

Reactions of Phenyl-pyrylium Salts with Phenacylidene-
dimethylsulfurane

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Reactions of 2,4,6-triphenyl- (1) and 2,6-diphenyl-pyrylium (6) salts with phenacylidenedimethylsulfurane (2) gave corresponding addition products (3 and 7) which possess ylid structures. Alkali treatment of 3 and 7 afforded 2,4,6-triphenylthioanisole (4) and 4-benzoylmethylene-2,6-diphenyl-4H-pyran (8), respectively.

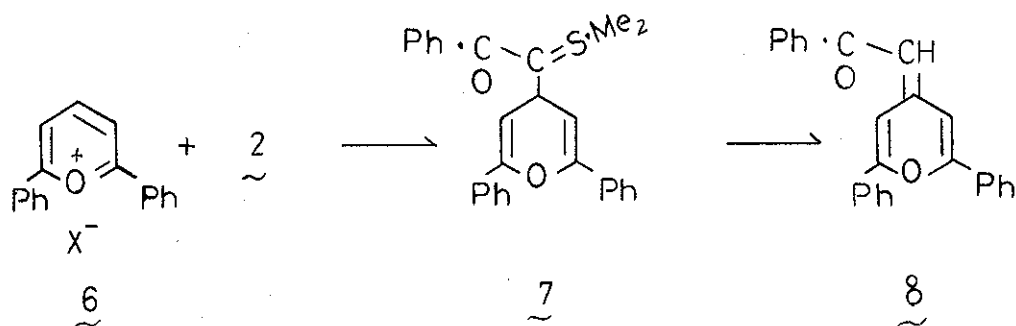
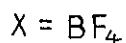
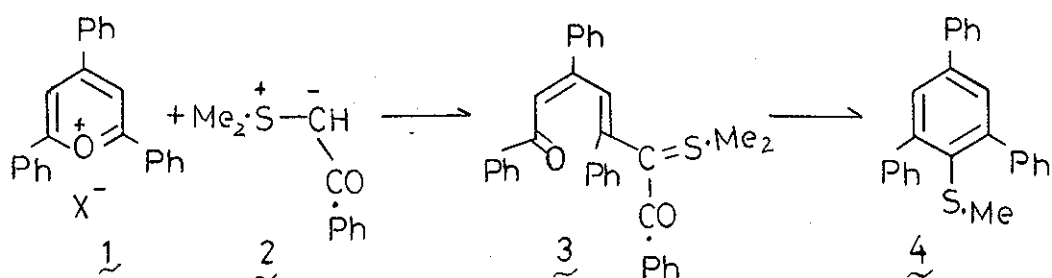
The reactions of pyrylium salts with anionoid reagents have extensively been studied until recently.¹⁾ However, only few examples have been known about the reactions of pyrylium salts and ylids.¹⁾ Very recently Katritzky and coworkers reported reactions of 2,4,6-triphenylpyrylium perchlorate and phenacylmethylphenylsulfenyl ylids to give furan derivatives.²⁾ We have independently studied the reactions of pyrylium salts and ylids, and wish to report here our results different from Katritzky's.

The reaction of 2,4,6-triphenyl fluoroborate (1) with phenacylidenedimethylsulfurane (2)³⁾ gave an addition product (3)

in an excellent yield (> 90%). The physical data of 3 are as follows: mp 153° (C₃₃H₂₈O₂S);⁴⁾ IR (KBr); 1640, 1552, 1510 and 1204 cm⁻¹; nmr (CDCl₃); δ 2.73 (s, 6H, S-Me).^{3,5)} Heating of 3 with dilute alkali afforded a viscous oily substance (4) accompanied with formation of benzoic acid. Its elemental analysis (C₂₅H₂₀S) and spectral data (IR, no carbonyl: nmr; δ 1.80, s, 3H) suggest that the structure of 4 is 2,4,6-triphenylthioanisole. This was confirmed by the reduction of 4 with Raney nickel to give 1,3,5-triphenylbenzene (5) (mp 170°) which IR spectrum is superimposable with that of an authentic sample.^{6,7)}

Also, the reaction of 2 with 2,6-diphenylpyrylium fluoroborate (6) afforded an addition product (7), mp 175° (decomp. C₂₇H₂₄O₂S) in a very good yield (> 90%): IR (KBr); 1600, 1502 and 1273 cm⁻¹; nmr (CDCl₃); δ 3.12 (s, 6H), 4.18 (t, 1H) and 5.52 (d, 2H).^{3,5)} The nucleophilic attack should be occurred at the C₄-position in 6 as known from the spectral data of 7 and an analogy of other reactions.¹⁾ Treatment of 7 with dilute alkali gave an yellow substance (8), mp 156° (C₂₅H₁₈O₂): IR (KBr); 1660, 1520 and 1210 cm⁻¹; nmr (CDCl₃), δ 6.20 (s, 1H): uv; λ_{max}^{MeCN}, nm (log ε), 224 (4.34), 249 (4.29), 309 (4.25) and 412 (4.46). The uv spectrum of 8 is similar to that of 4-formylmethylene-2,6-diphenyl-4H-pyran.⁸⁾

Thus, the reaction scheme of 1 and 6, and the structures of the reaction products (3, 4, 7 and 8) can reasonably be depicted as shown in the following figure.



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Received, 10th January, 1976