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TETRAVINYLETHYLENE

Lars Skattebøl
Union Carbide Research Institute
Box 278, Tarrytown, N. Y.

and

J. L. Charlton and P. deMayo[1]
Department of Chemistry, University of Western
Ontario, London, Canada.

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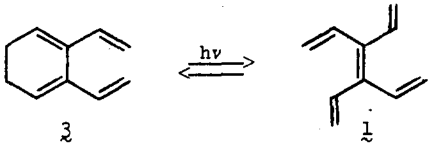
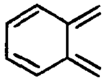
The hydrocarbon tetravinylethylene (1) represents an example of extended conjugation and cross-conjugation in a small molecule. Simple HMO calculations indicate a delocalization energy of 1.92 β[2] suggesting stabilization comparable with that in 2.[3] The present availability of the tetraene 3,[4] suggested that a route to 1 might be available through a photochemically induced electrocyclic reaction analogous to that well known in homoannular dienes.[5]



3 1



2

Irradiation of 3 as a 10% solution in n-pentane at -78°[6] in a Rayonet reactor with light of essentially 2537 Å for one hour, followed by removal of the solvent by fractional distillation at 0°, gave material which was separated by gas-liquid chromatography,[7] and which consisted of starting material and 1. There was about 25% polymer. The isolated yield of 1 was 6-7%, but compounds 3 and 1 were present in the reaction mixture in the ratio of 4:1. Irradiation of 1 led to the regeneration of 3, identified by retention time and I.R. and U.V. spectra.[4] Pyrolysis of 1 at 320° through a quartz tube packed with pyrex glass wool also regenerated 3.

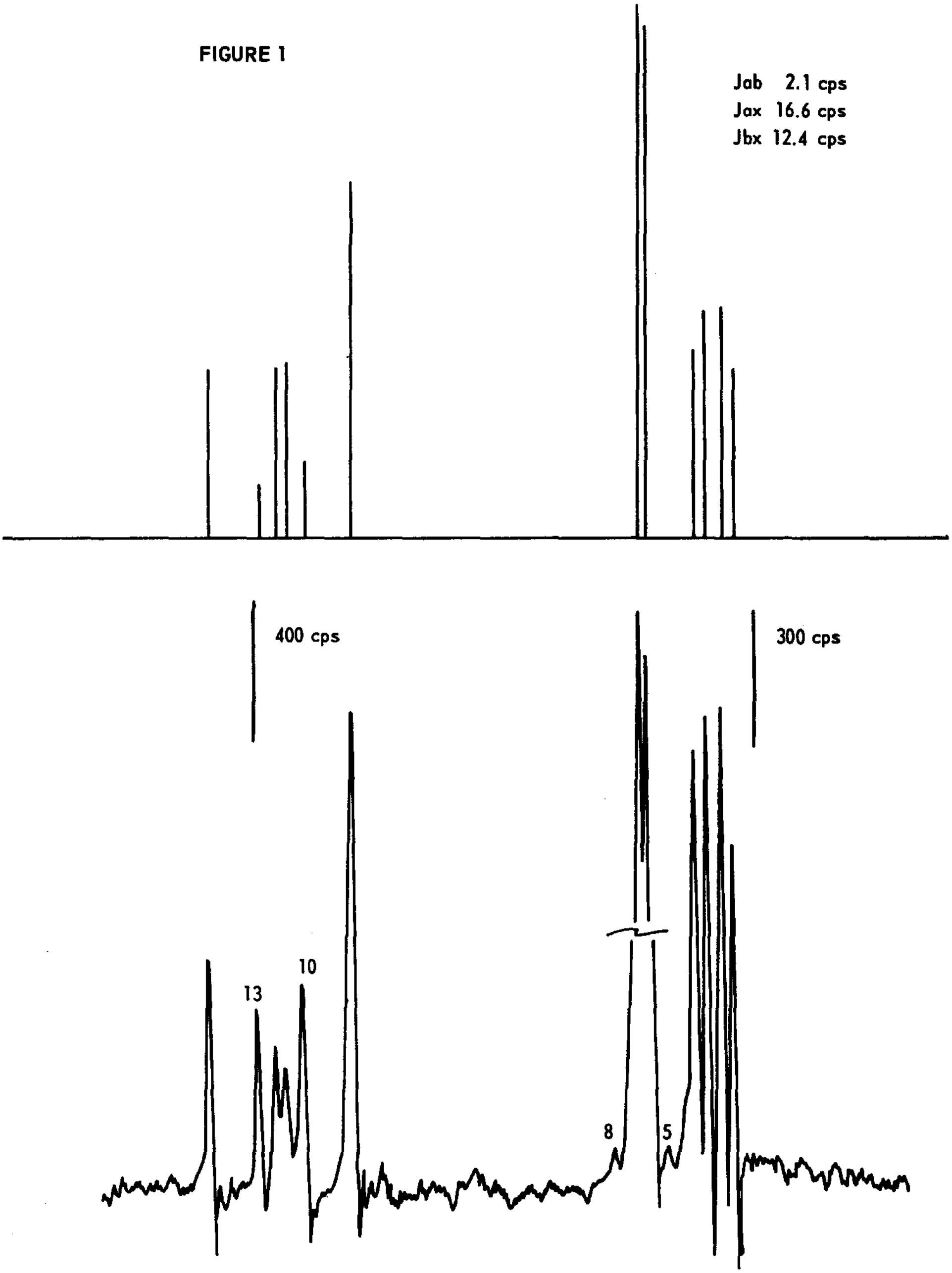
Irradiation of 3 in the presence of a sensitizer (benzophenone), both at -78° and 0°, such that the light was absorbed by the sensitizer led to accelerated polymer formation and no trace of 1.

The structure 1 is established on the basis of the following observations. The ultraviolet spectrum exhibits λ_{max} (EtOH) 224 (ϵ 16,300)[8] and 284 mμ (ϵ 23,300), compatible with the presence of a conjugated triene system.[9] The infrared spectrum (in CCl_4) shows characteristic vinyl absorption at 3090, 1610, 988, 930 and 910 cm^{-1}, which is also the main part of the spectrum. The presence of the two last bands, when normally one is observed, may indicate that 1 exists as a confirmational mixture in solution.

The n.m.r. spectrum (in CCl_4), Fig. 1, can be assigned as a perturbed ABX system to the approximation that couplings between protons in different vinyl groups can be ignored. The AB spins are strongly coupled, causing rather intense combination bands to appear in the X part of the spectrum (peaks 10, 13) and the outer lines of one of the two AB sub-spectra to become weak. Because of this the spectrum is sensitive to the sign of J_{AB}. Assuming all coupling constants to have the same sign, the computed[10] spectrum is shown in the Figure. The failure to obtain exact agreement is probably a consequence of the neglect of long-range couplings.[11] The parameters observed are reasonable for a vinyl group attached to a carbon atom.

Confirmation of the nature of the carbon skeleton was obtained in the following manner. Hydrogenation of the crude irradiation mixture over a 5% Pd/C catalyst gave a product from which 3,4-diethylhexane was isolated. This was shown to be identical with an authentic sample[12] by comparison of the mass spectra.[13]

FIGURE 1



REFERENCES AND FOOTNOTES

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2. See also M. Chowdhury, Proc. Nat. Inst. Sci. (India) 27A, 27 (1961).
3. J. D. Roberts, A. Streitweiser, and C. M. Regan, J. Am. Chem. Soc. 74, 4579 (1952).
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5. For a review, see W. G. Dauben, Chem. Weekblad 60, 381 (1964); see also N. J. Turro, "Molecular Photochemistry", Benjamin, Inc., New York 1965.
6. The solution was degassed and sealed in quartz. At high temperatures polymerization predominated even in dilute solution.
7. 5% Silicone SE 30 at 100°.
8. Because of the instability the intensities are only approximate.
9. The cross conjugated compound 1-phenyl-2-vinyl-1,3-butadiene absorbs at 285 mμ; P. Miginiac and M. Miginiac, Contr. rend. 258, 236 (1964).
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11. With the sign of J_{AB} opposite to those of J_{AX} and J_{BX} an entirely different spectrum was obtained by computation. We want to thank Dr. E. B. Whipple for the calculations and valuable discussions.
12. H. Koch and F. Hilberath, Ber. 73, 1171 (1940).
13. Kindly carried out by Dr. P. O. Schissel.