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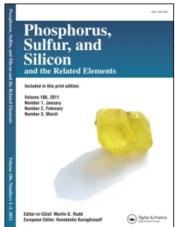
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SYNTHESIS AND PROPERTIES OF SOME NEW, STABLE THIETES (THIACYCLOBUTENES)

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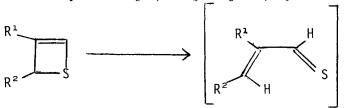
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SYNTHESIS AND PROPERTIES OF SOME NEW, STABLE THIETES (THIACYCLOBUTENES)

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Simple alkyl substituted thietes are liquids which decompose at room temperature presumably via electrocyclic ring opening to give polymeric material.



Introduction of an aromatic substituent on the carbon-carbon double bond (R^1 = phenyl, 2-naphthyl, 2-thienyl; R^2 = H) yields thietes which are stable solids (mp 89-90°, 125° and 65°, respectively).

The synthesis of 3-phenylthiete illustrates the general method.

PhCOCH₃ + (CH₃)₂NH
$$\frac{\text{TiCL}_4}{\text{C}_6\text{H}_6,0^\circ}$$

$$\frac{\text{CH}_3\text{SO}_2\text{CL}}{\text{C}_6\text{H}_6,0^\circ,(\text{C}_2\text{H}_5)_3\text{N}}$$
Ph $\frac{\text{LiA}_2\text{H}_4}{\text{ether}}$
Ph $\frac{\text{CH}_3\text{SO}_2\text{CL}}{\text{C}_6\text{H}_6,0^\circ,(\text{C}_2\text{H}_5)_3\text{N}}$
Ph $\frac{\text{CH}_3\text{SO}_2\text{CL}}{\text{C}_6\text{H}_6,0^\circ}$

$$\frac{\text{CH}_3\text{SO}_2\text{CL}}{\text{C}_6\text{H}_6,0^\circ,(\text{C}_2\text{H}_5)_3\text{N}}$$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$

$$\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$

$$\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$$

$$\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$$

$$\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$

$$\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$$

$$\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{H}_6,0^\circ}$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{I}}$
Ph $\frac{\text{CH}_3\text{I}}{\text{C}_6\text{$

The phenylthiete can be purified by sublimation $(60^{\circ}, 0.02 \text{ mm})$ without decomposition. Its ring opening appears to be catalyzed by zero-valent cobalt since treatment of 3-phenylthiete with cyclopentadienyl cobalt dicarbonyl affords a stable complex best formulated, according to the spectroscopic data, as a derivative of 2-phenylpropenethial.