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SYNTHESIS OF 1-PHENYL-1-THIONIUMCYCLOBUT-2-ENE PERCHLORATES AND THEIR REARRANGEMENT THROUGH 1-S-PHENYLTHIACYCLOBUTADIENE*

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Cyclodehydration of β-phenylmercaptoethyl alkyl/aryl ketones 1, by treatment with perchloric acid to yield a mixture of thianaphthalenium perchlorates 3 and the corresponding thiachromans 4, has been reported by us earlier [1-3]. Apart from these products, which were obtained by disproportionation (involving hydride transfer) of the intermediate Δ^3-thiachromenes 2, we have now found that a small quantity of the rearranged product pairs 5 and 6 were also formed. The formation of the rearranged product pairs 5 and 6 may be rationalized by postulating the intermediate formation of 1-S-phenyl-1-thioniumcyclobut-2-ene perchlorate 7. The latter will lead to 5 and 6 through the intermediate Δ^2-thiachromene 8 (Chart 1).

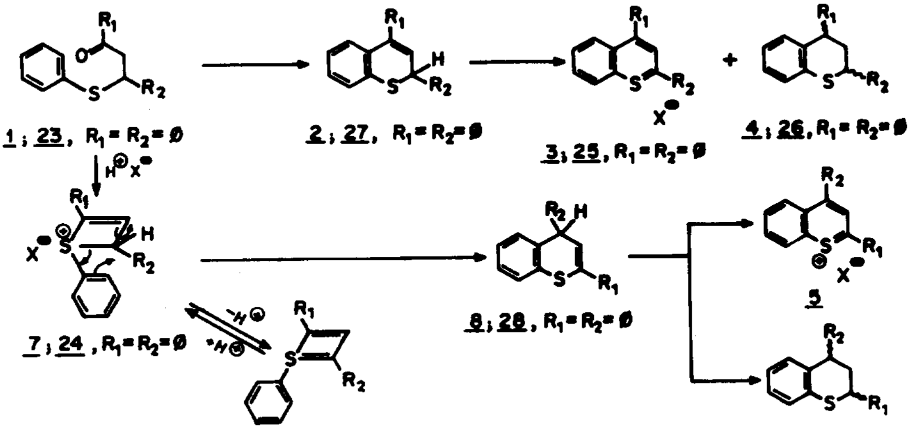

CHART-1.

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To confirm the involvement of 7 in the cyclodehydration reactions shown in Chart 1, β-phenylmercapto-n-propyl phenyl ketone 9 was reacted with phosphorous oxychloride followed by treatment with 70% perchloric acid. Saturation of the reaction mixture with diethyl ether gave 4-methyl-2-phenyl-1-S-phenyl-1-thioniumcyclobut-2-ene perchlorate 10, m.p. 229° (dec.) [PMR; 60 MH$_z$, CF_3COOH, TMS, δ ppm: C-4 methyl (2.9, d, 3p), aromatic protons and C-3H (7.5 - 8.4, m, 11p). Spectrum: $\lambda_{max}^{HClO_4/AcOH}$ mμ(log ε): 276 (3.80), 394 (4.03)]. Once isolated, 10 was quite stable. β-Phenylmercapto-β-phenylethyl methyl ketone, 21, on $POCl_3/HClO_4$ treatment as above, yielded 2-methyl-4-phenyl-1-S-phenyl-1-thioniumcyclobut-2-ene perchlorate, 13, m.p. 212° (dec.) [PMR; 60 MH$_z$, CF_3COOH, TMS, δ ppm: C-2 methyl (3.5, s, 3p); aromatic protons and C-3H (7.6 - 8.4, m, 11p). Spectrum: $\lambda_{max}^{HClO_4/AcOH}$ mμ (log ε): 268 (3.99), 297 (3.24), 391 (3.72)].

On warming with 70% perchloric acid, 10 rearranged to a pair of thianaphthalenium perchlorates 15 and 18 and a pair of thiachromans 16 and 19. The formation of these compounds may be due to double bond migration in 10 to give the isomeric perchlorate 13. Compounds 10 and 13 will then lead to pairs 15,16 and 18, 19 via the intermediate Δ^2-thiachromenes, 14 and 17 respectively. Compound 13, on warming with perchloric acid, however, gave only 18 and 19 presumably through 17.

To confirm the above possibility, the PMR spectrum of 10 and 13 in 70% perchloric acid was studied and changes followed by monitoring the methyl signals. It was indeed noted that 10 gets converted to 13 by treatment with 70% perchloric acid, whereas 13 itself remained unaltered. The synthesis of 18 and 19 from 9 and of 15 and 16 from 21 by perchloric acid cyclodehydration where no rearrangement is involved, probably proceeds through the relevant Δ^3-thiachromenes 20 and 22 respectively, whereas the formation of the rearranged cyclodehydration products (15 and 16 from 9 and 18 and 19 from 21) probably proceeds through the thionium salts 10 and 13 respectively as shown in Chart 2.

Compound 10 was also converted to 13 in another interesting manner by proton abstraction from 10 by treatment with sodium hydride in tetrahydrofuran and diethyl ether followed by reprotonation. In this process the yellow coloured 10 was converted into a deep olive green coloured product (not isolated and

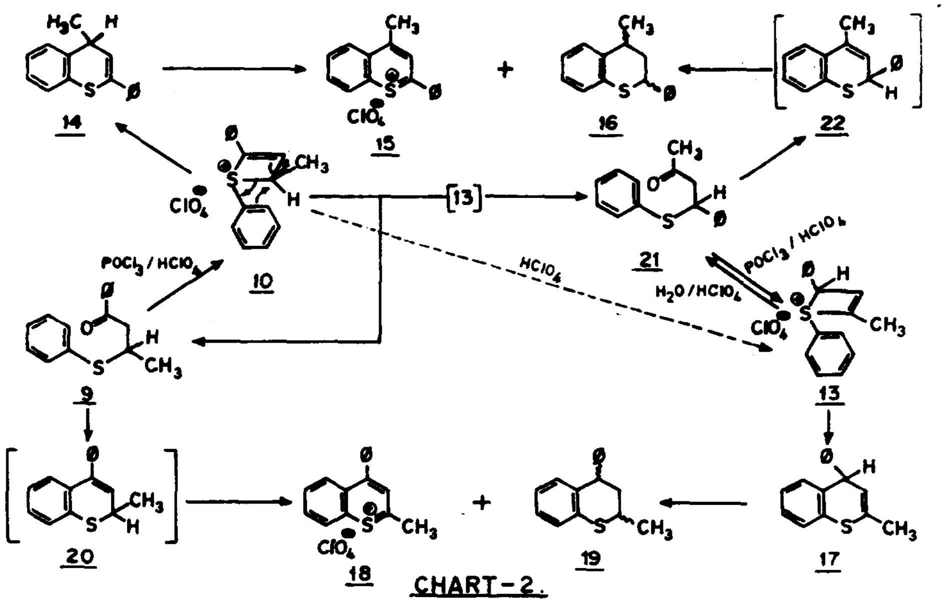

CHART-2.

in solution) which appears to be 2-methyl-4-phenyl-1-S-phenylthiacyclobuta-1,3-diene (11↔12). The formation of 13 and not 10 on reprotonation of the thiacyclobutadiene (11 12) seems to indicate the dominance of the diplolar form 12A as compared to 11A among the different resonance forms 11 ↔ 12 ↔ 11A↔12A.

When 13 was treated with sodium hydride as above, a green coloured solution possibly of the thiacyclobutadiene (11↔12) was again obtained which on perchloric acid treatment yielded back 13 and not 10. This further confirms the above observation regarding the greater contribution of 12A as compared to 11A to the resonance forms of the intermediate thiacyclobutadiene.

The absorption and PMR spectra of thiacyclobutadienes obtained by hydride abstraction from 10 and 13 were identical [PMR: 60 MH$_z$, CCl$_4$, TMS, δ ppm: C-2 methyl (3.2, s, 3p); aromatic protons and C-3H (7.7 - 8.7, m, 11p). Spectrum (EtOH): 240, 430, 460, 720 (broad mμ).

There may yet be another explanation to account for the formation of 15, 16, 18 and 19 starting from 10 viz. the conversion of 10 under acidic conditions to either 9 or 21 (via 13) and their normal cyclodehydration followed by disproportionation of the intermediate Δ^3-thiachromenes 20, and 22. Indeed when 10 was treated with water containing a few drops of perchloric acid, it

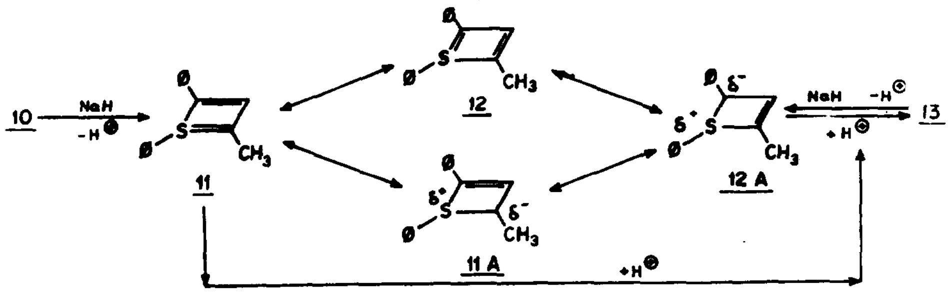

CHART-3.

gave a mixture of 9 and 21 in which 21 predominated. Under similar conditions, however, 13 yielded essentially 21 and not 9, again indicating the greater stability of 13.

The above study was then extended to β-phenylmercapto-β-phenylethyl phenyl ketone 23 which on treatment with POCl$_3$/HClO$_4$ gave 2,4-diphenyl-1-S-phenyl-1-thioniumcyclobut-2-ene perchlorate 24, m.p. 180° (dec.). Both 23 and 24 on treatment with 70% perchloric acid yielded, 2,4-diphenylthianaphthalenium perchlorate, 25 and 2,4-diphenylthiachroman 26 through probably Δ^3- and Δ^2-thiachromenes 27 and 28 respectively. Proton abstraction from 24 by treatment with sodium hydride yielded 2,4-diphenyl-1-S-phenyl-1-thiacyclobutadiene, 29 [PMR; 60 MH$_z$, CCl$_4$, TMS, δ ppm: C-3H (5.3, s, 1p), aromatic protons (7.0 -8.2, m, 15p). Spectrum : λ_{max} 434, 460, 483 and 775 (broad) mμs].Reprotonation of 29 with perchloric acid gave back 24. (Chart 1).

All new compounds mentioned herein gave satisfactory elemental analysis.

Further work on the isolation and/or trapping of the thiacyclobutadienes is in progress.

REFERENCES

1. B.D. Tilak and V.M. Vaidya, Tetrahedron Letters 487 (1963).
2. B.D. Tilak, H.S. Desai, C.V. Deshpande, S.K. Jain and V.M. Vaidya, Tetrahedron 22, 7 (1966).
3. B.D. Tilak and G.T. Panse, Indian J. Chem. 7, 191 (1969).