with the other isomer possessing little or no activity under these conditions.

[18] Danforth Fellow, 1968–1972.

Stephen T. Wilson,[18] John A. Osborn*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
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Critical Distance for Functional Group Interaction on Electron Impact

Sir:

Numerous recent studies[1–6] suggest that the electron impact induced fragmentation of organic compounds can be influenced by interaction between remote functional groups. Such interactions are demonstrated most unambiguously when they result in direct bond formation between the functional groups. In open-chain bifunctional molecules these interactions appear to be essentially independent of the distance between the two functionalities, and charge transfer with coiling of the carbon chain has been invoked.[7]

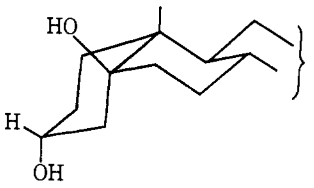
We have used the steroid molecule as a rigid template to determine how far apart two functional groups can be moved before detectable interaction ceases. A number of steroidal diols, in which both hydroxyl hydrogens had been exchanged with deuterium, were examined for loss of D_2O on electron impact induced fragmentation.[8] We chose to study this particular intramolecular interaction on the basis of prior work[9] with 1,2-cyclohexanediol, in which water loss was shown to occur by a variety of paths, including significant loss of D_2O (as well as H_2O and HDO loss) from the dideuteroxy derivative of 1,2-cyclohexanediol.

Table I

Steroidal diol	Loss of D_2O	Closest distance O–H---OH, Å
$3\beta,17\beta$-Dihydroxy-5α-androstane	No	10.8
$3\alpha,12\alpha$-Dihydroxy-5β-pregnan-20-one[a]	No	4.9
$3\beta,6\beta$-Dihydroxy-5α-cholestane	No	4.7
$3\alpha,5\beta$-Dihydroxy-5β-cholestane	No	3.5
$16\alpha,17\beta$-Dihydroxy-4-androsten-3-one[a]	Yes	3.2
$3\beta,4\beta$-Dihydroxy-5α-cholestane	Yes	2.4 (2.1)[b]
exo,exo-2,3-Dihydroxybicyclo[2.2.1]-heptane	Yes	2.0 (1.4)[b]
$3\beta,5\beta$-Dihydroxy-5β-cholestane	Yes	1.6 (1.5)[b]

[a] Kindly supplied by Dr. T. L. Popper, Schering Corporation, Bloomfield, N. J. [b] From measurements of Dreiding models. Numbers in parentheses are distances calculated from $\Delta\nu$(OH) by method of Kuhn.[11]

Our results are summarized in Table I, and we note first that no D_2O loss was detected for $3\beta,17\beta$-dihydroxy-5α-androstane (**1**), $3\alpha,12\alpha$-dihydroxy-5β-pregnan-20-one (**2**), or $3\beta,6\beta$-dihydroxy-5α-cholestane (**3**) as the dideuteroxy compounds. These observations reassured us that neither intermolecular deuterium transfer nor indiscriminate intramolecular scrambling of hydrogen and deuterium is a significant process under our experimental conditions. The contention that D_2O loss indeed comes from direct interaction of the two OD groups and does not involve bond cleavage or scrambling was further supported by a study of $3\alpha,5\beta$-dihydroxy-5β-cholestane (**4**) and $3\beta,5\beta$-dihydroxy-5β-cholestane (**5**) as the dideuteroxy derivatives. These compounds differ only in the configuration of the C-3 hydroxyl group, and whereas the $3\beta,5\beta$-diol (**5**) lost D_2O, the $3\alpha,5\beta$-diol (**4**) did not lose D_2O on electron impact. The dideuteroxy derivatives of $3\beta,4\beta$-dihydroxy-5α-cholestane (**6**), $16\alpha,17\beta$-dihydroxy-4-androsten-3-one (**7**), and bicyclo[2.2.1]-*exo*-2,3-heptanediol (**8**) also each fragmented with loss of D_2O.



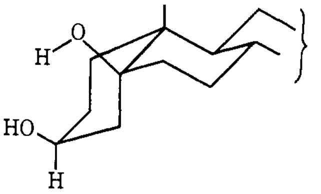


Table I shows that those compounds in our study which lose D_2O on electron impact are all 1,2- or 1,3-diols, and that these diols (except for the $16\alpha,17\beta$-dihydroxyandrostane derivative **7**) all show strong intramolecular hydrogen bonding in solution. Also shown are the closest O–H---OH distances[10] measured from Dreiding models, as well as the O–H---OH distances calculated[11] from infrared data in solution.

The range of O–D···OD distances within which D_2O loss occurs is, then, the range within which intramolecular hydrogen bonding occurs. The $16\alpha,17\beta$-dihydroxy steroid (**7**), for which intramolecular hydrogen bonding is neither expected nor demonstrated, is anomalous.

In conclusion, our measurements offer direct evidence that electron impact induced intramolecular interactions of functional groups will result in bond formation only when the atoms involved can be brought to within approximately normal bonding distances. This should allow other workers to assess the role played by ring opening and chain coiling in functional group interactions shown by cyclic and acyclic systems, respectively.

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(1) M. M. Green and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5190 (1967).

(2) M. Greff, R. E. Wolff, G. H. Draffan, and J. A. McCloskey, *Org. Mass Spectrom.*, **3**, 399 (1970), and references therein.

(3) S. Sloan, D. J. Harvey, and P. Vouros, *ibid.*, in press, and references therein.

(4) J. Winkler and H. F. Grützmacher, *ibid.*, **3**, 1117 (1970).

(5) J. L. Holmes and T. St. Jean, *ibid.*, **3**, 1505 (1970).

(6) A. Guggisberg, H. J. Veith, and M. Hesse, *Tetrahedron Lett.*, 3639 (1970).

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(8) The deuterium exchange was carried out in sealed glass capillaries with CH_3OD, and mass spectra were measured on a CEC-110 instrument at 70 eV, using the direct inlet system at source temperatures between 160 and 230°. In all cases the mass spectrum of the nondeuterated steroidal diol was run first; then the instrument was flushed several times with D_2O prior to analysis of the deuterated diol under otherwise comparable conditions. Although some d_1 and d_0 species were always present in the deuterated diols, analysis of the M^{+} and $M - 18$ groups conclusively demonstrated D_2O loss in some cases, as indicated in Table I.

(9) M. K. Strong and C. Djerassi, *Org. Mass Spectrom.*, **2**, 631 (1969).

(10) For our purposes, the O–H---OH distance is taken to be essentially the same as the O–D---OD distance for a given compound. Studies with hydrogen-bonded crystals [A. R. Ubbelohde and K. J. Gallagher, *Acta Crystallogr.*, **8**, 71 (1955)] have shown that substitution of deuterium for hydrogen produces very small changes in bond lengths. These changes are negligible compared with the errors involved in measurements from Dreiding models.

(11) $\Delta\nu(\mathrm{OH}) = 250/d(\mathrm{H{-}{-}{-}O}) - 74\ \mathrm{cm}^{-1}$: L. P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2492 (1952).

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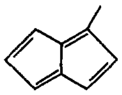
C. C. Fenselau,* C. H. Robinson
Department of Pharmacology
Johns Hopkins University, School of Medicine
Baltimore, Maryland 21205
Received March 26, 1971

1-Methylpentalene[1]

Sir:

Over the past years there have been many attempts to synthesize the hydrocarbon pentalene.[2] Up to the present success has attended on the preparation of aromatic derivatives[3,4] or the dianion[5] only. *In absentia* pentalene has been the subject of numerous calculations both in the ground state[6] and in the excited state,[7,8] the bond lengths being considered both as equal (symmetric) or unequal.

We wish to report experiments which lead us to believe that we have achieved the synthesis of 1-methylpentalene (**1**). It seemed likely, in view of the lack of success up to the present, that the object should be to generate pentalene in the absence of potential nucleo- or electrophiles. The retro-Diels–Alder was chosen as the generative step. Addition of 4-bromo-3-buten-2-one[9] to cyclopentadiene gave the adduct, which was then treated with the sodium salt of cyclopentadiene to give **2** in 51% yield. This was treated without purification with methylamine in methanol to give a mixture of two isomers. The major isomer **3** (80%) [*Anal.* Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.44; H, 7.82; λ_{max} 377, 278 nm (ϵ 620, 11,000)] was clearly a fulvene, and the 100-MHz nmr spectrum indicated the contiguity of the fulvene vinyl protons and the continuing presence of the methyl group. The mass spectrum confirmed the molecular weight (*m/e* 182) and, in addition, gave us encouragement since the base peak (*m/e* 116) indicated the loss of cyclopentadiene, *i.e.*, the formation of the **1** cation.



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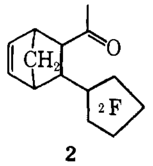

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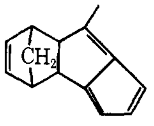

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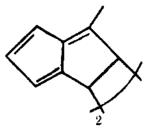

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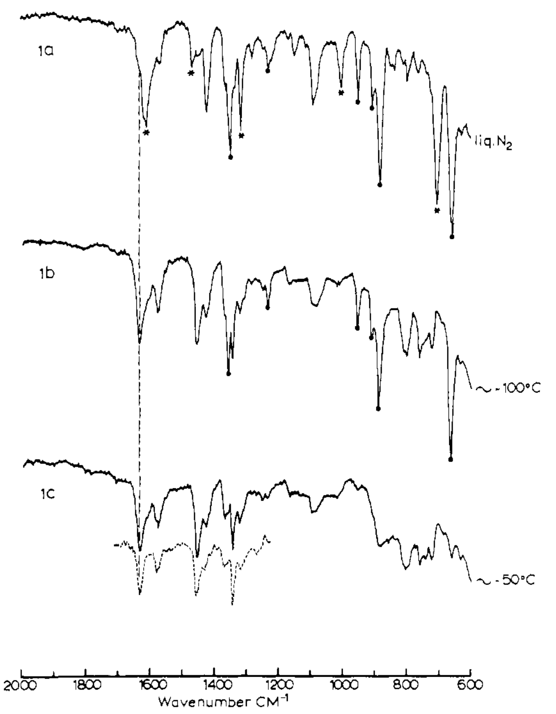

Figure 1. Infrared spectra of thermolysate of **3**: (a) at −196°; (b) at ~−100°; (c) at ~−50°; • bands assigned to cyclopentadiene; * bands assigned to **1**.

Thermolysis of **3** at 600° (<5 μ)[10,11] gave a crude product consisting essentially of cyclopentadiene and a mixture of two isomers. One of these has been obtained in crystalline form, mp 135–136° dec (pentane) [*Anal.* Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.30; H, 6.89; λ_{max} 387, 262 nm (ϵ 1400, 26,300)], and is assigned the structure **4** (or geometrical isomer). The molecular weight was confirmed mass spectrometrically, and the much more intense base peak was that for the methylpentalene cation (or isomer). The absorption spectrum of **4** indicates the presence of two fulvene moieties. The nmr spectrum[12] fully confirmed the gross structure. The circumstantial evidence that **1** had been generated by the retro-Diels–Alder reaction on **3** seemed strong. Further, more direct evidence was obtained as follows.

Flash thermolysis of **3** and condensation in a cryostat at −196° on a sodium chloride plate[13] gave the spectrum indicated in Figure 1a. This we believe to be the spectrum of **1** together with that of cyclopentadiene and a small amount of **3** or **4**. At −100° (Figure 1b) the bands attributed to **1** disappear and are replaced by those of **4**. At −50° (Figure 1c) the cyclopentadiene

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(1) Flash Thermolysis. VI. For part V see R. A. Marty and P. de Mayo, *Chem. Commun.*, 127 (1971).

(2) See, *inter alia*, E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959; G. M. Badger in "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969. The substance appeared on the end papers of the first two editions of Cram and Hammond, but although not synthesized did not achieve the third edition.

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(7) T. Nakajima, Y. Yaguchi, R. Kaeriyama, and Y. Nemoto, *Bull. Chem. Soc., Jap.*, 37, 272 (1964).

(8) N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 3072 (1971). Modified PPP calculations predict bands at 659 nm (forbidden), 335 nm (f = 0.45), 273 nm (f = 0.29), and 232 (f = 0).

(9) V. D. Nemirovskii, L. F. Chelpanova, and A. A. Petrov, *J. Gen. Chem. USSR*, **31**, 2380 (1961).

(10) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970).

(11) E. Hedaya, *Accounts Chem. Res.*, **2**, 267 (1969).

(12) It indicated the symmetry, the presence of the methyl groups, and, by double-irradiation, the proton sequence. We are very much indebted to Dr. M. Gordon for these determinations.

(13) The apparatus will be described in the full paper.