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PREPARATION AND REACTIONS OF TRIPHENYLARSORANYLIDENEKETENE

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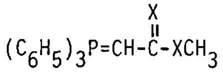
Abstract: Preparation and some reactions of the first cumulated ylide of arsenic, viz. triphenylarsoranylideneketene are described.

The cumulated-phosphonium ylides (1) form a unique group within the ylides, which have been recently used as very versatile synthones in organic synthesis.[1] The first cumulated-phosphonium ylide (1a) was prepared by Matthews and Birum[2] from the thermolysis of the adduct obtained from the interaction of CO_2 with hexaphenylcarbodiphosphorane. A simple method was later developed for the preparation of this ylide and its thioanalogue, which involved ß-elimination of CH_3XH (X=O,S) from the ylide, 2 by sodium bis(trimethylsilyl)amide.[3] We have now extended this method to the synthesis of the first cumulated ylide of arsenic, viz. triphenylarsoranylideneketene (3).

$(C_6H_5)_3P{=}C{=}C{=}X$

1

a, X=O
b, X=S
c, X=N-Ar



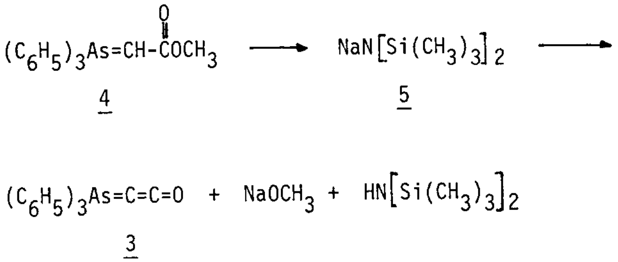
$(C_6H_5)_3P{=}CH{-}\overset{\overset{X}{\|}}{C}{-}XCH_3$

2

X=O;S

All the reactions were carried out under nitrogen. Methoxycarbonylmethylenetriphenylarsorane[4] (4, m.p. 161-63°; 1 equiv.) was stirred in toluene with sodium bis(trimethylsilyl)amide (5,1.1 equiv.) overnight at room temperature. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to a syrupy mass which on crystallization from toluene/ether afforded pale yellow crystals of 3, m.p. 141-43° (yield, 60%). IR (KBr), strong absorption at 2030 cm^{-1} (ν C=C=O); ^1H-NMR ($CDCl_3$), δ 7.3-8.0 ppm (aromatic H); ^{13}C-NMR, ($CDCl_3$), -5.5 ppm (C_α), 128.5-133.5 ppm (aromatic C), 150.0 ppm (C_β=O); $M^{+\cdot}$ = 346 m/e.

Scheme I



$$(C_6H_5)_3As{=}CH{-}\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow{\quad} NaN[Si(CH_3)_3]_2 \xrightarrow{\quad}$$

4 5

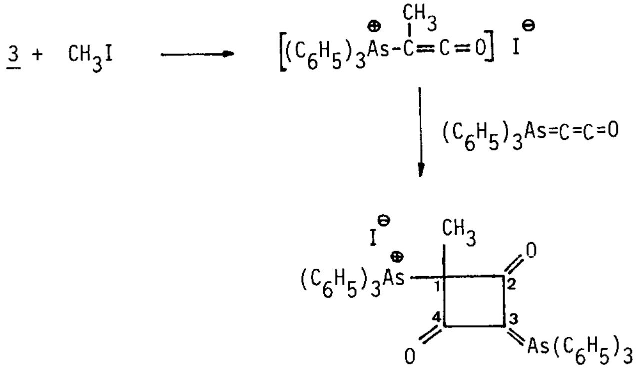
$$(C_6H_5)_3As{=}C{=}C{=}O + NaOCH_3 + HN[Si(CH_3)_3]_2$$

3

In the light of various interesting reactions shown by the cumulated-phosphonium ylides[1], a few representative reactions of the ylide, 3 have been carried out.

To the stirred solution of 3 (2 equiv.) in benzene was added methyl iodide (1 equiv.) dropwise and the resulting solution was stirred for 72 hrs. at room temperature. A pale yellow solid separated out which was filtered, washed with ether and dried, m.p. 163-65^{0} (decomp.) (yield, 50%). IR (KBr), 1760 cm^{-1} (w) and 1640 cm^{-1} (s); ^{1}H-NMR ($CDCl_3$); δ2.0 ppm (3H, CH_3), 7.3-8.0 ppm (30 H, aromatic H); ^{13}C-NMR ($CDCl_3$), δ16.7 ppm (CH_3), 72.9 ppm (C_1), 82.7 ppm (C_3), 120.0 - 134.5 (aromatic C) and 181.7 ppm (C_2 and C_4); Mass, 707 m/e ($M^{+\bullet}$-J, i.e. $C_{41}H_{33}O_2As_2$). On the basis of these results, structure 6 was assigned to this compound which is formed as shown in Scheme II. Thus, the reaction of 3 with methyl iodide proceeds similar to that of the corresponding phosphonium ylide, 1a.[5]

Scheme II



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To the ylide, 3 (1 equiv.) suspended in toluene was added ethanethiol (1 equiv.) and the solution was heated at 70-80^0 for 4 hrs. The solvent was then removed and the residue on crystallization from ethyl acetate/ether afforded pale yellow crystals of thioethylcarboxymethylenetriphenylarsorane (7), m.p. 168-170^0 (yield, 74%); IR (KBr), ν_{CO} 1550 cm^{-1}; ^{1}H-NMR(CDCl$_3$), δ 1.3 ppm (t, 3H), 2.75 ppm (q, 2H), 3.93 ppm (s, 1H), 7.3 - 7.9 ppm (m, 15H).

Scheme III

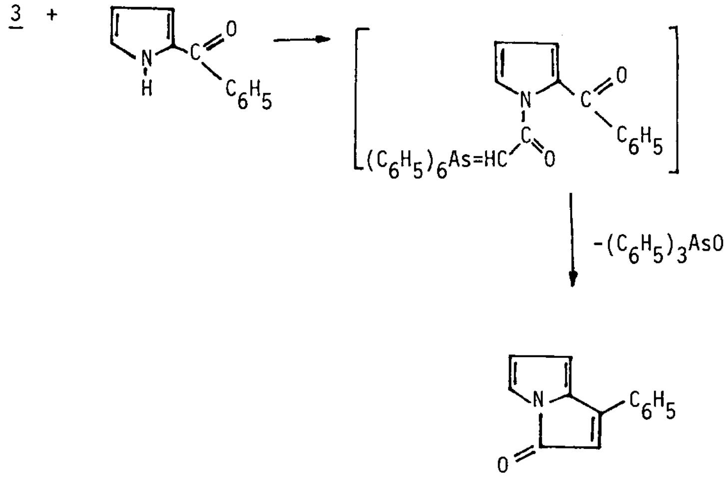
$$\underline{3} + CH_3CH_2SH \xrightarrow{\Delta} (C_6H_5)_3As{=}CHCOSCH_2CH_3$$

7

Dale and Froeyen[4] have reported the temperature-dependence of PMR spectra of methoxycarbonylmethylenetriphenylarsoranes. A similar phenomenon has been observed in the case of analogous phosphonium ylides.[6] In the view of this, PMR spectrum of the ylide, 7 was studied (in pyridine) at different temperatures. On increasing the temperature, the signal for C$\underline{H}$ at 3.93 ppm broadened slowly and at 110^0 a clear tendency was observed for splitting each peak into two.

To the ylide 3, (1 equiv.) dissolved in methylene chloride was added 2-benzoylpyrrole (1 equiv.) in methylene chloride slowly at room temp. A deep red colour developed within 1 hour. The solution was, however, stirred overnight. The solvent was removed under reduced pressure and the semi-solid on chromatography over silica-gel (eluent, benzene) afforded a red compound (8) which was recrystallized from toluene/pet. ether, m.p. 78-80^0 (yield, 85%). IR (KBr), ν_{CO} 1730 cm^{-1}. It was found to be identical with 1-phenylpyrrolizin-3-one[7].

Scheme IV



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The ylide, 3 like the analogous phosphonium ylides is expected to show other interesting reactions which are being investigated.

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