Tetrahedron Letters No.28, pp. 2357-2360, 1965. Pergamon Press Ltd.
Printed in Great Britain.

The reaction of stable phosphoranes with phthalic anhydride - a case of cis-trans isomerism.

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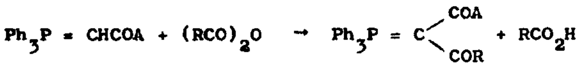
(Received 20 May 1965)

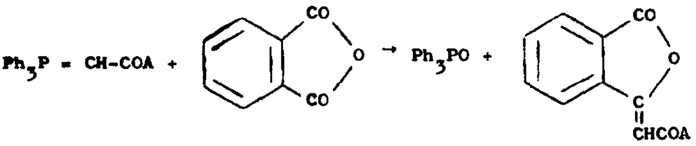
We have recently reported the reaction between stable phosphoranes, I, and carboxylic acid anhydrides to give diketo phosphoranes II,



$$\underset{\text{I}}{Ph_3P = CHCOA} + (RCO)_2O \rightarrow \underset{\text{II}}{Ph_3P = C\begin{matrix} COA \\ COR \end{matrix}} + RCO_2H$$

I II

The corresponding reaction with phthalic anhydride leads to the product of the normal Wittig reaction III,



III

where A = $-NC_4H_8O$, -OMe, -OEt, -Ph and -Me.

This reaction proceeds readily in the absence of a solvent, the stereochemistry of the product depending on the nature of A, as shown in Table 1.

TABLE 1

The ratio of CIS to TRANS olefin in the reaction of $Ph_3PCHCOA$ with phthalic anhydride

	A	%CIS	%TRANS	I P.(a)	$q_\pi(O)$(b)	K_H(c)	K_H(d)
IIIa	$-NR_2$	60	~ 0	8.8	> 0.62	~ 200	-
IIIb	-OMe	60	~ 0	10.27	0.62	-	-
IIIc	-OEt	60	~ 0	10.27	0.62	8.1	2.0
IIId	-Ph	12	50	9.27	0.59	6.8	1.76
IIIe	-Me	~ 0	64	9.67	0.54	8.5	2.9

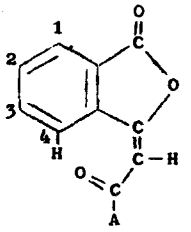
(a) Ionisation potentials of CH_3COA compounds[2].

(b) π-Electron charge density[3] on the oxygen atom of RCOA.

(c) Association constants[4], K_H, for the equilibria between CH_3COA and PhOH in CCl_4 at 25°.

(d) Association constants[5], K_H, for the equilibria between CH_3COA and EtOH in CCl_4 at 20°.

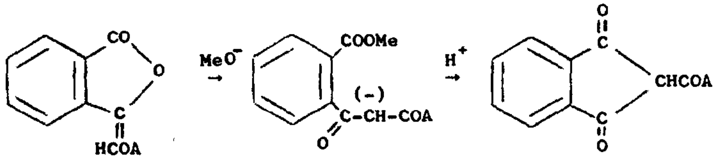
The isomers were recognised by differences in their p.m.r. and i.r. spectra, produced by the perturbation of the H^4 proton in the aromatic ring, probably caused by the carbonyl group, viz.,



IV

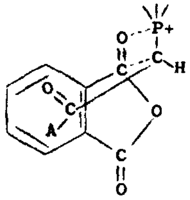
This interaction leads to a decrease in τ value of the p.m.r. spectrum of between 0.9 and 1.3 ppm. with respect to the other 3 aromatic protons and the 4 equivalent protons of the trans isomer, prepared by independent routes.

The cis-isomer is converted to the trans-isomer on u.v. irradiation and both isomers give the indanedione on treatment with sodium methoxide,



The specific formation of the cis isomer III a-c and the preferential formation of III d, is probably due to the interaction of the group -COA with either the aromatic ring, which is an electron acceptor owing to the -CO groups, or to the proton. We find however that the tendency to form the *cis*-compound, i.e. $A = R_2N \approx RO > Ph >> Me$ is quite different from the order of the association constants for hydrogen bonding, i.e. $R_2N >> Me >> EtO > Ph$, and the order of the ionisation potential of CH_3COA, i.e. $R_2N > Ph > Me > OEt$. The ratio CIS/TRANS decreases with electron release to the CO π-orbital, i.e. $R_2N >> RO > Ph >> Me$ as shown e.g. by the π-electron density on the carbonyl oxygen atom $q_\pi(O)$.

The Wittig reaction probably proceeds through a cyclic transition state (Structure V) which thus forces the group -COA into a plane parallel to the benzene ring.



V

In this configuration the lone pair (n) electrons of oxygen, which are used in complex formation, cannot interact with the system, but the p_{π} electrons (of A and C=O) can interact strongly with the electron deficient aromatic system. This $\pi \rightarrow \pi^*$ interaction is not normally observed with systems of this kind since the RCOA group forms $n \rightarrow n^*$ or $n \rightarrow \sigma^*$ complexes preferentially.

We wish to thank Dr. E.A.C. Lucken for the interpretation of the N.M.R. spectra, Dr. G. Klopman with whom several helpful discussions were held, and Mr. F. Devitt for technical assistance.

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