

Carbomethoxymethylene Triphenylarsenanes

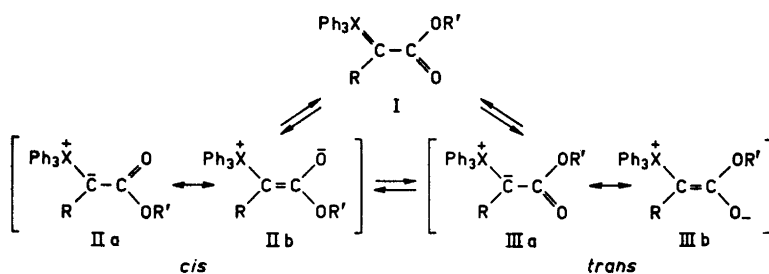
Calculation of the Barrier to Rotation About the C—COOCH₃ Carbon Bond by NMR

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Arsenanes of the formula $(\text{Ph}_3)_3\text{As}=\text{CR}-\text{COOCH}_3$ ($\text{R}=\text{H}$, Ph, CN) are studied. Evidence for partly double bond character of the C—COOCH₃ bond is given by the information obtained from an NMR variable temperature experiment. The free energy of activation, calculated for the rotational process, increases in the order: $\text{R}=\text{H}$, Ph, CN. These results are compared to those of corresponding phosphorus compounds.

The intramolecular dynamics of α -carbonyl stabilized phosphoranes has been studied in some details.¹⁻⁴ In the case of α -alkoxycarbonyl compounds, the importance of several resonance structures was considered^{1,4} (Scheme 1,



Scheme 1

$\text{X}=\text{P}$). The existence of a *cis/trans* equilibrium was demonstrated by the observation of two chemically different OR' groups from an NMR experiment at sufficient low temperatures. For $\text{R}=\text{H}$, two CH signals were also detected.² Raising the temperature led to coalescence, an observation in accordance with increased rate of internal rotation. It should also be mentioned that traces

of proton acids catalyze the *cis/trans* conversion, as the intermediate compound is assumed to be the phosphonium ion produced by protonation of the CR-carbon atom.^{6,7}

The main purpose of this study is to test whether the reaction scheme given for ester stabilized phosphoranes also applies to the analogous arsenanes. On the basis of the similarity between the chemical reactions, undergone by phosphorus and arsenic compounds, this is expected to be the case.

EXPERIMENTAL

α-Cyanocarbomethoxymethylene triphenylarsenane was synthesized according to the method of Horner and Oedinger.⁸ The reaction was carried out by dropwise addition of 0.05 mol of bromine to a solution of 0.05 mol of triphenylarsine in absolute benzene, then 0.1 mol of triethylamine, and finally 0.05 mol of methyl cyanoacetate was added. The reaction was carried out under dry nitrogen with vigorous stirring. After the addition of the reactants, the mixture was heated 10–15 min. Triethylammonium bromide was then filtered off and the product crystallized by stripping off the benzene. A chloroform solution of the ylide was passed onto a column of Merck No. 1077 aluminium oxide. The eluted product was recrystallized from chloroform-petroleum ether, m.p. 195–96°, lit.⁸ 193–94°.

α-Carbomethoxybenzylidene triphenylarsenane. To a suspension of 2×10^{-2} mol of triphenylbenzylarsonium iodide in absolute benzene was added 2×10^{-2} mol of phenyllithium. The resulting solution of triphenylarsine benzylidene was stirred for 2 h, whereafter 0.1 mol of methyl chloroformate was added. The reaction mixture was filtered, and most of the benzene distilled off. The product crystallized from the concentrated solution, and was recrystallized two times from benzene-petroleum ether, m.p. 169°.

Carbomethoxymethylene triphenylarsenane was synthesized according to literature.⁹ A solution of 15 g (0.05 mol) of triphenylarsine and 7.6 g of methyl bromoacetate in ethanol was heated overnight. The mixture was cooled and filtered into 1 l of dry ether. The precipitate was crystallized and dried, whereafter it was converted to the corresponding ylide by treatment with potassium hydroxide. The product was crystallized four times from benzene-petroleum ether, m.p. 160°, lit.⁹ 133–140°. Strong band (KBr) at 1608 cm^{-1} (6.21μ), lit.⁹ 6.13μ .

NMR measurements. Samples intended for NMR study were prepared as 0.3 M solutions in deuteriochloroform. To prevent possible acid catalysis, minute quantities (mg) of basic Al_2O_3 were introduced into the NMR tubes.

NMR spectra were recorded on a JEOL JNM-C-60H type spectrometer on internal lock (to TMS) conditions. Low temperatures, obtained by letting liquid nitrogen evaporate into the NMR probe, were measured using a copper/constantan thermocouple placed in vicinity of the NMR tube.

RESULTS AND DISCUSSION

R = H. At room temperature, the NMR spectrum of I ($X = \text{As}$, $R' = \text{CH}_3$, $R = \text{H}$) consisted of a complex low field signal (Ph_3) and two high field singlets (CH_3 and CH) in the intensity ratio 3:1. Lowering the temperature led gradually to broadening of both singlets, complete collapse, and thereafter splitting up into a total of four peaks.

R = Ph. The CH_3 signal appeared at room temperature as a broad singlet, being sharpened by increasing the temperature and splitted up into an unequal doublet on temperature decrease.

R = CN. The result is analogous to that for $R = \text{Ph}$, the intensity difference between the two peaks obtained by lowering the temperature being however greater in this case.

The result of the NMR temperature experiment can be interpreted in terms of *cis/trans* equilibria according to Scheme 1 ($X = \text{As}$, $R' = \text{CH}_3$), the contribution from carbon-carbon double bond resonance structures thus being accounted for.

To obtain the free energies of activation for the *cis/trans* isomerization process, the NMR method of Lynden-Bell is applied.^{10,11}

Experimental results and calculations based on the OCH_3 signal are listed in Table 1. Assignment of the *cis* and *trans* configurations were made on electrostatic grounds; the *trans* form being shielded to a greater extent than

Table 1. Coalescence temperatures ($^{\circ}\text{K}$), *cis/trans* ratios (p_c/p_t), ΔG -values for the *cis/trans* equilibrium (kcal/mol), NMR chemical shifts (ppm downfield from internal TMS) and free energies of activation (kcal/mol) for the rotational process about the C-COOCH₃ bond in compounds of the type $\text{Ph}_3\text{X}=\text{CR}-\text{COOCH}_3$.

X	R	T_c^b	p_c	p_t	$p_c - p_t$	p_c/p_t^a	ΔG	δ_c	δ_t	$\delta_c - \delta_t$	$\Delta G^\ddagger_{c \rightarrow t}$	$\Delta G^\ddagger_{t \rightarrow c}$
As	H	259	0.67	0.33	0.34	2.0	0.36	3.65	3.30	0.35	13.5	13.2
	Ph	282	0.70	0.30	0.40	2.3	0.47	3.65	3.22	0.43	14.8	14.3
	CN	298	0.88	0.12	0.76	7.2	1.17	3.80	3.43	0.37	16.3	15.2
P ^a	H	308	0.82	0.18	0.64	4.6	0.93	3.62	3.36	0.26	16.8	15.9
	Ph	225	0.79	0.21	0.58	3.8	0.58	3.66	3.25	0.41	11.9	11.3

^a The *cis/trans* ratios at coalescence were estimated from the ratios observed at lower temperatures.

^b T_c values are accurate to $\pm 3^{\circ}\text{K}$ and thus give ΔG^\ddagger values accurate to ± 0.2 kcal/mol.

^c T_c and *cis/trans* ratios taken from Ref. 1.

the *cis* form. For $R = \text{H}$, further evidence for this assignment is given by inspection of the position of the CH signal. Also in this case, the *trans* form should be expected to experience the greater shielding, in accordance with observation. As the *trans* OCH_3 signal and the *cis* CH signal are of nearly the same intensity, the identification of these was the subject of some ambiguity. However, on expanding the spectrum, the right assignment could be made by observing that the smallest, and one of the intermediate peaks, showed considerably greater half line width as compared to the greatest and the other intermediate one. The greater half line width of the CH signal can be explained by quadrupole broadening from arsenic ($I = 3/2$). It should be mentioned that the simultaneous coalescence of the CH and OCH_3 signal is in accordance with $\Delta\delta(\text{CH}) = 0.34$ ($\delta_c = 3.38$, $\delta_t = 3.04$).

Table 1 shows that the *cis* configuration is the most populated state, and that the *cis/trans* ratio for $R = \text{H}$, Ph is considerably smaller than for $R = \text{CN}$. This conclusion can more stringently be drawn from the calculation of the *cis/trans* ratio at a fixed temperature. At -50°C , this was found to be 2.5, 2.8, and 8.3 for $R = \text{H}$, Ph and CN, respectively.

Table 1 also includes the NMR results obtained by Bestman¹ from a study of the corresponding phosphoranes. In the $R = \text{H}$ case, it is immediately seen

that $X = P$ has a greater *cis/trans* ratio than has $X = As$. A comparison of the *cis/trans* value for the arsenic derivative obtained at $-50^\circ C$ (above) with the one given for the phosphorus compound ($-48^\circ C$) gives a corresponding result for $R = Ph$, although the difference is less pronounced. It thus seems that the *cis* conformer of the phosphorus compound is energetically more favourable relative the *trans* conformer than is the case for corresponding arsenic derivatives. An explanation could of course be sought by postulating a stronger electrostatic interaction in the phosphorus *cis* conformer. However, the more electropositive character of the As atom contradicts such an explanation. The possibility of stabilizing the *cis* conformer by partly overlap between the oxygen $2p$ orbitals and the d orbitals of phosphorus or arsenic is usually thought to depend on the size of the orbitals involved.^{12,13} It is not unreasonable that the phosphorus orbitals overlap with the oxygen $2p$ orbitals more effectively than do the more diffuse arsenic orbitals. Stronger contraction of the arsenic orbitals should then lead to stronger bonding, a conclusion being supported by the *cis/trans* ratio in the $R = CN$ case.

The chemical shift of the methine proton ($R = H$) in the arsenic and phosphorus compounds is of some interest. For the latter, these are found from Ref. 5 to be $\delta_c = 3.05$ and $\delta_t = 2.86$. Comparison with the above values given for the arsenic derivative shows that $X = P$ produces the greatest shielding at the methine proton, for both conformers. A possible interpretation of this observation could be given by assuming that $X = P$ has a greater contribution from structures IIa and IIIa than has $X = As$. However, different neighbouring anisotropy effects from the phenyl groups and a greater paramagnetic shift in the $X = As$ case would possibly contribute to the observed chemical shift difference.

Theoretically, it should be possible to calculate the *cis/trans* ratio at any temperature above coalescence by simply observing the resonance frequency of the signal involved. This is, according to Gutowsky,¹⁴ the weighed average of the separate *cis* and *trans* frequencies. The following equation is found:

$$K = \frac{\delta - \delta_t}{\delta_c - \delta}$$

Thus, if δ_c and δ_t are obtained from measurements at temperatures below coalescence, and in addition assumed to be temperature independent, K at any temperature can be calculated. For example, the compound I ($X = As$, $R' = CH_3$, $R = Ph$) gives $\delta = 3.46$ at $60^\circ C$. Using the values of δ_c and δ_t , listed in Table 1, leads to $K = 1.31$, a result illustrating increasing *trans* population when the temperature is raised.

Comparison of ΔG^\ddagger values should be made at same temperatures. However, since the entropy of activation for rotational processes are generally found to be small^{15,16} (a few e.u. for the rotation about the C-N bond in amides¹⁷), comparison of ΔG^\ddagger values may still be meaningful.^{15,18} On this basis, our results show increasing free energies of activation in the order $R = H, Ph, CN$.

The smallest difference between ΔG^\ddagger values for the arsenic derivatives equals $14.8 - 13.5 = 1.3$ kcal/mol, corresponding to a T_c difference of $282 - 259 = 23^\circ K$. Thus, if the relative order of ΔG^\ddagger values given above is to be

fictitious, an entropy of activation greater than 50 e.u. must be involved. This is very unlikely for a rotational process.

Table I also includes the results of a calculation based on the data given by Bestman¹ for two of the analogous phosphorus compound, R=H, Ph. As can be seen, the order of free energies of activation is reversed in such a way that for R=H $\Delta G^\ddagger(\text{P}) > \Delta G^\ddagger(\text{As})$ and R=Ph $\Delta G^\ddagger(\text{P}) < \Delta G^\ddagger(\text{As})$. By a calculation similar to the one above, it can be argued that these relationships are not due to a temperature effect on ΔG^\ddagger . However, the difference between activation energies obtained for the phosphorus and arsenic derivatives cannot easily be explained. Besides the temperature dependence of ΔG^\ddagger , steric hindrance and intermolecular effects (self association and solvent interaction) would be possible factors able to influence on the height of the barrier to internal rotation.

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