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Reactions of Phenyl-pyrylium Salts with Phenacylidenedimethylsulfurane

Yoshizo Suzuki,* Takashi Toda, and Toshio Mukai

Department of Chemistry, Faculty of Science, Tohoku University,
Aoba, Aramaki, Sendai 980, Japan

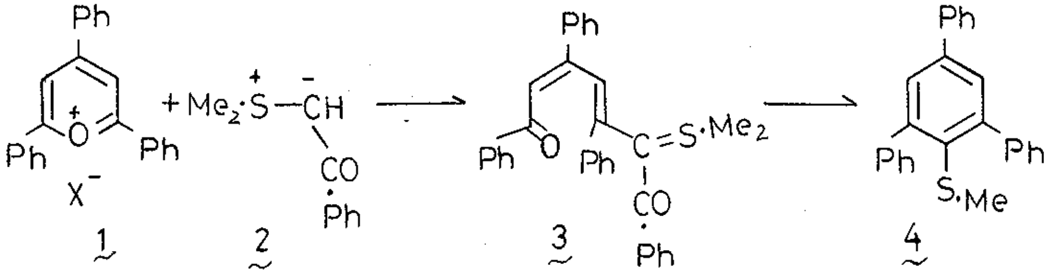
Reactions of 2,4,6-triphenyl- (1) and 2,6-diphenylpyrylium (6) salts with phenacylidenedimethylsulfurane (2) gave corresponding addition products (3 and 7) which possess ylid structures. Alkali treatment of 3 and 7 afforded 2,4,6-triphenylthioanisole (4) and 4-benzoylmethylene-2,6-diphenyl-4H-pyran (8),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

The reactions of pyrylium salts with anionoid reagents have extensively been studied untill 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.

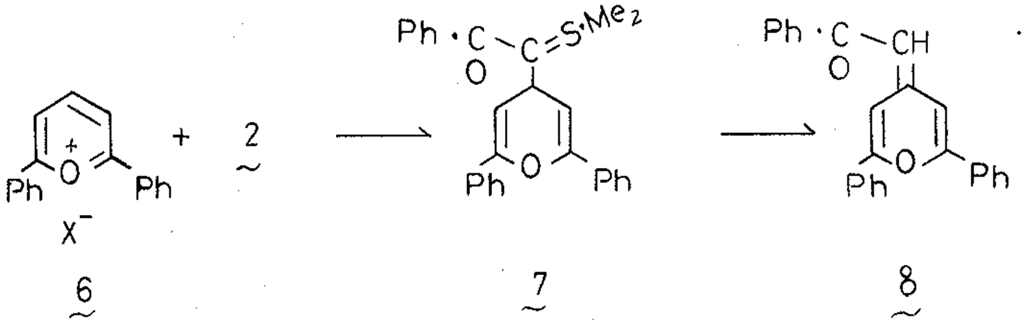
The reaction of 2,4,6-triphenyl fluoroborate (1) with phenacylidenedimethylsulfurane (2)[3] gave an addition product (3) in an excellent yield ($>$ 90%). The physical data of **3** are as follows: mp 153° ($C_{33}H_{28}O_2S$):[4] IR (KBr); 1640, 1552, 1510 and 1204 cm^{-1}: nmr ($CDCl_3$); δ 2.73 (s, 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 ($C_{25}H_{20}S$) 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. $C_{27}H_{24}O_2S$) in a very good yield ($>$ 90%): IR (KBr); 1600, 1502 and 1273 cm^{-1}; nmr ($CDCl_3$); δ 3.12 (s, 6H), 4.18 (t, 1H) and 5.52 (d, 2H).[3,5] The nucleophilic attack should be occurred at the C_4-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° ($C_{25}H_{18}O_2$): IR (KBr); 1660, 1520 and 1210 cm^{-1}: nmr ($CDCl_3$), 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.



$X = BF_4$



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3 A.W. Johnson and R.T. Amel, *Tetrahedron Letters*, 1966, 819. K.W. Ratts and A.N. Yao, *J. Org. Chem.*, 1966, **31**, 1185.

4 Correct analyses were obtained for all new compounds.

5 IR and nmr spectra of **3** and **7** show agreeable carbonyl bands and chemical shifts with those of so called ylid carbonyl band and ylid S-Me chemical shift. Cf. lit. 3; and H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, 1966, **22**, 2145.

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