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Preliminary communication

Reactivity of phosphonium diylids with aldehydes and ketones

Henri-Jean Cristau *, Yves Ribeill, Laurent Chiche and Françoise Plénat

Laboratoire de Chimie Organique E.N.S.C.M., Unité Associée au C.N.R.S. No. 458, Institut de Chimie Fine 8, rue de l'Ecole Normale, 34075 - Montpellier Cedex (France)

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Abstract

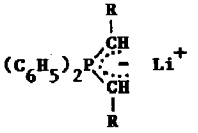
Non-stabilized and semi-stabilized phosphonium diylids of the type $(C_6H_5)_2P(CHR)(CHLiR)$ (**5**) show a greater nucleophilic reactivity toward carbonyl compounds than the corresponding monoylids $(C_6H_5)_2P(CHR)(CH_2R)$ (**8**). Thus diylid **5a** reacts readily at room temperature with sterically hindered ketones such as fenchone or di-t-butylketone. However, the residual negative charge in the intermediate adduct **13** slows the decomposition to Wittig products, and is probably responsible for the observed changes (generally enhancement) in the *E*-selectivity in the case of non-stabilized as well as semi-stabilized ylids.

Phosphonium ylids **1** and their aza analogues **2** are very useful in organic synthesis [1a,c,d], but their moderate nucleophilic character often limits their reactions to those with the most electrophilic carbonyl compounds, such as aldehydes and ketones, and sometimes to aldehydes only.

$(C_6H_5)_3P{=}CH{-}R$ **1** $(C_6H_5)_3P{=}N{-}R$ **2**

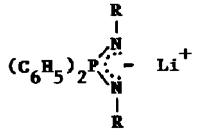
Because of this various more-nucleophilic organophosphorus reagents (such as α-metallated phosphinoxides, phosphonates, or phosphonamides) were soon developed [1b], but more recently, attention has turned to metallated phosphonium ylids either of the yldiid [2*] types **3** and **4**, or of the diylid [2*] types **5** and **6**. The synthesis and reactions of yldiid **3** were described by Schlosser [3] and by Corey [4], and we have presented reports on diylids **5** and **6** [5] and yldiid **4** [6]. In this paper,

$(C_6H_5)_3P{=}CH{-}Li$ **3** $(C_6H_5)_3P{=}N{-}Li$ **4**



$(C_6H_5)_2P(CHR)_2^{-}\ Li^+$

5



$(C_6H_5)_2P(NR)_2^{-}\ Li^+$

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* Reference number with asterisk indicates a note in the list of references.

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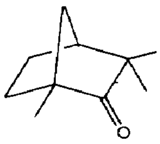
Table 1. ^{31}P NMR chemical shifts (ppm) for the diylids **5** and the corresponding monoylids **8** and salts **7**

	R	X	**7** ($CHCl_3$)	**8** (THF)	**5** (THF)
a	H	I	20.2	10.1	30.9 (green-yellow)
c	C_6H_5	Br	26.8	6.7	−1.2 (dark red)
d	$\underset{\overset{\|}{O}}{C}C_6H_5$	Cl	21.5	12.0	4.0 (pale yellow)

Table 2. Reaction of phosphonium mono- and di-ylids with aldehydes and ketones

Carbonyl compound	Monoylid **8** or diylid **5**		Conditions	Unreacted products [a] (%)	Wittig products **9** [b]	
					Yield (%)	Z/E
$R^1 = H$,		**8b**	5 h, −50 °C	90	10	98/2 [c]
$R^2 = C_6H_{13}$	$R = C_2H_5$		24 h, +25 °C			
		5b	idem	0	98	40/60 [c]
		8c	30 min, −50 °C	0	95	10/90 [d]
	$R = C_6H_5$		16 h, +25 °C			
		5c	idem	0	95	25/75 [d]
	$R = \underset{\overset{\|}{O}}{C}C_6H_5$	**5d**	24 h, +25 °C	100	0	–
$R^1 = H$,		**8c**	30 min, −50 °C	0	98	15/85 [e]
$R^2 = C_6H_5$	$R = C_6H_5$		16 h, +25 °C			
		5c	idem	0	98	5/95 [e]
		8d	24 h, +25 °C	60	35	*f*
	$R = \underset{\overset{\|}{O}}{C}C_6H_5$					
		5d	14 h, +25 °C	20	70	*f*
$R^1 = C_6H_5$		**8a**	30 min, −50 °C	25	75	–
$R^2 = C_6H_5$	$R = H$		90 min, +25 °C			
		5a	idem	10	63 [g]	–
		8c	30 min, −50 °C	55	45	–
	$R = C_6H_5$		90 min, +25 °C			
		5c	idem	20	80	–
	$R = \underset{\overset{\|}{O}}{C}C_6H_5$	**5d**	24 h, reflux	100	0	–
	$R = H$	**5a**	2 h, 20 °C +1 equiv. $C_6H_5CO_2H$ 24 h, 20 °C	2	98	–
$R^1 = R^2 = t\text{-}C_4H_9$	$R = H$	**5a**	48 h, 20 °C+1 equiv. $C_6H_5CO_2H$ 24 h, 20 °C	15	85	–

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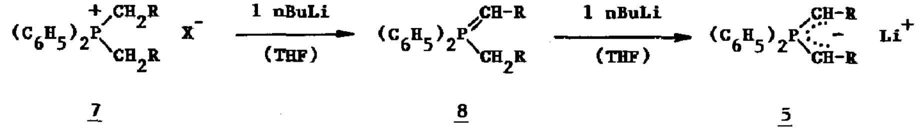
[a] Percentage of unchanged carbonyl compound and of the phosphonium salt **1** formed by hydrolysis of unchanged **8** or **5**. [b] Similar quantities of the corresponding phosphine oxides $(C_6H_5)_2P(O)CH_2R$ were isolated in all cases. Yields are after chromatographic separations. [c] The dominating isomer is that indicated by ^{13}C NMR spectroscopy; the exact ratio was determined by ^1H NMR (360 MHz) by integration of the methyl signals in the ^1H spectrum. [d] Z/E ratio determined from the vicinal olefinic coupling in the ^1H NMR spectrum at 360 MHz. [e] Z/E ratio of stilbene obtained by GLC. [f] Stereochemistry not determined. [g] Products **10** (23%) and **11** (5%) were also obtained in this case.

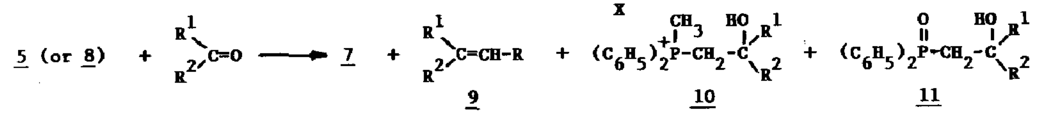
we report initial results [7] on the comparison of the reactivity of diylids **5** [8*], with that of the corresponding monoylids **8** toward aldehydes and ketones.

Although the first phosphonium diylid was prepared by Wittig [9] as long ago as 1949, the chemistry of these compounds has been mainly developed by Schmidbaur in respect of their use as bidentate ligands for metal coordination [10]. Except for two special applications [9,11], they were not regarded as new organic reagents although dicarbanionic species have recently attracted increasing interest [12*].



a : R = H ; b : R = C_2H_5 ; c : R = C_6H_5; d : R = $\underset{\displaystyle O}{\overset{}{C}}\text{-}C_6H_5$

We have examined the reactions of non-stabilized (**a**, **b**), semi-stabilized (**c**) and stabilized (**d**) monoylids **8**, and the diylids **5** (Table 1). Standard acidic work-up gave some unchanged **7** and the Wittig product **9** (Table 2), together in one case (R = H, $R^1 = R^2 = C_6H_5$), with the adducts **10** (23%) and **11** (5%) [13*].



The smaller amounts of unchanged reactant **7** left in the reaction of diylids **5b** with heptanal, **5a** and **5c** with benzophenone, and **5d** with benzaldehyde, compared with those in the reactions with the corresponding monoylids **8** (see Table 2), show that diylids **5** are more nucleophilic than the monoylids. Thus, more sterically hindered ketones such as L-fenchone or di-t-butylketone, which are unreactive towards monoylid **8a**, afford the corresponding Wittig products in good yield with diylid **5a** (see Table 2). This strong nucleophilicity is easily accounted for, since the phosphorus *d*-orbitals, already engaged in the first ylidic bond, are less available for stabilizing the second carbanionic center. This effect, however, is not strong enough to allow reaction of the stabilized diylid **5d** with a ketone or even heptanal.

Reaction of **8a** and **5a** with benzophenone reveals yet another unique feature of the diylids; the fact that the product **11** was isolated shows the decomposition of the intermediate metallated betainic adduct to be slow. The diylids **5** show a better nucleophilicity together with higher stability of the intermediate adducts, than the Horner reagents, which they closely parallel.

It is noteworthy that the use of diylids **5** induces changes in stereoselectivity of the carbonylolefination in contrast to the reactions of the analogous monoylids **8**. The increased *E*-selectivity, recently corroborated by Walker [15] in the case of semi-stabilized diylids, is not so high as that reported for the Schlosser modification using *β*-oxydo ylids [16,17], but is probably in the same way accounted for by intramolecular proton transfer owing to the residual negative charge in the diastereomeric intermediate adducts.

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13 A solution of the crude product in the minimum of $CHCl_3$ was slowly added to well stirred Et_2O ($CHCl_3/Et_2O$ 10/1). Any precipitate (which is filtered off) is made up of the phosphonium salts **7** and **11**; the latter was characterized by spectroscopy and elemental analysis. Column chromatography of the concentrated mother liquor gave pure Wittig products **9** and phosphine oxides, which were characterized by spectroscopy and GC–MS. Significant data for products not commercially available are: **9** ($R = C_2H_5$, $R^1 = H$, $R^2 = C_6H_{13}$): GC–MS m/e (140 M^+); the ^{13}C NMR spectrum of the Z/E mixture is the exact superimposition of pure Z and E isomers [14]. **9** ($R = C_6H_5$, $R^1 = H$, $R^2 = C_6H_{13}$): ^1H NMR ($CDCl_3$, 360 MHz), 1.0–1.1 (m, 3H, CH_3), 1.3–1.7 (m, 8H, CH_2), 2.3 (q, $=CCH_2$, E, J 6 Hz), 2.4 (q, $=C–CH_2$, Z, J 7.0 Hz), 5.8 (dt, =CHC, Z, J 11.6 and 7.0 Hz), 6.8 (dt, =CH–C, E, J 16.0 and 6.0 Hz), 6.49 (d, Ar–CH=, E, J 16.0 Hz), 6.05 (d, ArCH=, Z, J 11.6 Hz), 7.2–7.6 (5H, C_6H_5); GC–MS: m/e 188 (M^+). **9** ($R = R^1 = R^2 = C_6H_5$): GC–MS m/e 256 (M^+). 5 ($R^1 = R^2 = C_6H_5$): m.p. 123° C; ^{31}P NMR ($CHCl_3$) 20.9; ^1H-NMR ($CDCl_3$) 2.73 (d, 3H, CH_3, J 14 Hz), 4.50 (d, 2H, CH_2, J 13 Hz), 5.47 (s, 1H, OH, disappears upon addition of CF_3COOH) 6.8–8.0 (m, 20H, C_6H_5). **12** ($R^1 = R^2 = C_6H_5$): m.p. 190 ° C; ^{31}P NMR ($CHCl_3$), 32.9; ^1H NMR ($CDCl_3$) 3.45 (d, 2H, CH_2, J 10 Hz), 6.90 (s, 1H, OH, disappears upon addition of CF_3COOH), 7.0–7.8 (m, 20H, C_6H_5).

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