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ACYLATION OF ARSENIC β-KETOYLIDES BY CARBOXYLIC ACID HALIDES

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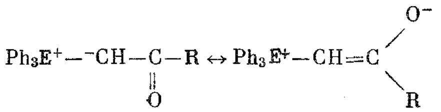
Ketophosphonium and ketoarsonium ylides of type (I) can react at O and C nucleophilic centers



$$Ph_3E^+-{}^-CH-\underset{\overset{\|}{O}}{C}-R \leftrightarrow Ph_3E^+-CH=C\begin{matrix}O^-\\R\end{matrix}$$

(I)

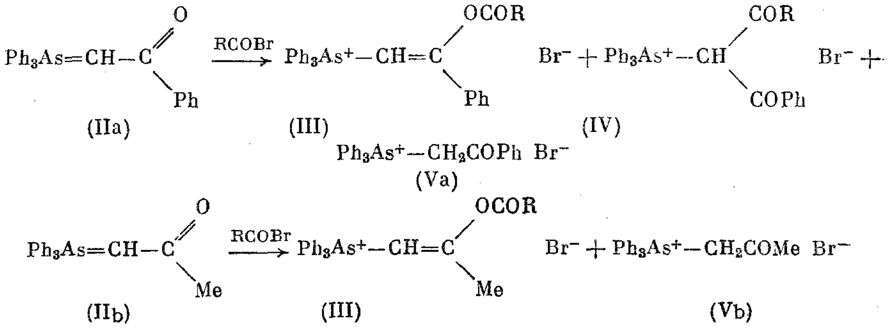
E = P, As.

Phosphonium ylides of this type are acylated by acid chlorides at the O atom exclusively, and the O-acylvinylphosphonium salts formed do not undergo any O→C rearrangement [1, 2]. The reaction of P and As ylides with trifluoroacetic anhydride leads to an O-acylation product, which on heating rearranges into a C-substituted product [3, 4]. Acetic anhydride acylates ylides (I) at the C atom only [1, 5]. We relate this difference in reactivity to a decrease in nucleophilicity in the series of anions $MeCOO^- > CF_3COO^- > Cl^-$ and to the fact that rearrangement occurs due to the reversibility of the O-acylation and irreversibility of C-acylation [3]. It can be assumed that $MeCOO^-$ readily removes acyl from O, CF_3COO^- only on heating, and Cl^- practically does not react in this way.

In the present work, we studied the acylation of arsenic ketoylides (IIa) and (IIb) by acyl halides, and the O → C rearrangement of acyloxyvinylarsonium salts.

The course of the reactions was monitored by IR and PMR spectra, and also by TLC on aluminum oxide.

During acylation of triphenylarsinebenzoylmethylene (IIa) by benzoyl bromide, only the product of O-acylation, α-benzoyloxystyryltriphenylarsonium bromide, was obtained in [5]. In contrast, we showed that ylide (IIa) is acylated by acetyl and benzoyl halides not only at O, but also at C (5-7%). The analogous phosphorus ylides are acylated by acyl halides at O only [1, 2]. This difference in the behavior of P and As ylides was observed in alkylation by alkyl iodides [6]. The acylation of triphenylarsineacetylmethylene (IIb) by the same acid halides leads to O-acylation products only



R = Me, Ph.

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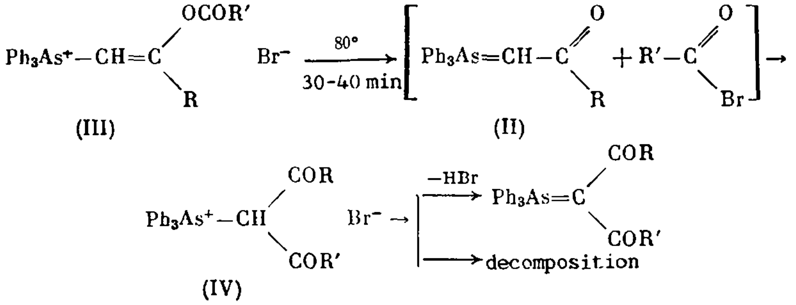
TABLE 1. Ratio of Rearrangement Products According to PMR Spectra Data

Number of reaction	R	Ratio of ylides	
		$Ph_3As{=}C(COR)(COPh)$	$Ph_3As{=}C(COR)(COMe)$
1	Me *	1	2
1	Ph **	1	2
2	Me *	1	3
2	Ph **	1	2,5

*Spectra of reaction mixtures were taken.
†Spectra of ylides were taken after separation by TLC.

In contrast to the corresponding phosphonium salts [2], the acyloxyvinylarsonium salts (III) formed give 5-10% of rearrangement products when heated. Their low yield is explained by the thermal instability of salts (IV)



(III) (II) (IV) (VI)

Here and below R = Ph, R' = Me (a); R = R' = Ph (b); R = R' = Me (c); R = Me, R' = Ph (d).

It has already been shown [1] that the phosphorus analog of (IIIc) rearranges by the action of tetrabutylammonium acetate into diacyl ylide, analogous to (VIc). In [5] a rearrangement of arsonium salt (IIIb) by the action of sodium acetate was observed, but to our surprise only one and not even the main product (VIb), was isolated. If we assume that the rearrangement proceeds as in the case of alkoxyvinylphosphonium and arsonium salts, the formation of an ylide with acetyl group (VIa) should have been expected, since the mixed anhydride formed during rearrangement should acylate ylide (IIa) obtained mainly with the MeCO group.

In fact, by the action of sodium acetate on (IIIb) and (IIId) or sodium benzoate on (IIIa) and (IIIc), one and the same mixture of ylides is formed in a ratio given in Table 1.

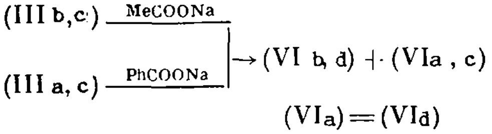
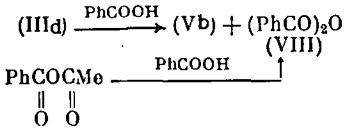


Table 1 shows that, as expected, more of the acetylation product is obtained. The formation of the benzoylation product can be explained by the acylation of the intermediately formed initial ylide by the PhCO group of the mixed anhydride, or, more probably, by its reaction with symmetric anhydride, formed as the result of symmetrization of the mixed anhydride itself, and also as the result of splitting of salts (III) formed in the reaction by acids RCOOH



(VII)

Such possible processes have been confirmed by experiments specially carried out.

It can thus be assumed that as the result of the action of carboxylic acids salts, the acetate or benzoate anion attacks the C atom of the acyloxy group to form the corresponding

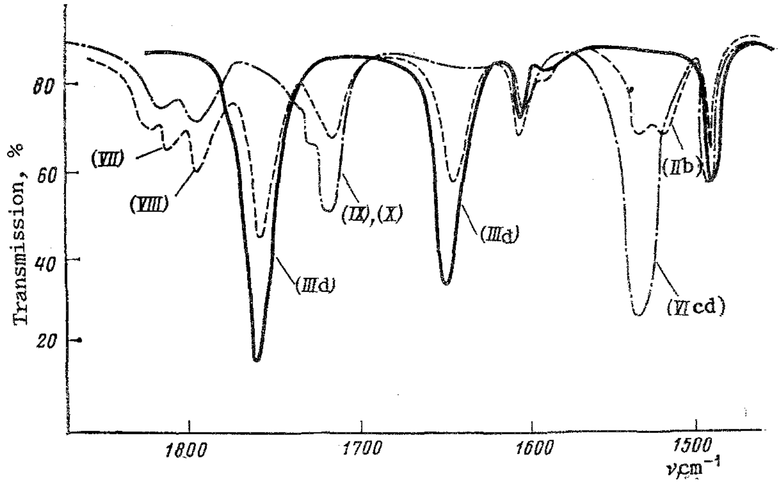
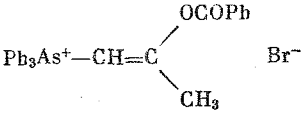


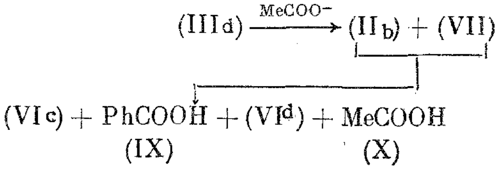
Fig. 1. IR spectrum of reaction mixture



$Ph_3As^+{-}CH{=}C(OCOPh)(CH_3)\ Br^-$

(IIId) and CH_3COON_a in DCE: dashed curve — after 2 min, 80°C; dot - dashed curve — after 15 min, 80°C; solid curve — (IIId).

initial ylide (IIa, b), and first a mixed, and then a symmetrical anhydride. Ylides (IIa, b) then react with the anhydrides to give mixtures of ylides (VI)



$$(IIId) \xrightarrow{MeCOO^-} (IIb) + (VII)$$

$$\underset{(IX)}{(VIc) + PhCOOH} + \underset{(X)}{(VId) + MeCOOH}$$

The IR spectrum of the reaction mixture (Fig. 1) shows that 2 min after the start of the reaction, "ylide" bands appear at 1520 cm^{-1} (IIb) and 1540 cm^{-1} (VIc) and (VId), and bands characteristic of the carboxylic acids at 1720 cm^{-1} ($\nu C{=}O$) (IX) and (X), and mixtures of anhydrides at 1820 and 1800 cm^{-1} ($\nu C{=}O$) (VII) and (VIII). After 15 min, bands of the initial salt (IIId) and the "ylide" band (IIb) disappear in the spectrum, and the band of the diacyl ylides (VIc) and (VId) strongly increases. Similar spectral changes are also observed for the remaining salts (IIIa, b, c).

Due to the ease of the occurrence of the reaction of benzoic acid with the O-acylated salt, a practically individual mixed anhydride could be obtained

$$(IIIc) \xrightarrow{PhCOOH} (Vb) + (VII)$$

In the reaction of an authentic anhydride (VII) with ylide (IIb), the same mixture of ylides is formed as in the rearrangement, with the ratio of the products (VIc):(VId) = 2.5:1. The use of the Bu_4N^+ salt, which is soluble in DCE, instead of the Na salt leads to the formation of the same mixture of ylides and in the same ratio.

When salts (III) are heated in the presence of carboxylic acid salts, a mixture of ylides (VI) is formed with predominance of the ylide with a larger number of MeCO groups in the reaction mixture.

EXPERIMENTAL

All the operations were carried out in absolute solvents. The IR spectra were recorded on a UR-20 spectrophotometer in CH_2Cl_2 and DCE, the PMR spectra on Varian T-60 and Bruker WP-200SY spectrometers in $CDCl_3$. The products were separated by preparative TLC on Al_2O_3 (grade II of activity according to Brockmann) in a benzene—acetone system (3:2). The course of the reaction was monitored by using IR spectra. The characteristics of salts (IIIa-d) are given in Table 2.

1. Reaction of (IIb) with Benzoyl Bromide. A 0.32-ml portion (2.8 mmoles) of benzoyl bromide was added to a solution of 1 g (2.8 mmoles) of ylide (IIb) in 10 ml of benzene. (2-

Benzoyloxypropen-1-yl)triphenylarsonium bromide (IIId), precipitated in the form of an oil, crystallized after 12 h. Weight of precipitate 1.42 g (2.6 mmoles). After reprecipitation from acetonitrile, the weight of salt (IIId) was 1.2 g (2.2 mmoles).

2. Reaction of (IIa) with Benzoyl Bromide. A 0.48-ml portion (4.1 mmoles) of benzoyl bromide was added to a solution of 1.6 g (3.8 mmoles) of (IIa) in 15 ml of benzene. The oil formed after decantation of the benzene solution was washed with two 10-ml portions of benzene. According to the data of IR spectra and TLC, the solid reside (2.1 g) consists of two arsonium salts: (α-benzoyloxystyryl)triphenylarsonium bromide (IIIb) and phenacyltriphenylarsonium bromide (Va). Acetonitrile was added to the precipitate. The insoluble salt (Va) was filtered (0.5 g). From the filtrate, after partial distillation of the solvent, 1.3 g (2.1 mmoles) of (IIIb) were precipitated by ether.

Solvent was distilled in vacuo from the combined benzene solutions. From the residue (0.3 g), 0.14 g (7%) of triphenylarsinedibenzoylmethylene (VIb) was isolated by the TLC method; mp 210°C (cf. [7]).

3. Reaction of Ylide (IIb) with Acetyl Bromide. A 0.43-ml portion (5.9 mmoles) of acetyl bromide was added to a solution of 2 g (5.6 mmoles) of (IIb) in 20 ml of benzene. The oily precipitate was washed several times with benzene to solidification. After two reprecipitations of the precipitate formed (2.6 g) from acetonitrile by ether, 1.5 g (3.1 mmoles) of (2-acetyloxypropen-1-yl)triphenylarsonium bromide (IIIc) were obtained.

4. Reaction of Ylide (IIa) with Acetyl Bromide. A 0.2-ml portion (2.7 mmoles) of acetyl bromide was added to a solution of 1 g (2.4 mmoles) of (IIa) in 10 ml of benzene. The precipitate formed was washed thrice with benzene. The residue (1.2 g) was reprecipitated twice from acetonitrile by ether. The yield was 0.8 g (1.46 mmole) of β-acetoxystyryltriphenylarsonium bromide (IIIa). After the benzene filtrates were treated as described above (experiment 2), 0.05 g (5%) of triphenylarsineacetylbenzoylmethylene (VIa) was isolated; mp 173.5-174.5°C (cf. [7]).

5. Rearrangement of (IIId) in the Presence of Sodium Acetate. A mixture of 0.8 g (1.46 mmoles) of salt (IIId) in 8 ml of DCE and 0.6 g (7.3 mmoles) of sodium acetate was boiled for 15 min and the solvent was then distilled. According to PMR data, the residue (0.88 g) consisted of a 1:2 mixture of ylides (VId) and (VIc). After twofold separation of the reaction mixture by the TLC method, 0.1 g ylide (VId) (mp 172-173°C) and 0.1 g of ylide (VIc) (mp 155-156°C) were isolated (cf. [7]).

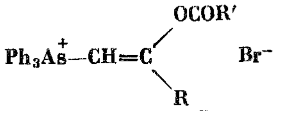
6. Rearrangement of (IIId) in the Presence of Tetrabutylammonium Acetate. A mixture of 0.4 g of salt (IIId) and 0.22 g of tetrabutylammonium acetate in DCE was boiled for 10 min. The solvent was distilled in vacuo. From the residue, 0.45 g of a mixture of ylides (VId) and (VIc) (1:2.5, according to PMR) was isolated by the TLC method.

7. Rearrangement of (IIIb) in the Presence of Sodium Acetate. a) A mixture of 0.9 g (1.5 mmoles) of salt (IIIb) and 0.8 g (9.7 mmoles) of sodium acetate in DCE was boiled for 20 min. The solution was then filtered, and the solvent was distilled in vacuo. From the residue, 0.45 g of a mixture of ylides (VIa) and (VIb) (2:1) was isolated by the TLC method.

b) A mixture of 1 g (1.65 mmoles) of salt (IIIb) and 0.9 g (10.9 mmoles) of sodium acetate in DCE was boiled for 20 min. The solution was filtered, and the solvent evaporated. The residue was ground in hexane. A 5-ml portion of a 1:1 benzene–ether mixture was added to the precipitate formed. According to TLC data and IR and PMR spectra, the insoluble precipitate is triphenylphenacylarsonium bromide (Va), mp 175°C (cf. [8]).

The solvent was distilled from the filtrate in vacuo. From the residue (0.8 g), 0.04 g of ylide (VIb) (mp 212°C [7]), 0.12 g of ylide (VIa) (mp 174°C [7]), 0.15 g of a mixture of ylides (VIa) and (VIb), and 0.07 g of ylide (IIa) (mp 165°C [5]) were isolated by the TLC method.

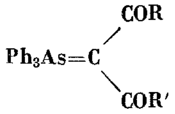
8. Rearrangement of (IIIc) in the Presence of Sodium Benzoate. A mixture of 0.8 g (1.65 mmoles) of salt (IIIc) and 0.7 g (4.9 mmoles) of sodium benzoate in DCE was boiled for 15 min, and then filtered. The solvent was distilled from the filtrate in vacuo. According to PMR data, the residue consisted of a 3:1 mixture of ylides (VIc) and (VId). After twofold separation by TLC method, 0.06 g of ylide (VId) (mp 173°C [7]) and 0.2 g of ylide (VIc) (mp 156°C [7]) were isolated.

TABLE 2. Acyloxyvinyltriphenylarsonium Bromides  $Ph_3\overset{+}{As}{-}CH{=}C(OCOR')(R)\ Br^-$ (III)

Com-pound	R	R′	Yield %	mp, °C	Found/Calculated, %			Empirical formula	IR spectrum (ν, cm^{-1})		PMR spectrum (CDCl$_3$, δ, ppm)			
					C	H	As		C=C	C=O	$OCOCH_3$	CH_3	—CH=	Ph
(IIIa)	Ph	Me	61	142	$\frac{60,86}{61,44}$	$\frac{4,50}{4,42}$	$\frac{13,70}{13,69}$	$C_{28}H_{24}AsBrO_2$	1620	1790	1,49 c	–	7,55 s	7,6–7,9 m
(IIIb) *	Ph	Ph	56	179 *	–	–	–	–	1620 *	1745 *	–	–	6,45 s *	7,3–8,1 m
(IIIc)	Me	Me	55	131	$\frac{56,33}{56,93}$	$\frac{4,63}{4,57}$	$\frac{15,46}{15,44}$	$C_{23}H_{22}AsBrO_2$	1650	1790	1,40 c	2,53 d $J=0,9$ Hz	7,48 s	7,5–7,9 m
(IIId)	Me	Ph	78	162	$\frac{61,17}{61,44}$	$\frac{4,49}{4,42}$	$\frac{13,70}{13,69}$	$C_{28}H_{24}AsBrO_2$	1650	1760	–	2,65 d $J=0,9$ Hz	7,48 s	m7,5–7,9 m

*Data from [5].

TABLE 3. Triphenylarsinediacylmethylenes



$Ph_3As{=}C(COR)(COR')$

(VI)

Salt (III), mmoles	Ylide (VI)	Time of reaction, h	Yield, %	mp, of ylide (VI), °C (cf. [7])
(IIIa) (0,36)	(VIa=d)	0,3	6,0	171
(IIIb) (0,5)	(VIb)	1,5	8,0	210–211
(IIIc) (0,41)	(VIc)	0,3	12,2	154–155
(IIId) (0,4)	(VIa=d)	1,0	Traces	–

9. Rearrangement of (IIIa) in the Presence of Sodium Benzoate. A mixture of 1 g (1.8 mmoles) of salt (IIIa) and 0.8 g (5.5 mmoles) of sodium benzoate in DCE was boiled for 20 min, and then filtered. The solvent was distilled from the filtrate in vacuo. The residue was was washed twice with hexane and 7 ml of a 1:1 benzene–ether mixture were added. The insoluble precipitate (0.11 g) that consisted of salt (Va) (IR spectrum, TLC) was filtered. The solvent was distilled from the filtrate. After separation by the TLC method, 0.52 g of a mixture of ylides (VIa) and (VIb) was isolated from the residue in the ratio of 2.5:1 (according to PMR). After repeated separation of the mixture on aluminum oxide, 0.12 g of ylide (VIa) (mp 171°C [7]) and 0.04 g of ylide (VIb) (mp 210°C [7]) were isolated

10. Rearrangement of Salts (IIIa-d) without Addition of Salts. Salt (III) in DCE was boiled to complete disappearance of $\nu_{C\equiv C}$ and $\nu_{C=O}$ bands in the IR spectrum of the reaction mixture. The mixture was filtered, and the solvent was distilled in vacuo. The corresponding ylide (VI) was isolated by the TLC method from the residue. The yields and constants of the compounds obtained are listed in Table 3.

11. Reaction of Salt (IIIc) with Benzoic Acid. A 0.18-g portion (1.48 mmoles) of benzoic acid was added to a solution of 0.9 g (1.86 mmoles) of salt (IIIc) in DCE. The mixture was boiled for 10 min, and then was filtered. The solvent was distilled from the filtrate, and 10 ml of ether were added. The insoluble salt (IIb) was filtered (0.6 g). After distillation of ether from the filtrate, 0.28 g of mixed anhydride were obtained. IR spectrum (CH_2Cl_2, ν, cm^{-1}): 1820 and 1740. PMR spectrum ($CDCl_3$, δ, ppm): 2.3 s (CH_3), 7.5 m (Ph).

CONCLUSIONS

1. In contrast to the corresponding phosphorus ylide, triphenylarsinebenzoylmethylene is acylated by acyl bromides at two reaction centers: at the O and C atoms. Triphenylarsineacetylmethylene gives only an O-acylation product.

2. In contrast to the phosphorus analogs, acyloxyvinylarsonium salts rearrange on heating into the C-acylated analogs.

3. During rearrangement of β-substituted benzoyloxyvinyltriphenylarsonium bromides in the presence of sodium acetate and β-substituted acetoxyvinyltriphenylarsonium bromides in the presence of sodium benzoate, one and the same mixture of diacyl ylides is formed. It was shown that the rearrangement proceeds via the stage of splitting of the acyl group, followed by C-acylation of the ylide formed by an anhydride.

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