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PREPARATION AND DECOMPOSITION OF CYMANTRENYLDIPHENYLBENZYLPHOSPHONIUM HYDROXIDE

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The mechanism of decomposition of most quaternary phosphonium hydroxides is reasonably well established and consists of the following steps:[1,2]

(1) $R_4P^+ + OH^- \xrightleftharpoons{\text{fast}} R_4POH$

(2) $R_4POH + OH^- \xrightleftharpoons{\text{fast}} R_4PO^- + H_2O$

(3) $R_4PO^- \xrightarrow{\text{slow}} R_3PO + R^-$

(4) $R^- + H_2O \xrightarrow{\text{fast}} RH + OH^-$

It is also well established that the relative ease of departure of an R group as R^- parallels its stability as an anion. For example, a benzyl group departs more rapidly in step (3) of a typical decomposition reaction than a methyl,[1] ethyl,[1] phenyl,[1] ferrocenyl,[3] p-methoxybenzyl,[2] or p-methylbenzyl[2] group and less rapidly than a m-bromobenzyl[2] or a p-chlorobenzyl[2] group. We have now found that, in the reaction of cymantrenyldiphenylbenzylphosphonium bromide with sodium hydroxide, cymantrene (cyclopentadienylmanganesetricarbonyl) is obtained in 92.3% yield and toluene in 6.3% yield. This strongly implies that the cymantrenyl anion is distinctly more stable than the benzyl anion, particularly since it is known that steric effects do not exert any major effect on either the rate or product distribution of the decomposition of quaternary phosphonium hydroxides.[3,4,5] The surprising stability of the cymantrenyl anion may possibly be attributable to overlap of the orbital of the unshared pair of electrons with an antibonding orbital of a carbonyl group, but most likely it results because of the strongly electron-withdrawing inductive field effect of the manganesetricarbonyl group. That the operation of mainly an inductive field effect can strongly influence the stability of a carbanion has been strikingly demonstrated by Streitwieser and Holtz[6] in the case of the conjugate base of 1H-undecafluorobicyclo[2.2.1]-heptane.

The rate of reaction of cymantrenyldiphenylbenzylphosphonium bromide with sodium hydroxide in 50% 1,2-dimethoxyethane-water (0.4M in potassium chloride, 0.01M in NaOH and in R_4P^+, Br^-) at 55.0° was 8.78×10^3 $l.^2mole^{-2}min.^{-1}$, compared to 5.20×10^2 $l.^2mole^{-2}min.^{-1}$ and 7.54 $l.^2mole^{-2}min.^{-1}$ for the analogous reactions of triphenylbenzylphosphonium bromide and ferrocenyldiphenylbenzylphosphonium bromide, respectively. All reactions were clearly third order, as required by the mechanism cited above. The greater reactivity of the cymantrenylphosphonium salt as against the other salts is also attributable to the strongly electron-withdrawing inductive field effect of the manganesetricarbonyl group. This is consistent with substituent effects on rate of reaction reported previously.[1]

Further evidence for the electron-withdrawing effect of the cymantrenyl group was obtained by measurement of the pK_A of cymantrenoic acid in 70% by volume ethanol-water solution at 25.0°. The value was 5.44 as against values of 6.12 and 6.61 for benzoic acid and ferrocenoic acid, respectively, in the same medium.

Cymantrenyldiphenylbenzylphosphonium bromide, m.p. 195-197° (dec.), was prepared by the reaction of benzyl bromide with cymantrenyldiphenylphosphine. The latter compound was prepared by the reaction of the Grignard reagent (prepared in tetrahydrofuran solution in the presence of 1,2-dibromethane by the entrainment method) of iodocymantrene with diphenylchlorophosphine. Iodocymantrene,[7] in turn, was obtained by treatment of chloromercurycymantrene[8] with iodine in carbon tetrachloride. Complete elemental analyses were obtained for cymantrenyldiphenylbenzylphosphonium bromide and found to be in agreement with the theoretical values.

The unusual stability of the cymantrenyl anion indicated by the results described above suggests that it should prove to be a valuable intermediate in syntheses of cymantrene derivatives. Work designed to explore this possibility is in progress.

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