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Abstract

Full Text

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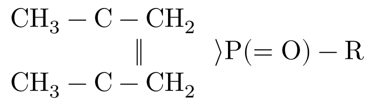
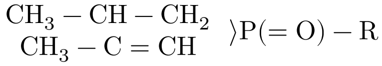
STRUCTURE AND FEATURES OF PROTON N.M.R. SPECTRA OF PHOSPHACYCLOPENTENE DERIVATIVES WITH ASYMMETRICALLY ARRANGED SUBSTITUENTS IN THE RING

It was reported earlier (1,2) that the reactions of phosphorus trihalides with dienes open up broad possibilities for obtaining various phosphacyclopentene derivatives. It was established (3) that they can exist in isomeric forms differing in the position of the double bond in the ring. It was shown that in the case of 3,4-dimethylphosphacyclopentenes, i.e., symmetrically substituted structures, the position of the double bond on going from P-, P-, P-trihalides to cyclophosphinic acid derivatives depends on the nature of the halogen. The use of bromides leads exclusively to structures with the double bond in the 3–4 position, whereas chlorides give predominantly 2–3 unsaturated rings. The position of the double bond was determined unambiguously with the aid of n.m.r. spectra, by the presence or absence of an ethylenic proton.



$$\begin{array}{rl} CH_3-C-CH_2 & \\ \| & \rangle P(=O)-R \\ CH_3-C-CH_2 & \end{array}$$

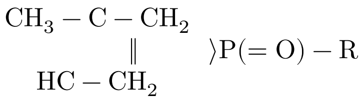
(A)



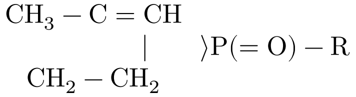
$$\begin{array}{rl} CH_3-CH-CH_2 & \rangle P(=O)-R \\ CH_3-C=CH & \end{array}$$

(B)

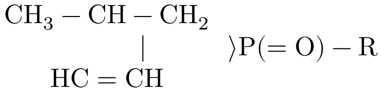
The present communication is devoted to phosphacyclopentene derivatives obtained on the basis of isoprene, which are more complex from the standpoint of structural proof. The presence of a single methyl group, which disrupts the symmetry of the molecule, permits three structural variants to be assigned to them:



$$\begin{array}{lll} \mathrm{CH_3 - C - CH_2} & & \\ \qquad\qquad \| & \rangle \mathrm{P(=O) - R} & \mathrm{(C)} \\ \quad \mathrm{HC - CH_2} & & \end{array}$$



$$\begin{array}{lll} \mathrm{CH_3 - C = CH} & & \\ \qquad\qquad | & \rangle \mathrm{P(=O) - R} & \mathrm{(D)} \\ \quad \mathrm{CH_2 - CH_2} & & \end{array}$$



$$\begin{array}{lll} \mathrm{CH_3 - CH - CH_2} & & \\ \qquad\qquad | & \rangle \mathrm{P(=O) - R} & \mathrm{(E)} \\ \quad \mathrm{HC = CH} & & \end{array}$$

To elucidate the structure of the compounds obtained, p.m.r. spectra were recorded, and the method of double nuclear-nuclear resonance (d.n.m.r.) was also used. The principle of the method is that the nuclear spins of P^{31} are subjected to the action of a strong radio-frequency field with the resonance frequency of the phosphorus nuclei. At the same time, the resonance spectrum of the protons, excited by a weak radio-frequency field, is observed. In this process the indirect spin-spin coupling between the phosphorus and hydrogen nuclei is disrupted. The theory of the method was developed by Bloom and Shoolery $^{(4)}$ and further developed by Baldeschwieler $^{(5)}$. To obtain the double-resonance effect, a special nuclear probe and an interpolation generator were used, producing an intense radio-frequency···

field frequency of 9.853 MHz and a field strength of about 20 oersteds, described earlier (^{6}). The PMR spectra at a frequency of 24.342 MHz and the double-resonance NMR spectra were recorded on a YaMR-KGU-1 NMR spectrometer (^{7}).

In the PMR spectra of compounds V, VI, VII, and VIII, the doublet lines of the ethylene protons have an intensity corresponding to one proton. The peak of the methyl protons is not split, which is characteristic of a methyl group located at a double bond. As the spectra of compounds of type B (^{3}) have shown, there is spin-spin interaction between the protons of a methyl group located at a secondary carbon atom and the nucleus of the phosphorus atom in the chain P—C—C—C—H. In the spectra of these compounds a doublet line appears. The spin-spin coupling constant $J_{\mathrm{P^{31}-H}}$ varies, depending on the substituent R, from 5 to 7 Hz. The nature of the splitting was confirmed by double-resonance NMR. When an oscillating field with the resonance frequency of ^{31}P is applied, the peaks of the doublet merge. At the same time, in the spectra of compounds of types A and B (^{3}), the methyl protons at the double bond correspond to a singlet peak. Consequently, structure D is rejected.

Structures B and G have more subtle differences: the ethylene proton in structure B is located at the β-, and in structure G at the α-carbon atom; the methylene groups are equivalent in structure B and nonequivalent in structure G. The coupling constant $J_{\mathrm{P-H}}$ of the ethylene proton with the nucleus of the phosphorus atom was taken as the determining characteristic; its magnitude depends on the arrangement of the interacting nuclei. The limiting values of the constants were obtained from the spectra of the model compounds B (α-ethylene proton) and E (β-ethylene proton).

Fig. 1. PMR and double-resonance NMR spectra. *a* —PMR spectrum of compound I, *b* —double-resonance NMR spectrum of compound I, *v* —PMR spectrum of compound VI, *g* —PMR spectrum of compound V.

The double-resonance NMR spectra confirm that the doublet at $\tau = 4.18$ ppm is due to interaction of the ^{31}P nucleus with the protons at the C=C bond. When a secondary field at the resonance frequency of the phosphorus nucleus is applied, both lines merge into one peak of doubled intensity. At the same time, the peaks caused by the interaction of ^{31}P with the CH$_2$ protons merge (Fig. 1).

Table 1

Structure B	R	J_{P-H}, Hz	Structure E	R	J_{P-H}, Hz
$CH_3-CH-CH_2\backslash$ $CH_3-C=CH/$ P(= C)−R	Cl	26.8	$H-C-CH_2\backslash$ $H-C-CH_2/$ P(= C)−R	Br	39.1
$CH_3-CH-CH_2\backslash$ $CH_3-C=CH/$ P(= C)−R	OH	24.3	$H-C-CH_2\backslash$ $H-C-CH_2/$ P(= C)−R	OCH$_3$	32.5
$CH_3-CH-CH_2\backslash$ $CH_3-C=CH/$ P(= C)−R	OCH$_3$	22.6	$H-C-CH_2\backslash$ $H-C-CH_2/$ P(= C)−R	OC$_2$H$_5$	36

Comparison of the values in Table 1 shows that, for substituents R of the same type, the value of J_{P-H} for the β-ethylene protons is approximately 1.5 times higher than for the α-protons. These values of J_{P-H} are anomalously high-

those compared with acyclic compounds, where the interaction through 2 bonds is equal to 12 Hz, and through 3 bonds to 10 Hz. Although the reason for such a difference in J_{P-H} for the interaction of α- and β-ethylene protons with the phosphorus nucleus in unsaturated heterocycles is not clear and requires special study, the very fact of this difference may be used for analytical purposes in determining the structure of the isomeric products obtained.

Table 2

Compound	R	J_{P-H}, Hz
V	Br	28.8
VI	Cl	28.0
VII	OH	23.8
VIII	OCH$_3$	36.5

From the cited values of J_{P-H} for the compounds studied (Table 2) it follows that compounds V—VII must have a structure of type G, and ester VIII, structure V.

Thus, we arrive at the conclusion that the position of the double bond in derivatives of phosphacyclopentene depends not only on the nature of the halogen ([3,8]) or on the route of synthesis ([3]), but also on the character of the diene, on the degree of symmetry in the arrangement of substituents in the ring.

Table 3

No.	Compound	Yield, %	m.p., °C	b.p., mm Hg	n_D^{20}	d_4^{20}	MR_D*	P*, %
I	H– C– CH_2‖ \\ OH –C– CH_2 P– Br	38	46–8 ‖	72– 40.53 O	1.5593	1.7037	34.3134.6	17.3417.11
II	H– C– CH_2‖ \\ OH –C– CH_2 P– Cl	15	52–3 ‖	112– 311 O	–	–	–	22.9522.69
III	H– C– CH_2‖ \\ OH –C– CH_2 P– OCH_3	49	– ‖	113– 414	1.4882 O	1.1891	32.0232.3	23.5423.45
IV	H– C– CH_2‖ \\ OH –C– CH_2 P– OC_2H_5	51	– ‖	71– 20.53	1.4801 O	1.1361	36.5436.9	21.2421.20

No.	Compound	Yield, %	m.p., °C	b.p., mm Hg	n_D^{20}	d_4^{20}	MR_D*	P*, %
V	CH_3 –	32	–	123–60.02	1.5682	1.6216	39.36 39.32	15.36 15.88
	C==CH	|	\					
	O CH_2 – CH_2 P– Br		‖		O			
VI	CH_3 –	16	–	91–20.02	1.5232	1.2604	36.50 35.96	20.67 20.57
	C==CH	|	\					
	O CH_2 – CH_2 P– Cl		‖		O			
VII	CH_3 –	30	116–7	174–60.02	1.5129	1.2165	32.70 32.25	23.43 23.45
	C==CH	|	\					
	O CH_2 – CH_2 P– OH_3		‖		O			
VIII	CH_3 –C–	31.5	–	11710	1.4847	1.1343	36.94 36.96	21.12 21.20
	CH_2 ‖ \							
	O HC – CH_2 P– OCH_3		‖		O			

* Upper figures are the values found; lower figures are calculated.

The constants of the substances obtained are given in Table 3. Compounds I and V were obtained from phosphorus tribromide and dienes with subsequent treatment with acetic anhydride, as described previously ($^{1-3}$). Compound VI was obtained

analogously from phosphorus trichloride. Acid VII was obtained by hydrolysis of haloanhydrides V and VI. Esters III, IV, and VIII were synthesized from the corresponding bromoanhydrides. Chloroanhydride II was obtained from ethyldichlorophosphite and divinyl by a known method ([9]).

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