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ON THE IRRELEVANCE TO THE NORCARADIENE PROBLEM OF CONROW'S "EUCARVONE ENOL TRIPHENYLMETHYL ETHER"

W. von E. Doering and M. R. Willcott, III

Department of Chemistry, Yale University, New Haven, Conn.

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NORCARADIENE was one of the hypothetical valence-tautomeric structures considered for tropilidene and its derivatives almost from the beginning.[1,2,3] But, as n.m.r. spectroscopy made it possible to exclude this structure for tropilidene[4] and "norcaradiene carboxylic acid,"[3] and as no unequivocally defined pair of molecules having the norcaradiene-cycloheptatriene relationship emerged, a serious consideration of the structure became less and less reasonable, at least, in uncomplicated cases. However, two years ago Conrow reported "the isolation and characterization of such a compound which exists in the norcaradiene valence tautomer."[5] The structure of this substance,

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[1] R. Willstätter, Liebigs Ann. 317, 204 (1901).

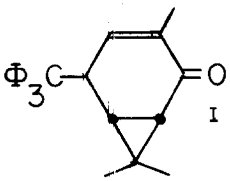
[2] H. Meerwein, H. Disselnkötter, F. Rappen, H. v. Rintelen and H. van de Vloed, Liebigs Ann. 604, 151 (1957).

[3] W. v. E. Doering, G. Laber, R. Vonderwahl, N.F. Chamberlain and R. B. Williams, J. Amer. Chem. Soc. 78, 5448 (1956).

[4] E. J. Corey, H. J. Burke and W. A. Remers, J. Amer. Chem. Soc. 77, 4941 (1955).

[5] K. Conrow, J. Amer. Chem. Soc. 82, 5504 (1960).

obtained by the reaction of sodio-eucarvone and triphenylmethyl chloride in 71% yield, was based on an absorption at 230 mμ (log ε 4.26) which was compared with the eucarvone enol esters of Corey (λ_{max} 270 mμ);[6] strong absorption in the infrared at 1643 cm^{-1}, attributed to an enol ether;[7] an n.m.r. spectrum showing two hydrogen atoms at 3.54 and 5.66τ, thought to be of the vinyl type, and three distinct and separate methyl groups at 8.3 to 8.9 τ, attributed to an allyl methyl and a geminate dimethyl group in an unsymmetrical environment; and the isolation of eucarvone (37%) and triphenyl carbinol (73%) by acid hydrolysis. It was concluded that "this evidence points unequivocally to the structure II for eucarvone enol triphenylmethyl ether."[5]



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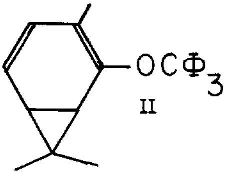

II

Having for some years been interested in various aspects of tropilidene and its derivatives, we wished to be well assured that the assignment of the norcaradiene structure was correct. A sample prepared according to the published procedure[7] showed substantially the same melting point (197-200° w. dec.), elementary composition (Found: C, 88.2; H, 7.6. Calcd. for $C_{29}H_{28}O$: C, 88.7; H, 7.2%); n.m.r. spectrum, (two vinyl hydrogen atoms at 3.6 and 5.6 τ), infrared

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[6] E. J. Corey and H. J. Burke, J. Amer. Chem. Soc. **78**, 174 (1956).

[7] K. Conrow, J. Amer. Chem. Soc. **83**, 2343 (1961).

(most intense band at 1650 cm^{-1}) and ultraviolet absorption spectra [λ_{max}^{EtOH} 230 mμ (ε 19,800)] as reported by Conrow.[5, 7] Much of this data affords questionable support for the assigned structure. Thus, cyclic, conjugated vinyl protons generally fall between 4.1 and 4.6 τ ;[8] enol ethers typically show very strong absorption about 1250 cm^{-1} whereas Conrow's substance shows only very weak absorption in this region;[9] and the ultraviolet absorption of a norcaradiene of this structure might be expected to fall between 256 and 265 mμ [10] (indeed, 2,3-dihydroanisole has its maximum absorption at 262 mμ [11]).

Chemical evidence has now been uncovered which cannot be interpreted by the hypothesis of an enol ether and is quite reasonably interpreted in terms of an α, β-unsaturated carbonyl function. When the substance is treated with lithium aluminium hydride a reduction product is obtained which shows a peak in the n.m.r. at 4.72 τ and absorption in the infrared at 3530 cm^{-1}, both facts attributable to an alcohol function. The single hydrogen at 3.6 τ has disappeared while the single hydrogen at 5.6 τ seems to have moved to the region between 6.2-6.7 τ which now has an area corresponding to two hydrogen atoms and appears to include the hydrogen of the secondary carbinol. The strong peak at 2.71 τ (15 hydrogen atoms) clearly arises from the

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[8] L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry p. 61. Pergamon Press, London (1959).

[9] L. J. Bellamy, The Infra-red Spectra of Complex Molecules p. 115. John Wiley and Son, New York (1958).

[10] A. E. Gillam and E. S. Stern, Electronic Absorption Spectroscopy p. 86; 90; 106. Edward Arnold, Ltd., London (1955).

[11] A. J. Birch, J. Chem. Soc. 1642 (1947).

trityl group.

The reaction of Conrow's substance with 2, 4-dinitrophenylhydrazine to give a derivative retaining the trityl group is strongly indicative of the presence of a carbonyl function [m.p. 180-181° w. dec.; λ_{max}^{EtOH} 381 mμ (ε 25, 300), 293 mμ (ε 7, 900) and 257 mμ (ε 14, 400) (Found: C, 73.2; H, 6.0; N, 9.9. $C_{35}H_{32}N_4O_2$ requires C, 73.4; H, 5.6; N, 9.8%)].

The ultraviolet absorption spectrum of the original substance has a maximum at 320 mμ (ε 126) which was not reported by Conrow. This band and the one at 230 mμ (ε 19, 800) are fully consistent with the location of the R and K bands found in monosubstituted α, β-unsaturated cyclohexenones.[10] The maximal absorption at 381 mμ shown by the 2, 4-dinitrophenylhydrazone is likewise indicative of an α, β-unsaturated cyclohexenone.[10]

Although the available evidence does not suffice for the establishment of a structure at the normally acceptable level of reliability, it does seem sufficient to permit the suggestion of I, as an alternative. Unnecessary as it is to elaborate here on the consistency of this formulation with all the experimental evidence, it should be mentioned that the formation of the substance would be rationalized as a C-alkylation[6] and the acid hydrolysis to eucarvone and triphenyl carbinol[5, 7] would be formulated as an "electrophilic fragmentation".

Insight into the properties of the norcaradiene system and into its thermodynamic and kinetic relationship to cycloheptatriene continues to await the availability of an appropriate pair of molecules.