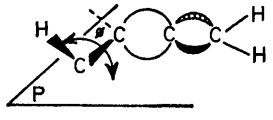
Long-range Proton Spin–Spin Coupling in Allenic Compounds

By M. SANTELLI

(*Laboratoire associé au C.N.R.S. No* 109, *Faculté des Sciences*, 13-*Marseille*, *France*)

Summary An equation relating the long-range coupling constant ^5J and the molecular geometry of allenic compounds is put forward.

MANY semi-empirical relationships between an angular value (*e.g.*, dihedral angle) and the magnitude of the related coupling constant have been reported for vicinal couplings,[1] allylic couplings,[2] and long-range couplings.[3] The case of ^5J in allenic derivatives (Figure) is less well



FIGURE

known,[4] and I describe a relationship which has been useful for cyclic derivatives. For the alcohols (I) and (II) taken as reference compounds, the following coupling constants were found:

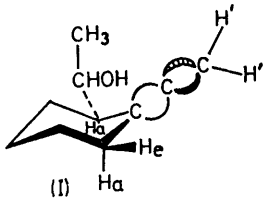
$$^5J(H_aH') = 3{\cdot}2 \text{ Hz} \quad \phi_a = 104°$$
$$^5J(H_eH') = 1{\cdot}2 \text{ Hz} \quad \phi_e = 5°$$

The dihedral angles ϕ_a and ϕ_e were evaluated by comparison with chair cyclohexanone.[5] On the basis of these reference coupling constants, we can write:

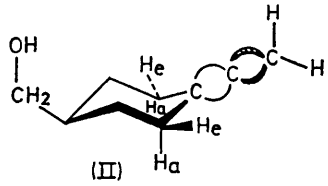
$$^5J = A \sin^2\phi + B, \text{ where } A \simeq 2{\cdot}25 \text{ Hz and } B \simeq 1{\cdot}18 \text{ Hz.}$$

The usefulness of this equation was tested on the compounds (III), (IV), and (V) (Table).

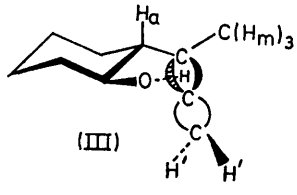
In the case of (III), the i.r. spectrum provides evidence of a strong intramolecular association, which is in agreement with the conformational model drawn from coupling-constant considerations. This is also the case for (IV). For the allenic ketone (V), the conformation which is the



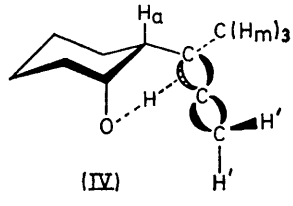
(I)



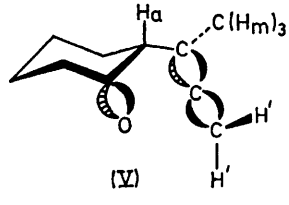
(II)



(III)



(IV)



(V)

most likely is probably the one where homoconjugation can be satisfied for the allenic and carbonyl groups.[6] Thus, atoms 1, 2, 3, 5, and 6 will be coplanar and the dihedral angle $\phi_a \simeq 120°$ which is exactly the value found from the equation.

This equation has been established using as reference *strainfree* compounds containing an allenic system with a terminal CH_2.

however, in the absence of any other relationship, the present one might be considered as useful although it needs further checking.

TABLE

	$^5J(H_aH')(CCl_4)$	ϕ_a	$^5J(H_mH')$	I.r.[a]	U.v. (EtOH)
(III)	1·05 Hz	0	3 Hz	3625 cm^{-1} (4·5%) 3602 cm^{-1} (75%) 3455 cm^{-1} (13%)	—
(IV)	2·6 Hz	127°	2·6 Hz	3624 cm^{-1} (7%) 3582 cm^{-1} (80%) 3455 cm^{-1} (13%)	—
(V)	2·75 Hz	123°	2·75 Hz	—	217 nm, ϵ 1200 290 nm, ϵ 260

[a] Solvent: CCl_4, conc.: 0·11 M.

Allenic systems are not very common, so that it was fairly difficult to check this equation on other molecules;

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