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NEW ROUTES TO 5,8,8-TRIPHENYLBENZO[c]HEPTAFULVENES FROM (3,4-BIS(DIPHENYLMETHYLENE)-2-OXOCYCLOBUTYLIDENE)TRIPHENYLPHOSPHORANE. ISOLATION OF EXCESSIVELY STABILIZED BETAINE

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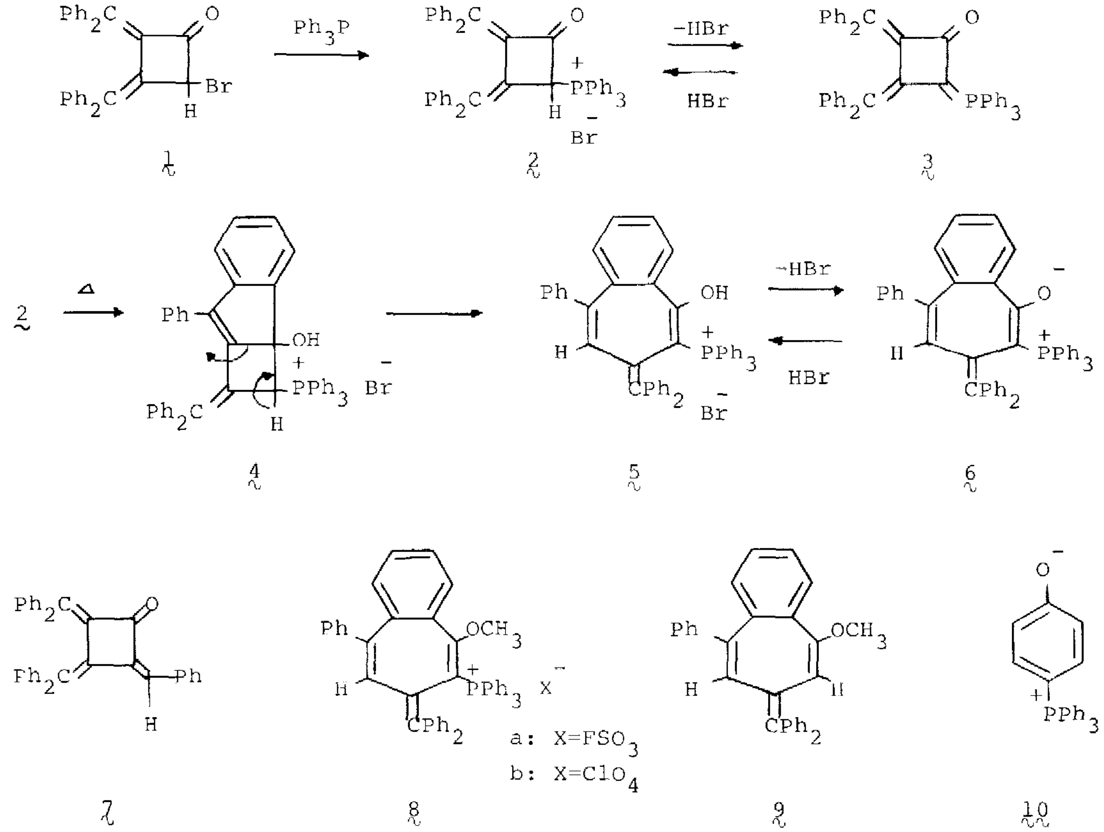
Summary: Thermal isomerization of HBr salt of the title phosphorane gave (2-hydroxy-5,8,8-triphenylbenzo[c]heptafulvenyl)triphenylphosphonium bromide, which upon dehydrobromination afforded excessively stabilized betaine. Thermal reaction of the title phosphorane with diphenylketene gave 5,8,8-triphenylbenzo[c]heptafulvene which is condensed with cyclopropene ring.

During the couse of the study of the title phosphorane (3), we found that thermal isomerization of the HBr salt of 3 (2) and thermal reaction of 3 with diphenylketene afford 5,8,8-triphenylbenzo[c]heptafulvene derivatives, 5 and 14, respectively. These reactions are worthwhile as simple synthetic routes to benzo[c]heptafulvenes, because only a few synthetic methods have been reported so far, one for benzo[c]heptafulvene itself[1] and three for its 8,8-disubstituted derivatives.[2,3] These synthetic routes are also interesting in the point of view of unusual reactions of phosphorous derivatives of four-membered ring compounds.

Heating of 2-bromo-3,4-bis(diphenylmethylene)cyclobutanone (1)[4] and Ph_3P in benzene under reflux for 4 h afforded the HBr salt of the title phosphorane, (3,4-bis(diphenylmethylene)-2-oxocyclobutyl)triphenylphosphonium bromide (2) as dark red prisms in 83% yield (mp 220 °C; ν(C=O) 1760 cm^{-1}), which upon treatment with $NaOCH_3$ in CH_3OH afforded the title phosphorane (3) as orange prisms in quantitative yield (mp 228-229 °C; ν(C=O) 1695 cm^{-1}). Heating of crystals of 2 at its melting point for 30 min gave (2-hydroxy-5,8,8-triphenylbenzo[c]heptafulvenyl)triphenylphosphonium bromide (5) as colorless prisms in 82% yield; mp 285-286 °C;

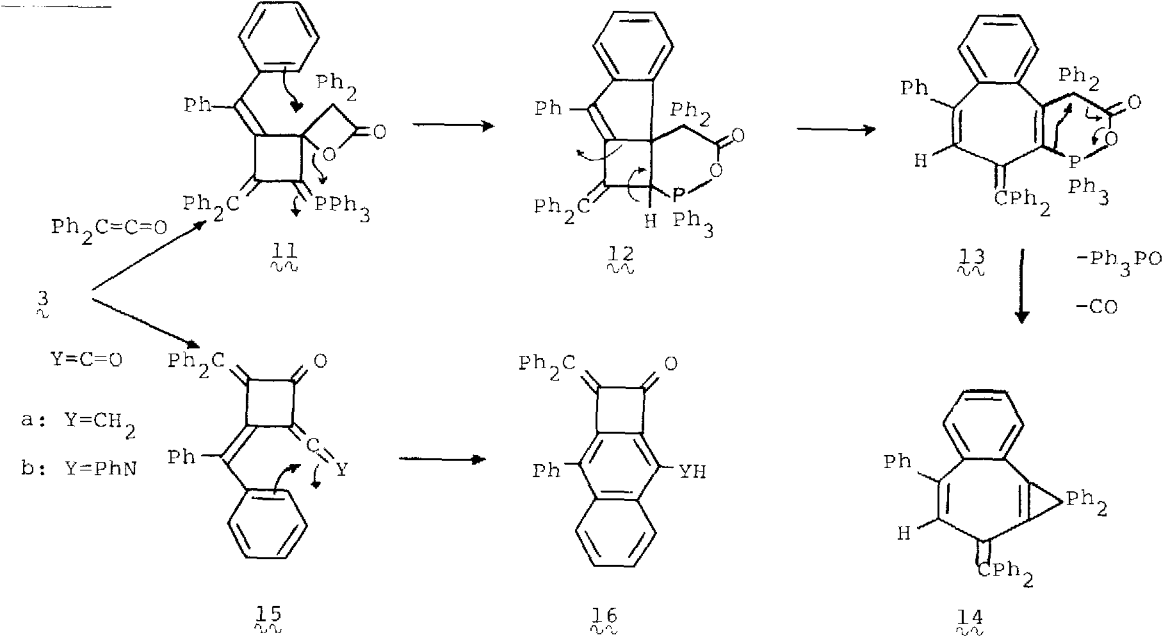
Scheme 1



ν(conjugated OH $\underset{5}{\text{to}}$ $Ph_3\overset{+}{P}$ group) 3000-2300 cm^{-1}; λ_{max} 253 (40000), 294 sh (14200), 365 nm (ε 6200). A plausible reaction pathway is that proceeds by ring opening accompanied by 1,3-hydrogen shift of the intermediate (4) which is initially formed from 2 by the reaction of phenyl to carbonyl carbon (Scheme 1). The carbonyl carbon of 2 might be positively charged because electrons of the carbonyl oxygen are strongly pulled by $Ph_3\overset{+}{P}$ group through space.

By treating with water, 5 is easily dehydrobrominated to give 6 as yellow prisms; mp 278-278.5 °C; $\nu(-\overset{-}{O})$ 1510 cm^{-1}; λ_{max} 320 (26900), 353 (11200), 385 nm (ε 11600). The O-methylation reactions of 6 with CH_3FSO_3 and CH_3I-$AgClO_4$ which afford 8a (76% yield; mp 219 °C; λ_{max} 250 (20500), 290 sh (6700), 360 nm (ε 2800)) and 8b (97% yield; mp 254 °C), respectively, also support the enolate structure of 6. Both the $KMnO_4$ oxidations of 5 and 6 afforded benzophenone and o-benzoylbenzoic acid. The following facts show that 6 is an excessively stabilized

Scheme 2



betaine and does not show reactivity as a phosphonium ylid. Heating of 6 and benzaldehyde in xylene under reflux for 5 h recovered 6 unchanged in quantitative yield. This contrasts with that 3 reacts easily with benzaldehyde to give 7.[6] 6 was also inert to KOH-catalyzed hydrolysis in boiling methanol, even though 8a was hydrolyzed under the same conditions to give 2-methoxy-5,8,8-triphenylbenzo[c]heptafulvene (9) in 79% yield as colorless prisms; mp 180-181 °C; λ_{max} 245 (24400), 298 (23800), 332 nm (ε 20600); ^{1}H NMR δ 6.71 and 6.38 (each s, =CH), 3.35 (s, OCH_3). As we are aware, no strongly stabilized betaine such as 6 has been reported except some stable aromatic betaines like 10.[7] However, it is not clear why 6 is strongly stabilized.

Heating of 3 and diphenylketene in xylene under reflux for 1 h also afforded 5,8,8-triphenylbenzo[c]heptafulvene derivative (14) as colorless prisms in 43% yield; mp 246-247 °C; λ_{max} 245 (21600), 294 (19500), 328 nm (ε 17800); ^{1}H NMR δ 6.00 (s, =CH); ^{13}C NMR δ 53.5 (s, CPh_2); m/e (relative intensity) 548 (M^+, 100), 381 ($M^+ - Ph_2CH$, 44), 167 (Ph_2CH^+, 38). A plausible reaction pathway is shown in Scheme 2. Thermal cycloaddition of diphenylketene to the carbonyl of 3 gives β-lactone intermediate (11). Ring expansion of the β-lactone of 11 accompanied by the attack of phenyl to the four-membered ring carbon gives δ-lactone intermediate

(**12**), which is then converted into **13**. Thermal degradation of **13** finally afford **14**, Ph_3PO (isolated), and CO. It is interesting that diphenylketene attacks on the carbonyl but not on the phosphonium ylid moiety of **3**. It is probably due to steric control, because ketene reacted with **3** at room temperature and afforded naphthocyclobutanone derivative (**16a**) as yellow prisms in 62% yield; mp 218-219 °C; ν(C=O) 1760 cm^{-1}; λ_{max} 253 (39400), 285 (25300), 324 (42900), 382 (14800), 430 nm (ε 13400). This reaction probably proceeds via the allene intermediate (**15a**) which is produced by normal phosphonium ylid-ketene reaction. Reaction of phenylisocyanate and **3** also gave naphthocyclobutanone derivative (**16b**) as orange prisms in 64% yield; mp 248-249 °C; ν(C=O) 1750 cm^{-1}; λ_{max} 248 (34900), 282 sh (29300), 344 (21900), 413 (17300), 453 sh nm (ε 10200).

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