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SYNTHESIS OF (2,4,6-CYCLOHEPTATRIEN-1-YLIDENE)METHYL TRIPHENYLPHOSPHONIUM TETRAFLUOROBORATE: A STRONGLY STABILIZED YLIDE ?

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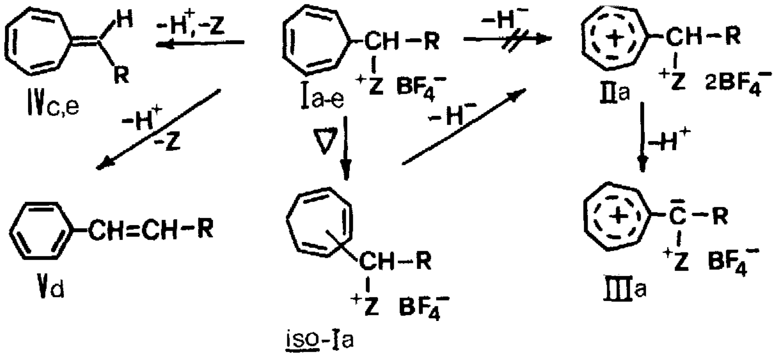
Abstract: The synthesis of (cycloheptatrienylmethyl)triphenylphosphonium tetrafluoroborates is reported. Hydride abstraction to the corresponding tropylium salt followed by proton abstraction afforded the title compound IIIa which shows little, if any, ylidic character.

Much work has been done on the stabilizing ability of electronwithdrawing groups such as carbonyl, cyano and sulphonyl groups in ylides. Many reports on pK_a's of several onium salts and the nucleophilic power of the corresponding ylides are in fact available[1]. However no information is available on the stabilizing power of aromatic cations such as cyclopropenylium, pyrylium and tropylium ions on the negative charge of ylides, except a brief report on the phosphonium ylides obtained from 2-chlorotropones[2]. For this reason and in consideration of the potential synthetic utility in the field of cycloheptatriene and tropylium derivatives, we considered the possibility of synthesizing onium salts and ylides of general structures I, II and III:



a: R = H ; Z = PPh_3

b: R = CO-R'; Z = PPh_3

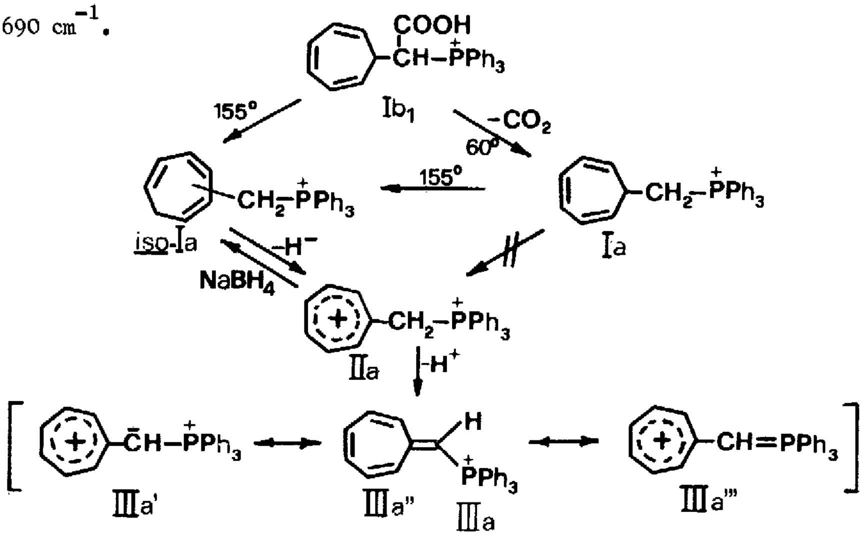
c: R = H ; Z = NMe_3

d: R = CO-R'; Z = SMe_2 or $AsPh_3$

e: R = H ; Z = $SOMe_2$

Earlier reports by two research groups[3,4] and by us[5] indicated that structures like I are not stable at r. t. when Z is SMe_2, $SOMe_2$ or $AsPh_3$ (Id, e) because of rapid elimination of the onium group with[3,5] or without[4] concomitant ring contraction. The only examples of stable onium salts of structure I are those reported by Doering and Wiley[6], who synthesized Ic and by our group (five salts of structure Ib[5]).

We wish to report here the synthesis of Ia and its conversion to IIa and IIIa. In a preliminary investigation we found that the easy direct approach to phosphonium salts of structure I by reaction of tropylium ion $C_7H_7^+$ with phosphonium ylides is limited to stabilized ylides[5], but fails when R = H because of the exceedingly high reactivity of methylenetriphenylphosphorane. However gentle heating of the easily available (carboxy)(2,4,6-cycloheptatrien-1-yl)methyl triphenylphosphonium tetrafluoroborate (Ib_1)[5] in ethanol led us to the desired Ia (n. c.[*]), m. p. 205°C from n-BuOH; nmr[§]: 1.9–2.3 (m, C$\underline{H}$-CH_2), 3.68 (dd, both J's 5, CH_2), three m's at 4.9–5.3, 5.9–6.3 and 6.6–6.8 (2+2+2 vinyl protons), 7.6–8.0 (m, arom.); IR[+]: 1590, 1440, 1190, 1115, $\underline{1060}$, 1000, 820, 750, 710 and 690 cm^{-1}.



Since direct hydride abstraction from Ia by trityl tetrafluoroborate failed, a preliminary isomerisation[7] to *iso*-Ia (n. c.) was necessary by heating for five hrs at 155°C in DMSO or DMF. Apparently one of the three possible isomeric Ia salts, m. p. 210–212°C from n-BuOH, is predominant in the reaction mixture, as only one $\underline{CH_2}$-P doublet appears in the nmr spectrum, at 4.50, J = 15 (vinyl protons: three m's at ca. 5.3, 6.0 and 6.6; C$\underline{H}$-CH_2: m at 2.1; aromatics: m at 7.7–8.1; IR: 1590, 1440, 1180, 1110, $\underline{1060}$, 1000, 840, 750 and 690 cm^{-1}). A one step conversion of Ib_1 to *iso*-Ia is also possible (see below). Hydride abstraction from *iso*-Ia was then smoothly accomplished by $Ph_3C^+BF_4^-$ in acetonitrile at r. t. affording IIa (n. c.), which can be converted back to *iso*-Ia (three isomers, as shown by the presence of three very close doublets at ca. 4.50) by sodium borohydride in acetonitrile. IIa shows strongly acidic properties. It is hydrolized to the corresponding conjugate base IIIa (n. c.) when exposed to moist air. Treatment with water or

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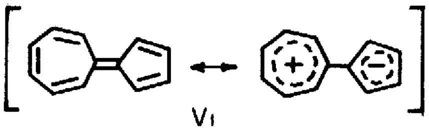
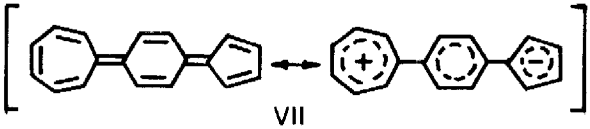
[*] n. c. = new compound. Satisfactory elemental analyses were obtained for all new compounds.

[§] All the nmr spectra were taken in CD_3CN (TMS as internal standard) on a Perkin Elmer R12 B spectrometer; chemical shifts are given in ppm (δ), J's in Hz.

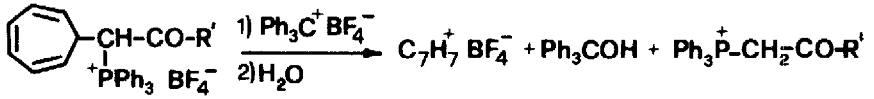
[+] All the IR spectra were taken in nujol on Perkin Elmer 700 spectrophotometer; only prominent peaks are reported, the strongest being underlined.

methanol rapidly converts it quantitatively into IIIa. The pK_a for the IIa-IIIa equilibrium, spectrophotometrically determined and extrapolated to zero ionic strenght[8], is -0.33±0.02 at 25°C in aqueous solution. IIIa is a red-orange solid, m. p. 188°C, the spectroscopic properties of which are clearly indicative of a heptafulvene structure (IIIa"). In fact its nmr spectrum shows a pattern characteristic of a cycloheptatriene structure (three m's at 6.2-7.5; d at 5.60, J = 17, =CHP; m at 7.6-8.2, arom.), while no absorption is observed in the tropylium region at ca. 9 ppm. Its UV-VIS spectrum in 95% ethanol shows a maximum at 365 nm (log ε = 4.58). In agreement with these data IIIa lacks almost completely ylidic reactivity. It doesn't react with p-nitrobenzaldehyde, acetic anhydride or phenylisocyanate in acetonitrile at 85°C for 8 hrs, although it can be methylated by methyl iodide/silver tetrafluoroborate in acetonitrile at ca. 50°C. In conclusion both the physico-chemical properties and the chemical behaviour are indicative of little, if any, contribution of the "ylidic"structures IIIa' and IIIa"' for IIIa, which can best be represented by structure IIIa". (Noteworthy is the remarkable stabilizing effect of the phosphonium group on the heptafulvene system, comparable with cyano or carbonyl groups[9]). This is in line with the well known fact that a negative charge on a carbon α to the tropylium ring, even if largely delocalized, as in VI and VII, becomes strongly involved in making a C=C bond, affording olefinic rather than aromatic structures[10].


VI


VII

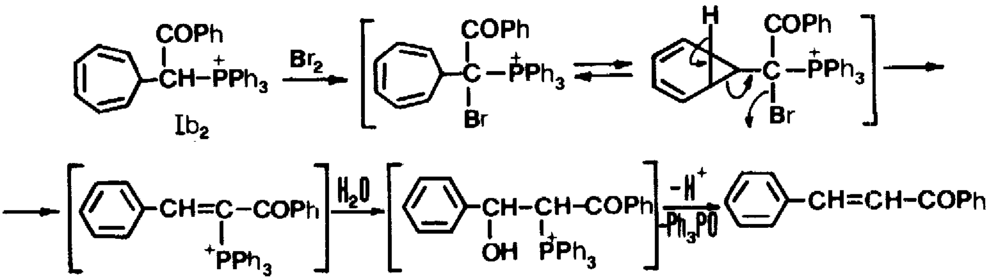
An attempt at hydride abstraction by $Ph_3C^+BF_4^-$ from the more acidic phosphonium salts Ib$_2$ and Ib$_3$ failed. In line with our previous observation[5], an acidic fragmentation occurred:



Ib$_2$: R'=Ph ; Ib$_3$: R'=OEt

On the other hand, an attempt at preliminary thermal isomerisation of Ib$_2$ and Ib$_3$ to iso-Ib$_2$ and iso-Ib$_3$ failed because of the limited thermal stability of Ib$_2$ and Ib$_3$.

A further attempt at oxidation of the cycloheptatriene moiety in Ib$_2$ to the corresponding tropylium salt by bromine in chloroform[11] was unsuccessful; triphenylphosphine oxide and trans-chalcone were in fact obtained. This is presumably due to the preferential attack of bromine on the α-carbon and the great leaving ability of bromide:



Experimental:

Thermal conversion of Ib_1 into iso-Ia. 2.0 g of Ib_1 in 5 ml of DMF were refluxed for 5 hrs; 100 ml of cold n-BuOH were added, the solution chilled and the crystals of iso-Ia (1.7 g, 85%) collected and recrystallized from n-BuOH, m. p. 212°C.

Hydride abstraction from iso-Ia: synthesis of IIa. 0.91 g (2 mmoles) of iso-Ia and 0.66 g (2 mmoles) of $Ph_3C^+BF_4^-$ were dissolved in 10 ml of acetonitrile. After one hr at r. t. 10 ml of ethyl acetate and 10 ml of hexane were added. A colourless ppt of IIa (0.43 g, 40%) was obtained, m. p. ca. 215°C (dec.). nmr: 5.45 (d, J = 18, CH_2), 7.5-8.3 (m, arom.), 8.8-9.5 (m, C_7H_6); IR: 1600, 1495, 1255, 1065, 860, 800, 760, 735 and 700 cm^{-1}.

Hydrolysis of IIa to IIIa. 0.17 g of IIa were suspended in 20 ml of water and stirred at r. t. until all the starting material was converted to an orange-red powder, IIIa (0.13 g, 91%), m. p. 188°C. It can be crystallized from acetone-hexane. IR: 1640, 1540, 1500, 1290, 1195, 1115, 1060, 1000, 875, 780, 730 and 695 cm^{-1}.

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