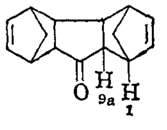
Communications to the Editor

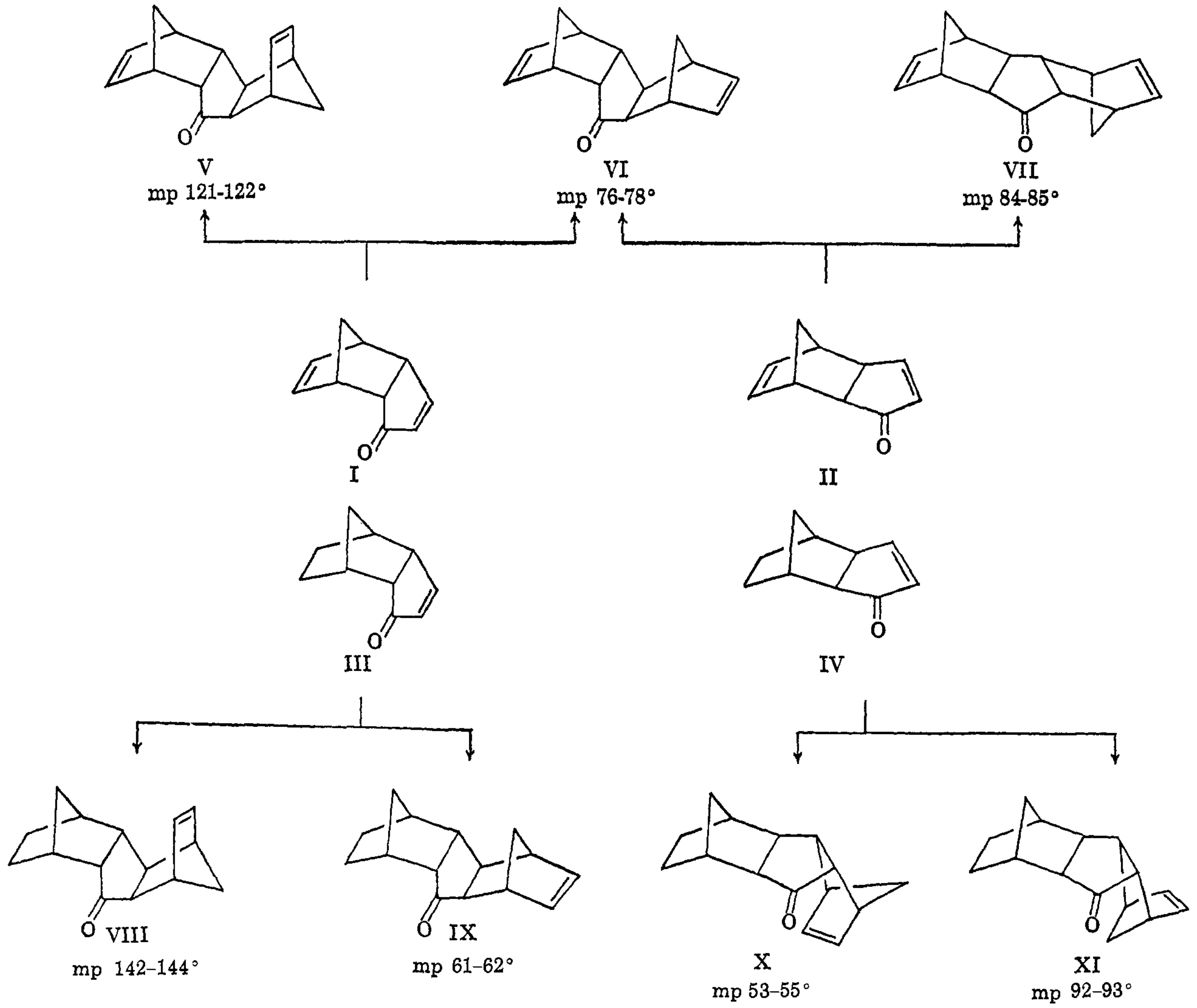
Synthesis of All the Stereoisomers of 1,4-5,8-Bismethylene-1,4,4aα,5aβ,5,8,8aβ,9aα-octahydrofluoren-9-one and Their Di- and Tetrahydro Derivatives

Sir:

Some years ago[1] we showed that the ketone formed by reaction of bicyclo[2.2.1]heptadiene with $Fe(CO)_5$ or $Fe_2(CO)_9$ had the gross structure A. The presence of a dyad axis along the CO bond was proved by chemical interconversions, leaving *endo,trans,endo* (V) or *exo,-trans,exo* (VII) as the only possible structure. Among several reasons which indicated the *endo,trans,endo* stereochemistry V for ketone A, the most compelling was the ultraviolet spectrum [λ_{max} 225 mμ (ϵ 2540) and 309 mμ (ϵ 137); *cf.* Table I][1,2] suggesting a charge-transfer interaction. However, Green and Lucken[3] pointed out later that the small vicinal coupling between the 1- and 9a-protons ($J < 1.0$ cps) was more consistent with the *exo,trans,exo* configuration VII. Thus there seemed to be a discrepancy between the two physical methods, *i.e.*, either the coupling constant deviated considerably from the Karplus equation or the charge-transfer and the exalted $n \rightarrow \pi^*$ transitions were due to a new type of chromophore. We have now settled this anomaly by synthesis of all three *trans* isomers.



A



endo-Dicyclopentadienone (I) and its dihydro derivative III have already been described.[4] The *exo* isomers II and IV were made from the known *exo*-dicyclopentadiene[5] and its dihydro derivative by oxidation with selenium dioxide and then chromic acid. Treatment

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(1) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (London) 20 (1960).

(2) R. C. Cookson, R. R. Hill, and J. Hudec, *ibid.*, 589 (1961).

(3) M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).

(4) K. Alder and G. Stein, *Ann.*, 504, 212 (1933); R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(5) A. A. Oswald and F. Noel, *J. Org. Chem.*, **26**, 3948 (1961). *exo*-Dicyclopentadiene was further purified by column chromatography on silica gel impregnated by 20% silver nitrate because the reaction product obtained by the method quoted in the reference cited was shown by nmr and glpc to be an approximately 1:1 mixture of *exo* and *endo* isomers.

of each ketone (I–IV) with cyclopentadiene in methylene chloride containing aluminum chloride[6] (0.3 mole) at 0–10° gave in every case a good yield of two stereoisomeric ketones (*exo* addition always predominating). In the diene series of adducts the isomer formed from both *endo*- (I) and *exo*-dicyclopentadienone (II) must be *endo,trans,exo* (VI); the configurations of the other two isomers then follow. In the dihydro series all four adducts are, of course, different, but the two *endo,trans,exo* isomers were easily identified by hydrogenation to the same saturated ketone, identical with the tetrahydro derivative of VI. Similarly, hydrogenation related V to VIII and VII to XI. For identification the melting points of the isomers are given under the formulae and their ultraviolet spectra are summarized in Table I. All the compounds had the expected elemental composition and infrared and nmr spectra.

Table I. Spectra of Dicyclopentadienones

Structure and Configuration	λ_{max}, mμ[a]	ϵ_{max}
III, *endo*	228	7850
	323	38
IV, *exo*	226	8250
	320.5	61
I, *endo*	226	7400
	323	36
II, *exo*	216.5	7390
	247.5[b]	1070
	323	48
VIII, *endo,trans,endo*		
	303	27.5
X, *endo,trans,exo*		
	302.5	37
IX, *exo,trans,endo*	224	1330
	307	79
XI, *exo,trans,exo*	224	1310
	309	84
V, *endo,trans,endo*		
	302	33.5
VI, *endo,trans,exo*	221	1410
	308	83
VII, *exo,trans,exo*	225	2540
	309	137

[a] Maxima of solutions in ethanol at wavelength longer than 210 mμ. [b] Shoulder.

The *exo,trans,exo* isomer VII was identical with the ketone from bicyclo[2.2.1]heptadiene and iron carbonyl.[7] The second double bond in the diene is not therefore involved in the reaction as we once thought,[1] but merely serves to increase the strain in the first and thus its reactivity. *exo* addition then occurs, as in the reaction with aqueous nickel carbonyl.[8] Indeed, some of the tetrahydro derivative of VII is formed when bicyclo[2.2.1]heptene reacts with iron carbonyl.

The chemistry of these compounds, including the rates of solvolysis of esters of the alcohols, will be reported later.

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(6) R. O. Williams, Ph.D. Thesis, Southampton University, 1961; P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **83**, 4436 (1960); R. Robinson and G. I. Fray, *ibid.*, **83**, 249 (1961).

(7) The configurations of the other ketones mentioned in ref 1 should also be revised from *endo* to *exo*.

(8) C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 410 (1963).

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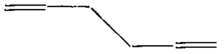
Received November 13, 1965

σ-Coupled p Electron Systems. A New Type of Chromophore

Sir:

Intense absorption of light in the near-ultraviolet region of the spectrum by compounds of the lighter elements generally involves electronic transitions on chains of three or more atoms having parallel p orbitals (dienes, enones, vinylamines, etc.) A second category was recognized more recently[1] in which the orbitals concerned are not on adjacent atoms (intramolecular charge transfer), and many further examples have since been described.[2] We now wish to draw attention to a third category which has remained unrecognized, namely σ-coupled transitions.[3,4]

Consider, for example, a 1,5-diene in a conformation where the central 3-4 bond is in a plane at right angles to both double bonds (B). The two π systems will be coupled by overlap with the central 3-4 σ bond, splitting both the π and π* levels and leading therefore to four possible transitions.[5]


B

The transition from the higher energy π to the lower energy π* orbital will then be shifted to longer wavelengths than in simple olefins, but this transition should be very sensitive to the precise geometry of the system. The coupling will decrease as the 3-4 bond is moved out of the plane normal to the double bond, until it is abolished when the 3-4 bond lies in the plane, and the spectrum will then become that of a normal olefin. Various classes of such coupled chromophores can be imagined, according to how the p orbitals at each end of the system are provided; *e.g.*, the C=C bonds might be replaced by C=O, N=N and so on, or by atoms with unshared electron pairs such as N or S. In unsymmetrical compounds the transition would have an element of charge transfer, which should become very marked in extremes such as β-amino ketones.

There are cases of what we believe to be such transitions in the region 220–260 mμ among hydrocarbons, γ,δ-unsaturated carbonyl compounds, γ,δ-unsaturated amines, and β-amino and β-thio ketones, some examples of which are given below.

The spectra of some ketones which demonstrate the exacting spatial requirement are summarized in Table I in the preceding communication. Among those with with two bicycloheptane units (V–XI) only those containing the cyclopentanone ring *exo* to a bicycloheptene (VI, VII, IX, XI) show an additional band at

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(1) R. C. Cookson and N. Lewin, *Chem. Ind.* (London), 984 (1956).

(2) *Inter alia*, H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); H. Birnbaum, R. C. Cookson, and N. Lewin, *J. Chem. Soc.*, 1224 (1961); R. C. Cookson and S. MacKenzie, *Proc. Chem. Soc.*, 423 (1961); S. Winstein, L. de Vries, and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961); N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960).

(3) In the $\pi \rightarrow \pi^*$ transitions of both the classical conjugated systems and those showing intramolecular charge transfer the σ bonds play no essential part in the transition, they merely hold the atoms together. In this new type of transition a σ bond is an integral part of the chromophore undergoing the transition.

(4) We originally referred to the excited state as σ*, since it has a node through the central single bond, but changed the description after helpful correspondence with Professor R. Hoffmann (Cornell), whom we thank for his interest.

(5) This elementary treatment neglects the more or less extensive mixing with other orbitals of appropriate symmetry that occurs in real molecules.