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ISOMER RATIOS IN FORMYLMETHYLENETRIPHENYLPHOSPHORANES AND THEIR ALKYLATION PRODUCTS

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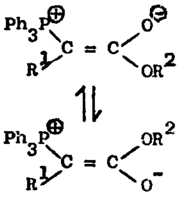
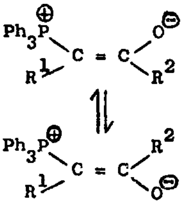
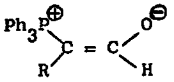
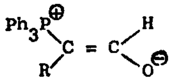
Isomer ratios, and the effect of changing solvent on these ratios, have been studied for both ester (1)[1] and keto (2)[2] stabilised ylids. Ester ylids exist as a mixture of <u>cis</u> (1a) and <u>trans</u> (1b) isomers in $CDCl_3$, the amount of <u>trans</u> increasing with the bulk of R'[1a] and/or increasing solvent polarity,[1b] while keto ylids show only the <u>cis</u> isomer (2a)[2b] unless R^1 or R^2 are very large.[2a] We have now studied isomer ratios for formyl stabilised ylids in various solvents since these provide a system with a minimum steric inhibition to solvation at oxygen[1b]

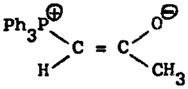

(1a)
(1b)


(2a)
(2b)

The <u>cis/trans</u> ratios for a number of substituted formyl ylids (3) are shown in Table 1. Unlike the keto ylids (2)[2] <u>trans</u> isomer is present in all cases. This can be explained in terms of the reduced interaction between phosphorus and hydrogen. The importance of this interaction is exemplified by a comparison of ylids (4) [100% <u>cis</u> in $CDCl_3$][2b] and (3; $R=CH_3$) [100% <u>trans</u> in $CDCl_3$]. For the ester ylids (1) in $CDCl_3$ the amount of <u>trans</u> isomer <u>increases</u> with the bulk of R^2 [1b] and an ingenious explanation has been proposed in terms of the energy gain from solvation forcing the Ph_3P^+ group <u>trans</u> in the face of increasing steric inhibition of solvation by R^2. However, variations in R in formyl ylids (3) effect isomer ratios in a similar way to analogous variations in R^1 in ester ylids (1).[1a]


(3a)

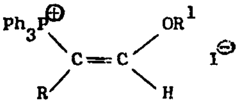

(3b)

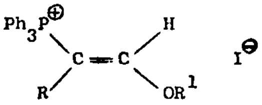

(4)

The isomer ratios for formylbenzylidenetriphenylphosphorane (3; R=Ph)[3] in various solvents are given in Table II. The polarity and solvating ability of a solvent are not necessarily directly related;[5] however in general the expected increase in the proportion of *trans* isomer with increasing solvent polarity is observed. The isomer ratio of (3; R=Ph) appears to be unaffected by the addition of LiBr, unlike that of the ester ylid (1).[1b]

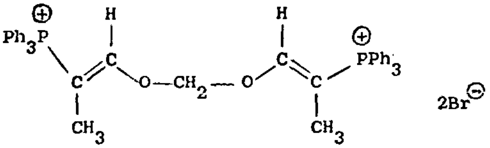
The ^{31}P nmr chemical shifts for the ylids (3; R=4-$NO_2C_6H_4$) and (3; R=Me) are given in Table I. The assignments are made on the basis of the presumed shielding in the *cis* case.[6]

Alkylation of the ylids (3) with methyl or ethyl iodide took place exclusively at oxygen to give the salts (5a) and (5b) in ratios (Table III) which differed from those observed in the corresponding ylids (3) and in some cases (3; R=$NO_2C_6H_4$) showed a marked dependence on the alkylating agent. The stereochemistries of (5) were assigned on the basis of J_{PCCH} values [28-34 Hz for (5a) and 11-13 Hz for (5b)]. The use of methylene bromide as an nmr solvent for ylids (3) above room temperature led to decomposition. The product from the decomposition of (3; R=Me) was isolated and assigned structure (6), with *trans-trans* stereochemistry, on the basis of its nmr spectrum; τ (CH_2Br_2) 2.04-2.50 m (30H), 2.80 bd, (2H, J_{PCCH} = 11 Hz), 3.90 s (2H), 8.06 dd (6H, J_{PCCH} = 13 Hz, J_{HH} = 1 Hz). Methylene diiodide gave a similar product.





(5a) R^1 = Me or Et (5b)



(6)

TABLE 1

		J_{PCCH}	(Hz)	^{31}P Chemical Shift $^{(a)}$	
R	cis/trans	cis	trans	cis	trans
H [4]	55/45	38	4	-15·0	-19·1
Ph	50/50	30	6	-	-
$3\text{-}NO_2C_6H_4$	50/50	30	5	-	-
$4\text{-}NO_2C_6H_4$	33/67	27	5	-16·4	-22·4
$3\text{-}ClC_6H_4$	54/46	27	5	-	-
CH_3	0/100	-	4	-	-25·4

(a) ppm from H_3PO_4

TABLE II

Solvent	D^b	E_T(kcal/Mole)	cis/trans
$CDCl_3$	4.80	39.1	1.17
CH_3SOCH_3	48.9	45	1
CH_2Br_2	7.2^c	-	0.85
CH_3OH	32.6	55.5	0.61
C_2Cl_4	2.3^d	-	>30
$CHCl_2CHCl_2$	8.2^e	-	>30

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TABLE III

Isomer Ratios in Alkylation Products of Ylids (3)

R	Methylation		Ethylation	
	(5a)	(5b)	(5a)	(5b)
H	55	45	55	45
C_6H_5	79	21	76	24
$3\text{-}NO_2C_6H_4$	28	72	100	0
$4\text{-}NO_2C_6H_4$	40	60	100	0
$3\text{-}ClC_6H_4$	60	40	-	-
CH_3	10	90	0	100

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