

THE 2-OXAPENTALENYL ANION

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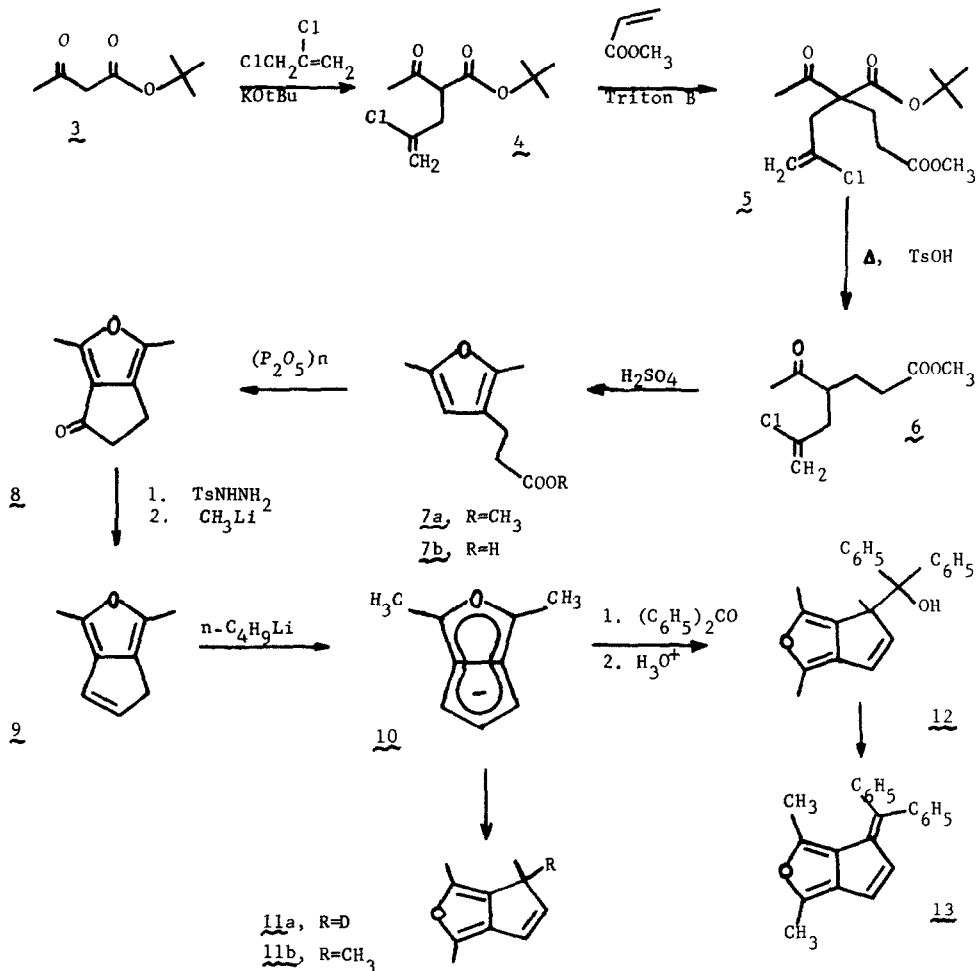
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Nonbenzenoid aromatic systems containing hetero atoms have been the subject of numerous recent investigations.^{2,3} As part of our program of study of 10 π -electron systems containing oxygen and/or sulfur, we prepared a dimethyl derivative of 1, the 2-thiapentalenyl anion. The present report concerns the preparation and properties of the 1,3-dimethyl-2-oxapentalenyl anion, 10.



1 Z = S
2 Z = O

Alkylation of t-butyl acetoacetate (3) with 2,3-dichloropropene by means of potassium t-butoxide in refluxing t-butanol gave 4 (64%). Michael addition of methyl acrylate to 4 (Triton B in DMF) proceeded in near-quantitative yield; the crude ester 5 underwent toluene-sulfonic acid-catalyzed elimination and decarboxylation in refluxing toluene to give the monoester 6 (2,4-DNP derivative⁵ m.p. 107-108°) quantitatively. Hydrolysis of the vinylic chloride function of crude 6 and cyclization of the resulting γ -diketone was accomplished by treatment with 90% sulfuric acid at 5-10°. ⁴ The methyl 2,5-dimethylfuran-3-propionate (7a) thus produced (25%) was hydrolyzed to acid 7b⁵ with 2N aqueous KOH (71%; m.p. 54-55°). Warming acid 7b in polyphosphoric acid (90°; 10 minutes) effected cyclization to ketone 8 [34%; m.p. 41.5-43°; semicarbazone⁵, m.p. 228° dec.; ν_{\max} 1710 cm^{-1} ; nmr (CCl_4): τ 7.38 (4H, methylenes) and 7.65 and 7.80 (3H each, singlets, methyls)]. The tosylhydrazone of 8 (m.p. 186-187.5° dec) was treated with 2.5 equivalents of ethereal methyllithium at 0-5° and stirred 5 hr. while warming to room temperature. Conventional workup⁶ gave the olefin 9 (61-75%; b.p. 50-55°/5mm;



nmr (CCl_4): τ 3.40 (1H, 3d, $J = 5.8, J' = 2.3, \text{H}-2$), 3.75 (1H, 3d, $J = 5.8, J' = 2.3, \text{H}-3$), 6.88 (2H, m, $-\text{CH}_2-$), and 7.67 and 7.74 (3H each, singlets, methyls); UV: $\lambda_{\text{max}}^{\text{EtOH}}$ 242 ($\epsilon = 4800$) and 218 nm ($\epsilon = 9900$). Addition of 1.1 equivalent of butyllithium in hexane to 9 in THF at -20° followed by warming to 0° gave the 1,3-dimethyl-2-oxapentalenyl anion 10 (nmr: τ 3.91 (1H, t, $J=3.2$), 5.58 (2H, d, $J=3.2$), and 7.90 (6H, s, methyls). Solutions of the anion could be stored at -20° for short periods, but deteriorated rapidly above 0° . Quenching of the anion with water led to recovery of olefin 9 in high yield; use of deuterium oxide in place of water gave the monodeutero olefin $11a$. The intensity of the methine hydrogen signal at τ 6.89 in the nmr

of 11a indicated the incorporation of $\geq 97\%$ of one atom of deuterium. Alkylation of 10 with methyl iodide gave the 3-methyl compound 11b (52%; nmr (inter alia): τ 8.82(3H, d, $J=7.5$).

Addition of a degassed THF solution of benzophenone to 10 at 0° and conventional workup gave alcohol 12⁵ (36%; white prisms from EtOH, m.p. 172-173°; ν_{\max}^{KBr} 3508 and 3590 cm^{-1} ; nmr (CDCl_3): τ 2.3-2.9 (10 H, m, aryl H's), 3.53 (1H, 2d, $J=5.8$, $J'=2.0$, H-2), 4.18 (1H, 2d, $J=5.8$, $J'=2.0$, H-3), 5.22 (1H, m, H-1), and 7.79 and 8.82 (3H each, broadened singlets, methyls).

Warming a benzene solution of 12 containing a trace of toluenesulfonic acid (50° ; N_2) gave the fulvene 13⁵ (74%; gold platelets from EtOH, m.p. 110-111°; $\lambda_{\max}^{\text{EtOH}}$ 375 ($\epsilon=11,000$) and 258 ($\epsilon=14,300$) nm; nmr (CDCl_3): τ 2.69 and 2.80 (5H each, singlets, phenyls), 3.63 (2H, s, vinyls), and 7.78 and 8.76 (3H each, singlets, methyls).

The simplicity of the nmr spectrum of 10 shows that it is indeed the symmetrical, delocalized species shown and not a covalent lithium compound. It is noteworthy that the methyl signal of 10 is shifted upfield ca. 0.2 p.p.m. relative to the methyl signals of the olefin 9, in contrast to the analogous sulfur series in which the methyl signals of the anion and neutral compound occur at essentially the same field.² The upfield shift of 10 could be accounted for by either the presence of a greater amount of negative charge in the heterocyclic ring of 10 than of 1 or by a weaker ring current effect in the oxygen heterocycle 10. The results of MO calculations and previous nmr studies⁷ on alkylfurans and alkylthiophenes indicate a smaller ring current in the furan series and a lower degree of aromaticity. It appears that oxygen heterocycles in general have a lower degree of aromaticity than the corresponding sulfur systems and that a weaker ring current effect in 10 is responsible for the upfield shift of the methyls.

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