Tetrahedron Letters No. 16, pp. 1069-1071, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE CHEMICAL EVIDENCE FOR TRIPLET STATE OF BIPHENYLENEMETHYLENE [≠]

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(Received 18 April 1963)

Recently Trozzolo, Murray and Wasserman [2] reported the ground state triplet biphenylenemethylene on the basis of its electron paramagnetic resonance study. We wish to report the chemical evidence to determine its electronic structure, singlet or triplet.

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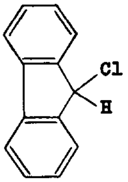
[2] A. M. Trozzolo, R. W. Murray and E. Wasserman, J. Am. Chem. Soc. 84, 4990 (1962).

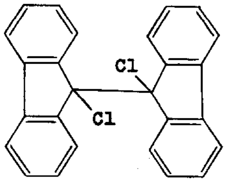
[≠] All compounds studied in the present experiment are known. Reaction products were successfully isolated by means of column chromatography. They were identified through comparison with each authentic samples. The structures of II and III were rigourously established by elemental analysis, IR and NMR studies. NMR spectrum of the compound II exhibited aromatic protons (2.25-2.90 τ), methyl(8.88 τ, triplet) and methylene (5.95 τ, quartet) of carboethoxy group, and protons on cyclopropane ring at 6.65 τ. The compound III gave quite similar pattern except the position of cyclopropane protons which appeared at 7.12 τ. This is reasonable because of the relative position of protons to the adjacent carboethoxy groups in these compounds, and therefore clearly supporting trans- and cis-configuration for II and III, respectively.

We have carried out the photochemical and thermal decomposition of 9-diazofluorene(I) in various olefins. The photochemical decomposition of I in diethyl maleate (*cis*-olefin) under irradiation of mercury lamp (2537Å) gave 1,1-biphenylenecyclopropane-2,3-*trans*-dicarboxylic acid diethyl ester [3] (II)(65%), its *cis*-isomer [3] (III)(2%) and a small amount of *bis*biphenylene-ethylene [4] (IV) and fluorenone-ketazine [5] (V). The photodecomposition of I in diethyl fumalate (*trans*-olefin) under the same condition as above similarly yielded the compound II (85%) and a small amount of IV and V.

VI



VII



The biphenylenemethylene from the thermal decomposition of I also produced the similar reaction products with II as a main product in diethyl maleate and fumalate.

All of these results clearly indicate that the addition of the biphenylenemethylene to a double bond proceeds non-stereospecifically [6], namely addition to the both *cis*- and *trans*-olefin resulted *trans*-adduct as a major product.

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[3] L. Horner and E. Lingnau, *Ann.* **591**, 46 (1955).

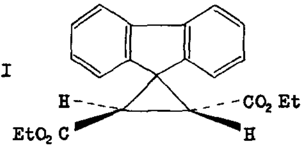
[4] J. R. Sawpey, *J. Am. Chem. Soc.* **69**, 234 (1947).

[5] H. Wieland and A. Roseau, *Ann.* **381**, 229 (1911).

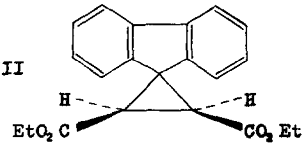
[6] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.* **78**, 5430 (1956); R. M. Etter, H. S. Skovronek and P. S. Skell, *ibid.* **81**, 1008, (1959).

The photodecomposition of I in *cis*- and *trans*-1,2-dichloroethylene gave 9-chlorofluorene [7] (VI)(85-89%) and a small amount of IV and fluorenone. Furthermore the photodecomposition of I in carbon tetrachloride resulted 9,9-dichloro-*bis*biphenylene-ethane [8] (VII) and a small amount of fluorenone. The formation of these chlorides can be understood as the result of radical abstruction reaction.

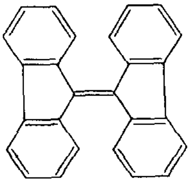
II



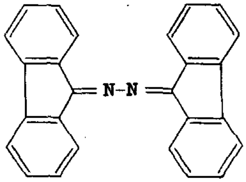
III



IV



V



In conclusion, the non-stereospecific addition of biphenylenemethylene to a double bond and the results of its reaction with chloro-compounds are providing the solid chemical evidences for the triplet state of biphenylenemethylene [6].

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[7] H. Staudinger, *Ber.* **39**, 3060 (1906).

[8] J. Schmidt and H. Wagner, *ibid.* **43**, 1796 (1910).