Tetrahedron Letters No. 12, pp. 791-794, 1963. Pergamon Press Ltd.
Printed in Great Britain.

LIGHT-INDUCED INTERCONVERSION OF CIS AND TRANS 2,3-DIMETHYLSPIRO[CYCLOPROPANE-1,9'-FLUORENE][1]

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(Received 21 February 1963)

LIGHT-INDUCED isomerizations include many basic types[3] but no examples of the stereoisomerization of a cyclopropane derivative.[4] During an investigation into the characteristics of the carbene fluorenylidene, an example of this type of isomerization has now been uncovered.

Photolysis of diazofluorene[5] in *trans*-butene leads to a mixture of products from which the addition product, *trans*-2,3-dimethylspiro[cyclopropane-1,9'-fluorene] (I) may be isolated by chromatography on alumina with cyclohexane-ether as the eluting solvent. The *trans* isomer, m.p. 104.5 - 105.5° (Found: C, 92.50; H, 7.31. $C_{17}H_{16}$ requires C, 92.67; H, 7.33%), has bands in the I.R. at 1932, 1897, 1860, 1825, 1792 and 1601 cm^{-1} characteristic of 9-substituted fluorenes and at 3090 and 1022 cm^{-1}, positions often associated with the cyclopropane system.[6] In the

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[1] This work has been supported by the National Science Foundation, Grant 11378.

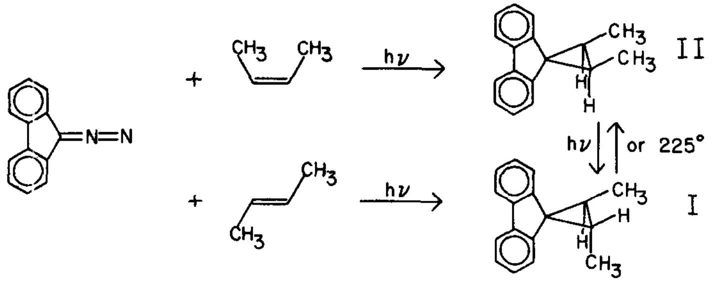
[2] DuPont Teaching and Assistantship Fellow, 1961-1962. National Science Foundation Summer Research Fellow, 1962.

[3] P. deMayo and S.T. Reid, *Quart. Rev.* (London) **15**, 393 (1961).

[4] G.W. Griffin, E.J. O'Connell and H.A. Hammond of Yale University have recently uncovered the photointerconversion of *cis* and *trans*-1,2-dibenzoylcyclopropane [*J. Amer. Chem. Soc.* in press (1963)].

[5] W. Kirmse, L. Horner and H. Hoffmann, *Liebigs Ann.* **614**, 19 (1958).

N.M.R. spectrum of I, the methyl groups appear at 1.47 p.p.m.[7] as a doublet (J = 4.5 c.p.s.), while the two cyclopropyl hydrogen atoms appear



as a multiplet, δ = 1.71 p.p.m. Aromatic hydrogen atoms (1', 2', 3', 6', 7' 8') appear as a group of relative area 6, δ = 7.15 p.p.m., while atoms 4' and 5' appear at 7.65 - 7.97 p.p.m.

Photolysis of diazofluorene in <u>cis</u>-butene gives a mixture of products from which the cyclopropane component is separated by chromatography on alumina and purified by fractional crystallization from cyclohexane. <u>Cis</u>-2, 3-dimethylspiro[cyclopropane-1, 9'-fluorene] (II), m.p. 121.5 - 122.5° (Found: C, 92.68; H, 7.24. $C_{17}H_{16}$ requires C, 92.67; H, 7.33%), has I.R. bands at 1938, 1900, 1864, 1830, 1793 and 1608 cm^{-1} (fluorene) and at 3095 and 1030 cm^{-1} (cyclopropane). In the N.M.R. spectrum of II, the methyl groups appear as a doublet at 1.32 p.p.m. (J = 5.1 c.p.s.) and the cyclopropyl hydrogen atoms appear as a multiplet at 1.90 - 2.15 p.p.m. In the <u>cis</u> isomer, there is a group of relative area 5 lying between 7.05 - 7.30 p.p.m. and a single hydrogen atom at 6.75 - 6.95 p.p.m., while the pair of hydrogen atoms, 4' and 5', appear

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[6] H. Weitkamp, U. Hasserodt and F. Korte, <u>Chem. Ber.</u> **95**, 2280 (1962).

[7] N.M.R. spectra were measured in a Varian A-60 Nuclear Magnetic Resonance Spectrometer and are reported in p.p.m. from tetramethylsilane (δ = 0.00 p.p.m.).

at 7.60 - 7.90 p.p.m.

Mixtures of I and II can be analyzed by g.l.p.c. on a 5-m kieselguhr column containing 5% Dow-Corning 710 silicone oil (*ca.* 1600 plates) at 220°. The *trans* isomer has the shorter retention time (*e.g.* 24 min compared with 30 min for the *cis* isomer).

Distinction between the *cis* and *trans* isomers rests on the method of synthesis, the emergence of a single aromatic hydrogen in the N.M.R. spectrum of II, and on the fact that I is favored thermodynamically over II by a factor of 1.75 (equilibrium can be established by heating either isomer at 230° for 24 hr).

The ultraviolet absorption spectra of the two isomers, as expected, are quite similar: *trans* (I): λ_{max} 302.5 mμ (ϵ = 11215), 291.5 (10535), 270 (19201); λ_{min} 297.5 mμ (ϵ = 7392), 287 (8921), 245 (9261). *Cis* (II): λ_{max} 302(10693), 291 (9843), 270 (17629); λ_{min} 297 (6890), 287 (8635), 243 (7829).

Irradiation was carried out in cyclohexane at 20° in Pyrex flasks with a sunlamp ("unfiltered radiation from mercury arcs passing through Pyrex") which furnishes radiation of λ 300 mμ. With pure *trans* or *cis* (containing 15% *trans*) as the starting material, identical photostationary states were reached after about 24 hr in which the ratio of *trans* to *cis* is 1.74. This photoisomerization presumedly involves electronic excitation of the fluorene portion of the molecule by absorption of light of λ 300 mμ (95 kcal/mole and less), homolytic cleavage of a 1,2-bond of the cyclopropyl ring to an intermediate in which free rotation permits the subsequent re-formation of the carbon-carbon bond to generate the 2,3-dimethylspiro[cyclopropane-1,9'-fluorene] in either the *cis* or the *trans* configuration. One of the interesting features of this isomerization is the cleavage of a bond one atom removed from the photoexcitable portion.

In this context, the reaction may be contrasted with stereochemical isomerizations of the androsterone-lumiandrosterone type[3] and may be compared with the flash photolysis of ethyl benzene to benzyl radical.[8]

Recognition of this stereochemical isomerization also serves as a cautionary note to the interpretation of the stereospecificity of the addition of certain carbenes to olefins. At the present time it is generally accepted[9] that stereospecific addition to *cis* and *trans*-butene implies a singlet carbene, whereas the absence of stereochemical specificity is considered to imply a triplet carbene. In reactions of photochemically generated carbenes to give absorbing product, one example of which is furnished by the present work and another by the extensive investigations of diphenyldiazomethane, it now becomes essential to prove that light-induced stereoisomerization of the product is not complicating the picture. In unfavorable cases, lack of stereochemical specificity would reflect less the true nature of the primary addition step than the incursion of a secondary transformation.

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[8] G. Porter and F.J. Wright, *Trans. Faraday Soc.* **51**, 1469 (1955).

[9] W. Kirmse, *Angew. Chem.* **73**, 161 (1961).