

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 Si₂Cl₆. 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 revert to 2 thermally at room temperature. Other reactions of 1 and 2 are also discussed.

Sir :

While ortho-xylene¹⁾ and various ortho-xylene derivatives²⁾ have been generated, isolated and characterized spectroscopically, isoindenes

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

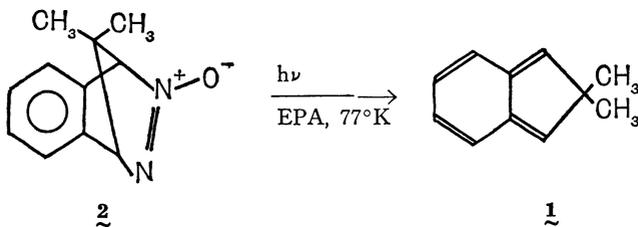
**Chemistry laboratory, Konan Women's College, Morikita Cho, Higashinada-Ku, Kobe City 658, JAPAN.

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

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

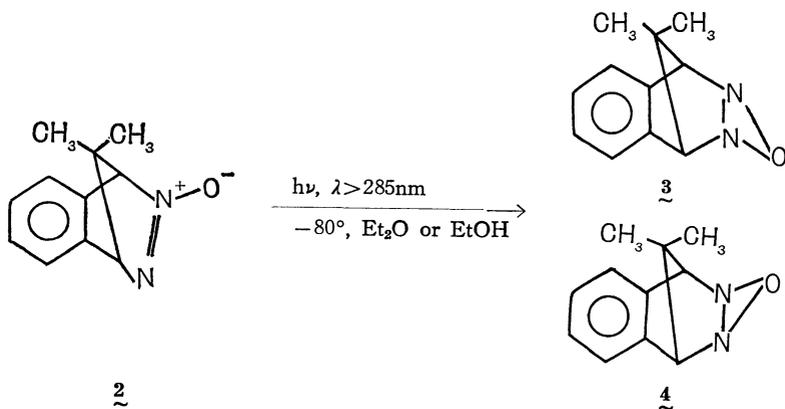
We have found that 2,2-dimethyl-2H-indene (2,2-dimethylisoindene), 1, may be generated and isolated in an EPA glass matrix at 77°K by irradiation of azoxy compound 2^{3b)} (high pressure mercury lamp and $\lambda > 285$ nm filter, or lowpressure mercury lamp). 1 exhibited a structured absorption band ($\lambda_{\text{max}} = 405\text{nm}$) 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^{2a)} as well as for orthoxylylene itself, but were red-shifted by about 2000cm^{-1} , presumably due to cyclic hyperconjugation.¹⁾ 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). As in the case of other reported spectra of o-xylylenes,^{1,2)} 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°C . At the latter

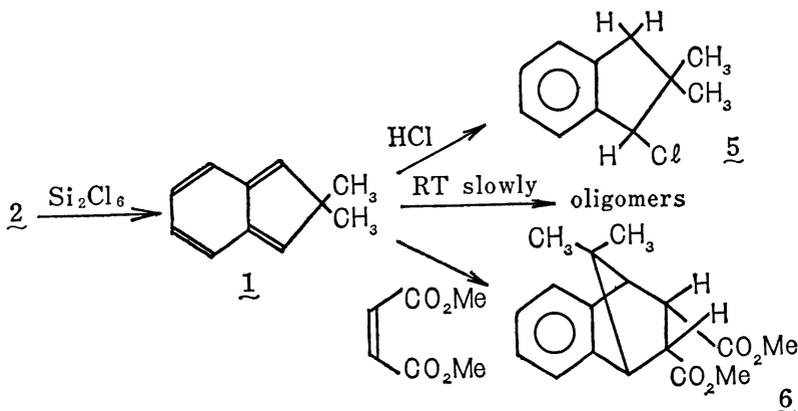
temperature there was a smooth conversion to species containing the benzene chromophore and isomeric with 2, stable for days at -80°C but reconverting to 2 in several hours upon warming to -20°C . NMR (CD_3OD) showed that two photoisomers were



formed in a ratio of about 2.5:1. Both contribute to a narrow multiplet at δ 7.38 (4H); the major isomer also has singlets at δ 4.64 (2H), 1.50 (3H), and 0.57 (3H), the minor isomer also has singlets at δ 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.⁴⁾

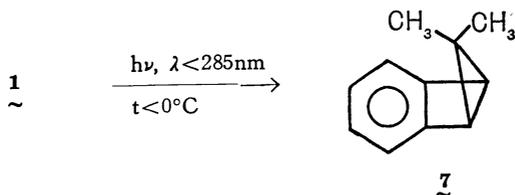
In view of the apparent ability of the gem dimethyl substituents to stabilize the isoindene toward oligomerization, we attempted to generate 1 at room temperature by an alternative method. Thus, it was found that 2 underwent deoxygenation by Si_2Cl_6 ⁵⁾ followed by loss of N_2 from the probable transient azocompound to produce 1.

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



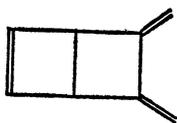
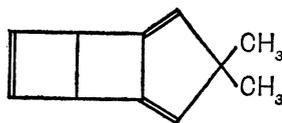
⁹⁾ o-carborane. The reported chemical shift for ring protons of paraxylene (δ 6.49) is indicative of a similar lack of aromaticity in ortho and para xylene-type molecules. The yellow color of the isoindene was rapidly discharged when the solution was treated with either HCl or dimethyl maleate with products **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°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 Si_2Cl_6 showed that 5,5-dimethylbenzobicyclo [2.1.0] pent-2-ene was the photoproduct.



7 gave an NMR with singlets at δ 0.94 (3H), 1.06 (3H), and 2.54 (2H) and a pair of symmetrical multiplets at δ 6.62 (2H) and 6.82 (2H). The singlet bridgehead proton absorption (δ 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 (δ 3.14¹⁰), the allylic protons of cyclobutene (δ 2.54¹¹) and the bridgehead protons of bicyclo [2.1.0] pent-2-ene (δ 2.0¹²). On the other hand, the bridgehead protons of the dewar-orthoxylylene species 8 are at δ 3.73¹³. This, plus the fact that 8 is relatively stable thermally, makes the alternative photoproduct structure 9 highly unlikely. The ready thermal

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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.

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