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REACTION OF THIOPYRYLIUM ION WITH ACTIVE METHYLENE COMPOUNDS

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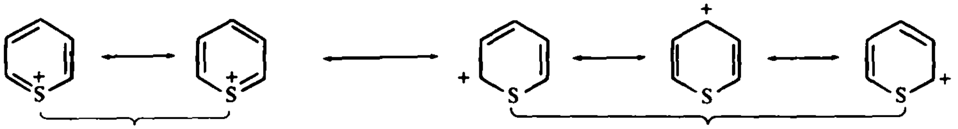
Abstract—The reaction of 2,4,6-triphenylthiopyrylium ion with several active methylene compounds in the presence of base has been found to yield 2,4,6-triphenylbenzene derivatives. In the case of the reaction of 2,4,6-triphenylthiopyrylium fluoroborate with nitromethane, an alkali treatment gave 2,4,6-triphenylnitrobenzene, and an acid treatment afforded 2,4,6-triphenylbenzene, respectively. From these results, the reaction behaviour of the thiopyrylium ion has been discussed.

THIOPYRYLIUM ION (I) has six π-electrons in the positively charged six membered ring containing one sulfur atom, and might be expected to have aromatic as well as carbonium ion character, because its ground state can be represented as a resonance hybrid of the sulfonium structures (Kekulé structure) and the carbonium ion structures as shown below.

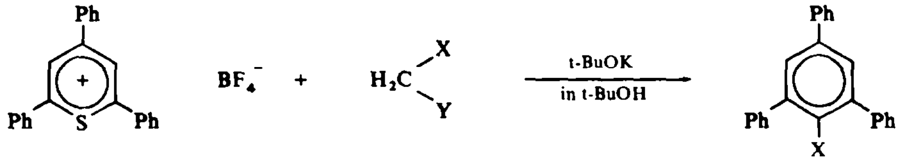


In order to investigate the characteristics of the thiopyrylium ion, it is of interest to attempt the reactions of thiopyrylium ion with nucleophiles. Although numerous nucleophilic reactions have been studied on the pyrylium ion,[1] isoelectronic to the thiopyrylium ion, reactions of the thiopyrylium ion have been confined to its reactions with PhLi[2] and Grignard reagent.[3] In the latter cases, the attack by the reagents occurs at sulfur to give thiabenzene derivatives, in which the unfilled 3d-orbital of the sulfur atom might be utilized to achieve through-conjugation at sulfur.

This paper is concerned with the reactions of 2,4,6-triphenylthiopyrylium ion (II) with active methylene compounds in the presence of base. The reaction behavior of II toward nucleophiles is discussed, together with the results obtained from Hückel MO treatment.

RESULTS AND DISCUSSION

When II was treated with active methylene compounds shown in Table 1 in the presence of t-BuOK in t-BuOH, the corresponding triphenylbenzene derivatives (III) were obtained. The results are summarized in Table 1. This reaction is useful as a new synthesis of 1-substituted 2,4,6-triphenylbenzene derivatives.



II III

TABLE 1. REACTION OF 2,4,6-TRIPHENYLTHIOPYRYLIUM FLUOROBORATE WITH ACTIVE METHYLENE COMPOUNDS IN THE PRESENCE OF BASE

	X	Y	yield (%)
III_a	CN	CN	58
III_a	CN	$CONH_2$	34
III_a	CN	COOEt	46
III_b	COMe	COMe	65
III_c	COOEt	COMe	11
III_d	NO_2	H	87
III_e	H	NO_2	74

All the results in Table 1 might be explained by a reaction course that the initial nucleophilic attack by active methylene compounds took place at α-carbon in II followed by ring opening and closure to give triphenylbenzene derivatives which are more stable than the thiopyrylium ion. The π electron densities (q_r) of II calculated by Hückel MO indicate that the positive charge distributes most largely on the sulfur (+0·525) as seen in Table 2. However, the reaction indices of II such as superdelocalizabilities (Sr) and localization energies (Lr) suggest that nucleophilic attack should take place exclusively at α-carbon (see Table 2).

TABLE 2. REACTION INDICES OF UNSUBSTITUTED THIOPYRYLIUM (I) AND 2,4.6-TRIPHENYLTHIOPYRYLIUM CATION (II) USING HÜCKEL PARAMETERS; $\alpha_s = \alpha + 0{\cdot}9\beta$ AND $\beta_{c-s} = 0{\cdot}6\beta$

	(I)				(II)			
	S	α	β	γ	S	α	β	γ
q_r	1·525	0·808	1·007	0·845	1·603	0·857	1·008	0·887
S_r	1·197	1·929	0·818	1·847	1·423	1·893	1·021	1·809
Lr(−β)	2·639	1·619	2·578	1·929	2·452	2·085	2·421	2·396

The probable reaction course, in which the initial attack at α-carbon is followed by ring opening and closure, is given in Fig. 1.

Initial adduct A may be considered to have a cyclohexadiene structure, whose ring-opening in the electrocyclic reaction is possible to occur photochemically, on the basis of the Woodward-Hoffman rule. Actually, a photochemical ring opening and reversible thermal closure of thiopyran derivative was reported by Becker and Kolc[4]

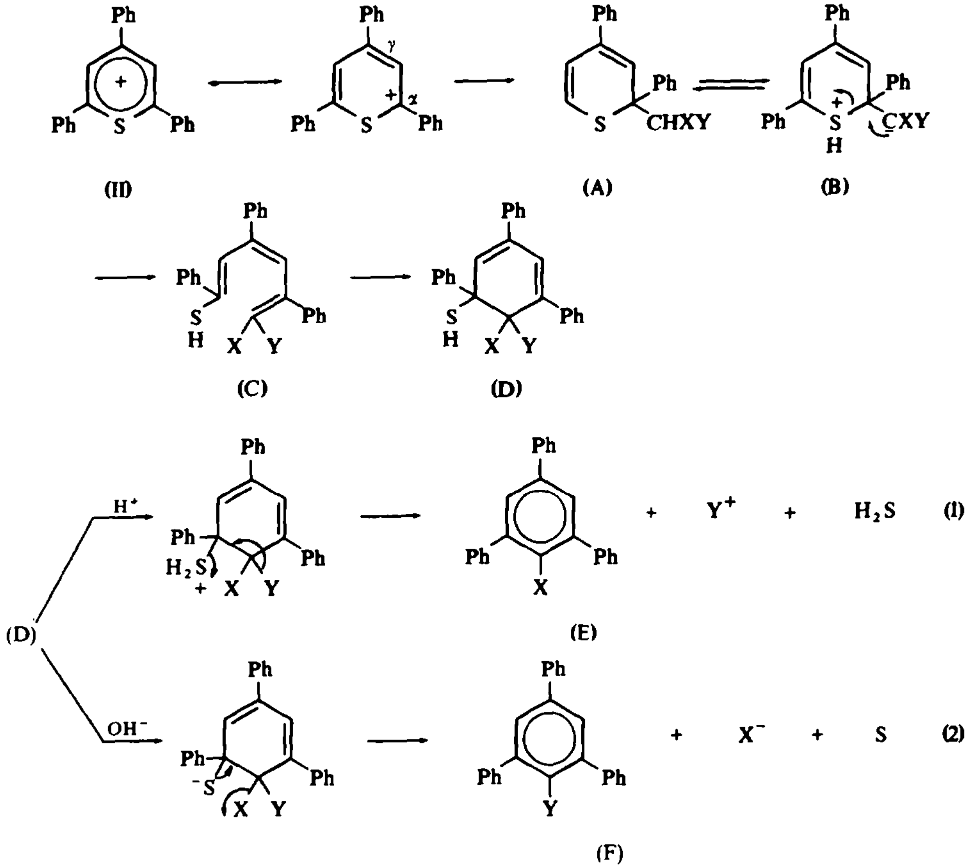
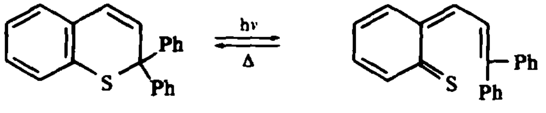


FIG 1. The probable course of the reaction of triphenylthiopyrylium ion with active methylene compound in presence of t-butoxide

as shown in Scheme 1. In our case, however, thermal ring fission is considered to take place by an accelerating effect of the electron-withdrawing sulfonium group in the intermediate (B) (Fig. 1). The ring-opened intermediate C, a hexatriene system, would cyclize again to give a cyclohexadiene derivative D. Thus, formation of products and the evolution of H_2S are explained by equation 1.

In the reaction of II with malodinitrile in the presence of t-BuOK in t-BuOH, an intense reddish violet colour appeared and faded away in about 30 min at reflux. The reddish violet coloured mixture could be attributed to the ring-opened intermediate C, which should change on heating to the uncoloured species D. The existence

SCHEME 1



of the intermediate C was confirmed by the fact that the same treatment of II in ether gave the rather stable red-violet oily matter and its UV spectrum was almost identical with that of 1,1′-dicyano-2,4,6-triphenyl hexatriene. When the reddish violet matter was heated in t-BuOH at 70°, product III was obtained.

In the reaction of II with $MeNO_2$, the difference in the products between acid treatment and alkali treatment can be interpreted by the reaction courses, 1 and 2, in Fig. 1. Acid treatment of D gives, with evolution of H_2S, the final product, 2,4,6-triphenylnitrobenzene (IIId). In this case, the leaving group (solvated H^+) in $MeNO_2$ should be more stable as a cation in an acidic solution. On the other hand, in an alkaline condition, sulfur was isolated and 2,4,6-triphenylbenzene (IIIe) was obtained. The leaving group (NO_2^-) in this case is a more stable species as an anion in an alkaline condition.

Treatment of unsubstituted thiopyrylium ion (I) with active methylene compounds in a similar reaction condition employed in the case of II was also attempted, but no reaction product was confirmed, because the reaction proceeded too fast and was followed by polymerization of the reaction intermediate. The reaction of γ-methoxythiopyrylium ion with malodinitrile in the presence of base has been also carried out and found to afford 7,7-dicyanomethylene thiopyran.*

In summary from the above results, it is concluded that triphenylthiopyrylium ion displays reaction behaviour as a carbonium ion. There remains the question of quite different reaction behaviour of II between PhLi or Grignard reagents and active methylene compounds with base. It can be rationalized by the following interpretation; the former reactions proceed *via* radical intermediates, and the latter, *via* ionic routes. The evidence of the radical route in the former has been recently provided by Hori[5] from measurement of the ESR spectrum of the 9-phenylthioxanthyl radical,† formed by treatment of 9-phenylthioxanthylium ion with organic metal (RM: R=Me, Ph; M=MgX, Li).

EXPERIMENTAL SECTION

NMR spectra were determined on Jeolco C-60H with TMS as internal standard. UV spectra were run on Hitachi EPS-3T recording photometer. IR spectra were recorded on Hitachi grating IR spectrophotometer Model-215.

2,4,6-*Triphenylthiopyrylium fluoroborate* (II). This compound was prepared by the method of Wizinger[7] from 2,4,6-triphenylpyrylium fluoroborate and Na_2S. m.p. 218° (decomp): NMR ($CDCl_3$) τ 0·9 (s, 2H), τ 1·2–2·5 (m, 15H): λ_{max}(MeOH): 375 mμ (ε 26,600), 407 mμ (ε 21,500). (Calc. for $C_{23}H_{15}SBF_4$: C, 67·02: H, 4·13. Found. C, 67·18, H, 4·34%).

Reaction between II *and malodinitrile.* To a suspension of 4·1 g (0·01 mol) of II in 50 ml of t-BuIH was added a solution of 0·66 g (0·01 mol) of malodinitrile and 0·11 g (0·01 mol) of t-BuOK in 50 ml of t-BuOH at room temp. When this suspension was stirred under reflux, the yellow solid (II) disappeared rapidly giving a red violet solution, and white crystals (KBF_4) separated out. After stirring for about 30 min, the reddish violet colour faded and the suspension again turned to yellow. Stirring was continued under reflux for an additional 2 hr and then the heated suspension was immediately filtered. The filtrate was cooled at 0° and the white solid precipitated was collected by filtration. This solid was recrystallized from MeOH, dried under vacuum, and the white fibres III_a were obtained with a yield of 58%; m.p. 166–167°. IIIa was shown to be 2,4,6-triphenylbenzonitrile by m.m.p. with an authentic sample.[8] The NMR spectrum of IIIa

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* Details will be published elsewhere.

† 9-Phenylthioxanthyl radical, formed by one electron reduction of 9-phenylthioxanthylium with zinc, was also reported by Price *et al.*[6]

showed a singlet at τ 2·4 (2H, the protons at β-positions in the parent ring) and a multiplet at τ 2·2–2·8 (15H, benzene ring). The IR spectrum of IIIa contained a peak at 2240 cm^{-1}, which was assigned to the C–N stretching vibration.

Reaction between II *and cyanoacetamide.* The method used here was identical with that described for malodinitrile, the same product (IIIa) was obtained in 34% yield: m.p. 166–167°.

Reaction between II *and ethyl cyanoacetate.* The method employed was identical with that described above, and the product (IIIa) obtained in 46% yield: m.p. 166–167°.

Reaction between II *and acetylacetone.* The procedure was virtually identical with that described for malodinitrile except that the nucleophile was replaced with 1·00 g (0·01 mole) of acetylacetone. The product was recrystallized from EtOH to give white needles (IIIb) in 65% yield, m.p. 128–129°. IIIb was shown to be 2,4,6-triphenylacetophenone by spectral data and elemental analysis. The NMR spectrum exhibited a singlet at τ 2·5 (2H, parent ring), a multiplet at τ 2·5–2·8 (15H, benzene ring) and a singlet at τ 8·1 (3H, Me). The IR spectrum contained a signal at 1690 cm^{-1}, which was assigned to the carbonyl stretching vibration. (Calc. for $C_{26}H_{20}O$: C, 89·39: H, 5·83: O, 4·50. Found: C, 89·66; H, 5·75: O, 4·59%).

Reaction between II *and ethylacetoacetate.* Procedure identical with that above, but in this case, ethyl acetoacetate was used as a nucleophile. Recrystallizztion of the product from EtOH gave white plates (IIIc) in 11% yield. This was determined to be ethyl 2,4,6-triphenylbenzoate by spectral data and elemental analysis. The NMR spectrum of IIIc showed a multiplet at τ 2·3–2·7 (15H, benzene ring), a quartet centered at τ 6·1 (2H, methylene) and a triplet centered at τ 9·2 (3H, Me). The IR spectrum of IIIc had a strong peak at 1725 cm^{-1}, which was assigned to the carbonyl stretching vibration. (Calc. for $C_{27}H_{22}O_2$: C, 85·70: H, 5·74: O, 8·39. Found: C, 85·71: H, 5·82: O, 8·47%).

Reaction between II *and nitromethane.* To a suspension of 4·1 g (0·01 mol) of II in 50 ml t-BuOH was added a solution of 0·61 g (0·01 mol) of $MeNO_2$ and 0·11 g (0·01 mol) of t-BuOK in 50 ml of t-BuOH at room temp. When the mixture was refluxed with stirring, the yellow solid (II) rapidly disappeared, the mixture turned to yellow, and white crystals (KBF_4) came out of solution. After adding 0·01 mol of t-BuOK, stirring was continued under reflux for 1 hr, when the colour changed to red brown. The heated mixture was immediately filtered, and the filtrate treated with a cooled HCl aq. White solid which separated was collected by filtration, recrystallized from glacial AcOH to give colourless crystals (IIId) with a yield of 87%: m.p. 145°. The product was identified as 2,4,6-triphenylnitrobenzene by m.m.p. with an authentic sample.[9]

To the red brown mixture obtained by the same procedure was added conc. NaOH aq, the mixtures was heated at 70° for one hr, and allowed to stand at room temp. The resulting red violet precipitate was collected by filtration, recrystallized from glacial AcOH to give colourless needles (IIIe) with a yield of 79%, m.p. 174°. The product (IIIe) was determined to be triphenylbenzene by m.m.p. with an authentic sample.

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