzocyclobutene ( $\delta$  3.14<sup>10</sup>), the allylic protons of cyclobutene ( $\delta$  2.54<sup>11</sup>) and the bridgehead protons of bicyclo [2.1.0] pent-2-ene ( $\delta$  2.0<sup>12</sup>). On the other hand, the bridgehead protons of the dewar-orthoxylylene species 8<sup>13</sup> are at  $\delta$  3.73. This, plus the fact that 8 is relatively stable thermally, makes the alternative photoproduct structure 9 highly unlikely. The ready thermal

89

reconversion of the photoproduct to isoindene 1 taken together with the simplicity of the NMR spectrum makes dimeric structures highly improbable. Hence, the benzobicyclo [2.1.0] pent-2-ene structure can be invoked with confidence.

## REFERENCES

- 1) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **96**, 3280 (1974); E. Migird-icyan and J. Baudet, *J. Am. Chem. Soc.*, **97**, 7400 (1975).
- 2) (a) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510 (1976).  
(b) G. Quinkert, J. Palmowski, H.-P. Lorenz, W.-W. Wiersdorff, and M. Finke, *Angew. Chem. internat. Edit.*, **10**, 198 (1971).
- 3) (a) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).  
(b) W. R. Dolbier, Jr., L. McCullagh, D. Rolison, and K. E. Anapolle, *J. Am. Chem. Soc.*, **97**, 934 (1975).  
(c) J. J. McCullough and A. J. Yarwood, *J. Chem. Soc., Chem. Comm.*, 485 (1975).
- 4) S. S. Hecht and F. D. Greene, *J. Am. Soc.*, **89**, 6761 (1967).
- 5) K. Naumann, G. Zon and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).
- 6) D. J. Williams, J. M. Pearson, and M. Levy, *J. Am. Chem. Soc.*, **92**, 1436

240 2,2-DIMETHYLISOINDENE AND 5,5-DIMETHYLBENZOBICYCLO  
[2.1.0] PENT-2-ENE  
(1970).

- 7) R. Bonnett and R. F. C. Brown, *J. Chem. Soc., Chem. Comm.*, 393 (1972).
- 8) U. E. Wiersun and W. J. Mijs, *J. Chem. Soc., Chem. Comm.*, 347 (1972).
- 9) D. S. Matteson and R. A. Davis, *Inorg. Chem.*, 13, 859 (1974).
- 10) G. Fraenkel, Y. Asahi, M. J. Mitchell and M. P. Cava, *Tetrahedron*, 20, 1179 (1964).
- 11) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, 83, 1226 (1961).
- 12) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, 88, 846 (1966).
- 13) F. R. Farr and N. L. Bauld, *J. Am. Chem. Soc.*, 92, 6695 (1970).