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PROPENYLTRIPHENYLARSONIUM IODIDE AND ITS REACTION WITH ALCOHOLS

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The phosphonioethylation reaction discovered in 1964 [1, 2] has served as a starting point for a study of the properties of vinyltriphenylphosphonium salts, which, in particular, have found common use in the synthesis of heterocyclic compounds [3]. The properties of the more available propenyltriphenylphosphonium salts have not been studied extensively [1, 4, 5]. Only Manske and Gosselek [6] have studied the analogous arsonium salts. These authors described the synthesis of vinyltriphenylarsonium bromide and the addition of a series of nucleophiles with a labile hydrogen atom to this salt.

In the present work, we studied the isomerization of allyltriphenylarsonium iodide (I) to propenyltriphenylarsonium iodide (II) and the addition of alcohols to (II).

The prolonged reaction of salt (I) with excess diethylamine or triethylamine in acetonitrile or upon the brief treatment of (I) with methanolic KOH gives a mixture of (I) and (II), as indicated by the appearance of a PMR signal for the methyl group at δ 2.29 ppm along with the signals of salt (I) and the IR band for the C=C bond at 1625 cm⁻¹, which is lacking in the spectrum of salt (I). Since the (I)/(II) ratio is 1:3 in all cases and does not change upon prolonged reaction with these amines, we may assume that equilibrium is established between (I) and (II). The isomerization is established through the intermediate ylid form from (I) by the action of the base.

$$\begin{array}{c} Ph_{3}As^{+}-CH_{2}-CH=CH_{2}I^{-}\xrightarrow{B} Ph_{3}As^{+}-CH-CH-CH_{2}\xrightarrow{HB} Ph_{3}As^{+}-CH=CH-CH_{3}I^{-} \\ (1) \end{array}$$

We should note that the analogous isomerization of allyltriphenylphosphonium salts proceeds to completion and leads exclusively to propenyltriphenylphosphonium salts [4]. This significant difference in the behavior of the phosphonium and arsonium salts may be attributed to the significantly greater electron-withdrawing capacity of the phosphonium group and, as a consequence, the greater acidity of the α -hydrogen atom in the phosphonium salts in comparison with arsonium salts, as shown in the case of acylmethyltriphenylonium compounds [7].

The action of sodium alcoholate in alcohol on a solution of salt (I) gives (2-alkoxypropyl)triphenylarsonium salts (III), apparently through intermediate salt (II), which rapidly and irreversibly adds the alcohol.



The structure of salts (III) was demonstrated by elemental analysis and spectral methods. Their IR spectra have a strong band at 1130-1140 cm⁻¹ (ν C-O-C) and their PMR spectra are given in Table 1.

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|---------------------------|---|---|----------------------------|-----------------|--|-----------------------------|
| Com- | 1 | | - | 6. ppm(J, Hz) | | |
| minod | <u> </u> | H1 ** (2, 3J) | (fc) 2H | H• (1) | H4 4# | H6 ** (3J) |
| (111a) CH | | 350 d.d (13.6; 11.5) 4.47 d.d (13.6; 3,1) | 3,75m (11,5; 4,6; 3,1) | 1,46 d (4,6) | 2,77 \$ | |
| (111b) CH | 2CH3 | 3,53 d_d (13,6; 11,2) 4,44 d_d (13,6; 3,4) | 3,90 m (11,2; 5,9; 3,4) | 1,46 d (5,9) | ${}^{3J=7,0;}_{(^3J=7,0;}, {}^{4J}_{J=8,95}, {}^{3A0}_{(0,4,4)}$ | 0,75 t (7,01) |
| (IIIc) ⁴ CH | 2cH3cH3 *** | 3,54 d_d (13,6; 5,7) 4,45 d_d (13,6; 3,4) | 3,89 m (5,8; 5,7; 3,4) | 1,47 d (5,8) | (*J = 7, 1; *J = 8, 9) (*J = 7, 1; *J = 8, 9) (*J = 7, 1; *J = 6, 0) | 1,14 m (8,9; 7,5; 6,0) |
| (p111) | CH, | 3,51 d.d (13,7; 11,0) 4,48 d.d (13,7; 3,5) | 4,18m (11,0; 5,9; 3,5) | 1,46 d (5,9) | 3,57 septet (*J=6,1) | 0,31d (6,1) 0,92 d (6,1) |
| (IIIe) [d] | l _z Ph | 3,544,d (10,7;0,8) 4,69 d,d (13,6; 3,1) | 4,14 m (5,8; 3,1; 0,8) | 1,60 d (5,8) | 3,54 d $(^2J=10,7)$ 4,43 d $(^2J=10,7)$ | 1 |

| in CDC1,* |
|--|
| (111) |
|)ORL ⁻ |
| GH ₃ |
| -CH(|
| PH ₃ As ⁺ -CH ₂ . |
| for |
| Data |
| Spectral |
| PMR |
| TABLE 1. |

*The phenyl group protons give multiplets at 7.5-8.2 ppm. **The increase in the signal multiplicity is due to a diastereotopic effect. ***H⁶ 0.62 t, 3H, ²J = 7.5 Hz.

EXPERIMENTAL

All the operations were carried out in absolute solvents. The IR spectra were taken in CH_2Cl_2 on a UR-20 spectrometer. The PMR spectra were taken on a Bruker WP-200SY spectrometer in $CDCl_3$. The chemical shifts in the PMR spectra are given relative to HMDS as the internal standard.

<u>Isomerization of (I) by the action of amines.</u> A solution of 1 mmole salt (I) and 5 ml Et_2NH or Et_3N in 20 ml acetonitrile was left for 24 h at 20°C. The solvent and amine were distilled off in vacuum. The residue was reprecipitated from CH_2Cl_2 by the addition of ether. The PMR spectrum indicates a 1:3 mixture of (I) and (II). PMR spectrum of

Ph₃As⁺-CH₂¹-C=C I⁻ (I) (in CDCl₃, δ , ppm, J, Hz): 4.66 d (2H¹, ³J = 7.4), 5.37 d (H⁴, ³J = H² H² H⁴

9.9, ${}^{4}J = 0.9$), 5.61 d (H³, ${}^{3}J = 16.9$, ${}^{4}J = 0.9$), 5.90 d. d. t (H², ${}^{3}J = 16.9$. ${}^{3}J = 9.9$, ${}^{3}J = \frac{16}{10}$

7.4), 7.60-7.82 m (3C₆H₅). PMR spectrum of Ph₃As⁺-C=C I⁻ (II) (in CDCl₃, δ , ppm, H_1 CH₃³ J, Hz): 2.29 d. d (CH³, ³J = 6.6, ⁴J = 1.6), 6.76 d. q (H², ³J = 16.7, ³J = 6.6), 7.38 d. q

J, Hz): 2.29 d. d (CH³, ${}^{3}J = 6.6$, ${}^{4}J = 1.6$), 6.76 d. q (H², ${}^{3}J = 16.7$, ${}^{3}J = 6.6$), 7.38 d. q (H¹, ${}^{3}J = 16.7$, ${}^{4}J = 1.6$), 7.60-7.82 m (3C₆H₅). The composition of the mixture did not change upon treatment of the solution for 100 h. The yields of (I) and (II) were 70-85%.

Isomerization of (I) by the Action of KOH. A solution of 1 mmole KOH in methanol was added to a solution of 1 mmole salt (I) in 10 ml methanol. After 2 h, the solution was neutralized by introducing HCl gas. Methanol was distilled off in vacuum. The products were extracted with CH_2Cl_2 . The solvent was distilled off until the solution volume was 3 ml and ether was added to precipitate a 1:3 mixture of salts (I) and (II) (as indicated by PMR spectroscopy) in 77% yield.

Synthesis of 2-Alkoxypropyltriphenylarsonium Iodide (III). A solution of 1 mmole sodium alcoholate in the same alcohol was added to a solution of 1 mmole salt (I) in 20 ml alcohol. After 30 min, the solution was treated as in the above procedure. Salts (III) were reprecipitated from acetonitrile by the addition of ether.

 $\frac{\text{Triphenyl}-(2-\text{methoxypropyl})\text{arsonium iodide (IIIa)}}{(\text{from CH}_2\text{Cl}_2-\text{ether})}.$ Found: C 52.77; H 4.83; As 14.88%. Calculated for C₂₂H₂₄AsIO: C 52.16; H 4.77; As 14.80%.

 $\frac{\text{Triphenyl}-(2-\text{ethoxypropyl})\text{arsoium iodide (IIIb)}}{(\text{from CH}_2\text{Cl}_2-\text{ether}).}$ Found: C 52.50; H 5.29; As 14.57%. Calculated for C₂₃H₂₆AsIO: C 52.89; H 5.42; As 14.35%.

<u>Triphenyl-(2-propoxypropyl)arsonium iodide (IIIc)</u> was obtained in 81% yield, mp 177-178°C (from CH_2Cl_2 -ether). Found: C 54.98; H 5.26; As 13.93%. Calculated for $C_{2.4}H_{2.8}AsIO$: C 54.04; H 5.29; As 14.04%.

 $\frac{\text{Triphenyl}-(2-\text{isopropoxypropyl})\text{arsonium iodide (IIId)}}{(\text{from CH}_2\text{Cl}_2-\text{ether})}.$ Found: C 54.22; H 5.48; As 13.84%. Calculated for C₂₄H₂₈AsIO: C 54.04; H 5.29; As 14.04%.

 $\frac{\text{Triphenyl}-(2-\text{benzyloxypropyl})\text{arsonium iodide (IIIe)}}{(CH_2Cl_2-\text{ether})}$ Found: C 57.69; H 4.75; As 12.83%. Calculated for C₂₈H₂₆AsIO: C 57.73; H 4.84; As 12.89%.

CONCLUSIONS

1. Allyltriphenylarsonium iodide rearranges in the presence of diethylamine or triethylamine to give propenyltriphenylarsonium iodide. The ratio of the starting and rearranged salts is 1:3.

2. Alcohols in the presence of sodium alcoholate add to propenyltriphenylarsonium iodide to form (2-alkoxypropyl)triphenylarsonium salts.

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POSSIBILITY OF THE FORMATION OF CHLOROSUBSTITUTED TROPONE RINGS UNDER ZINCKE-SUHL REACTION CONDITIONS

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The reaction of p-cresol with CCl₄ in the presence of AlCl₃ leads to the formation of 4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-one (I) in 18% yield [1]. As a consequence, this reaction has been used commonly as the major method for the synthesis of CCl₃-substituted cyclohexadienones [2]. This reaction has been assumed to proceed through electrophilic ipso attack of the benzene ring by cation of the intermediate CCl₃⁺AlCl₄⁻.

For a more complete understanding of the nature of this reaction and the reactivity of the para-semiquinoid species (I) generated [3], it is important to gain information on accompanying and side reactions. Merchant and Jadhav [2] have previously noted only the formation of polysubstituted benzoid aromatic derivatives. In the present work, we were the first to discover that traces of a nonbenzoid compound, namely, 4-methyl-5-chloro-2,4,6-cycloheptatrien-1-one (II), which could be isolated by taking large quantities of the starting reagents, were also formed under standard Zincke-Suhl reaction conditions.



It is interesting to note that a detailed study of the total composition of the products in an another method for the synthesis of halomethyl-substituted cyclohexadienones, namely, the "anomalous Reimer-Tiemann reaction," which we have termed the Auwers reaction [4], proceeding through the action of $CHCl_3/KOH/H_2O$ on p-cresol and leading to the formation of 4methyl-4-dichloromethyl-2,5-cyclohexadien-1-one (III) as the major product, also led to the formation of trace amounts of tropone derivatives, including a compound directly generated from the starting p-cresol by the action of dichlorocarbene and not containing chlorine in the seven-membered ring [5]. The formation of chloro derivative (II) in our reaction, in principle, may be related to the possibility of the intermediate formation of carbene species such as $[CCl_2][AlCl_3 \cdot Cl_2]$ (the aromatic p-cresol ring acts as a trap in this case) or cyclo- $C(O)(CH=CH)_2C(CH_3)CCl$ [6] or related to oxidative ring expansion in the intermediate carbocationic species, cyclo- $C(O)(CH=CH)_2C(CH_3)CCl_2^+$ according to rearrangements known for the corresponding gem- CH_2Hal -substituted derivatives and described by Cook and Koptyug [7]. The participation of CHCl_3 (as an impurity in the CCl_4 sample) may be excluded since we have found that the reaction of p-cresol with CHCl_3 and a two-fold excess of AlCl_3 under the same

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