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The Reaction of Thio-substituted Cyclopropenium Ions with Iminopyridinium and Sulfonium Ylides

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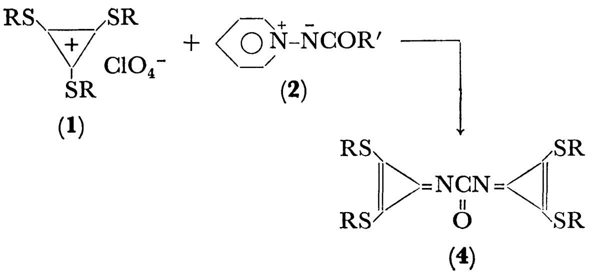
Synopsis. The reaction of several thio-substituted cyclopropenium ions with iminopyridinium and sulfonium ylides in organic solvents at reflux and room temperature under N_2 gave *N,N'*-dicyclopropenylidene urea derivatives, together with some unidentified compounds.

Amino-substituted cyclopropenium ions react with iminopyridinium ylides to give only cyclopropenimine derivatives.[1] It would be of interest to investigate what reaction takes place between heteroatom-substituted cyclopropenium ions[2] and ylides. As regards the reactions of cyclopropenium ions substituted with heteroatom, Yoshida *et al.* reported that tris(alkylthio)cyclopropenium ion reacts with trialkylphosphite to afford phosphonic acid esters and with hexamethylphosphorous triamide to give phosphonium salts and pyrrole derivatives, and with alkali to produce cyclopropenone and allene derivatives.[3]

Results and Discussion

When tris(ethylthio)cyclopropenium perchlorate (**1a**) was heated with three molar amount of *N*-benzoyliminopyridinium ylide (**2a**) in DMSO at 80 °C for 8 h under nitrogen atmosphere, *N,N'*-bis[bis(ethylthio)cyclopropenylidene]urea (**4a**) was formed in 60% yield; 7% of **1a** was recovered. The reaction of **1a** with *N*-(ethoxycarbonyl)iminopyridinium ylide (**2b**) under the same conditions gave **4a** in 39% yield.



R : Et for **1a** and **4a**, *t*-Bu for **1b** and **4b**,
p-*t*-BuC_6H_4 for **1c** and **4c**
R': Ph for **2a**, EtO for **2b**

Reactions of tris(*t*-butylthio)cyclopropenium perchlorate (**1b**) with **2a** and **2b** under the same reaction conditions afforded *N,N'*-bis[bis(*t*-butylthio)cyclopropenylidene]urea (**4b**) in 75 and 31% yields, respectively.

The reactions of tris(*p*-*t*-butylphenylthio)cyclopropenium perchlorate (**1c**) with **2a** in DMSO and **2b** in THF gave *N,N'*-bis[bis(*p*-*t*-butylphenylthio)cyclopropenylidene]urea (**4c**) in 87 and 89% yields, respectively.

The structures of **4a**, **4b**, and **4c** were confirmed by elemental analyses and spectroscopy.

When **1c** was reacted with *S,S*-dimethyl-*N*-acetylsulfimide (**3a**) in chloroform at room temperature for 8 h under nitrogen atmosphere with stirring, **4c** was formed in 89% yield.

$$\mathbf{1a—c} + (CH_3)_2\overset{+}{S}\text{-}\overset{-}{N}COR'' \longrightarrow \mathbf{4a—c}$$

(3)

R'': **3a** = Me, **3b** = EtO

However, reactions of **1a** and **1b** with **3a** under the same conditions did not give the corresponding ureas **4a** and **4b**, **1a** and **1b** being recovered quantitatively.

Reactions of **1a**, **1b**, and **1c** with *S,S*-dimethyl-*N*-(ethoxycarbonyl)sulfimide (**3b**) under the same conditions gave **4a**, **4b**, and **4c** in 42, 43, and 73% yields, respectively.

Experimental

All the melting points were uncorrected. IR spectra were determined with a Hitachi Model 215 spectrophotometer, UV spectra with a Hitachi Model EPS-3T spectrophotometer, and NMR spectra with a JEOL Model JNM-C-60H spectrometer with use of tetramethylsilane as an internal standard. Mass spectra were determined with a Hitachi RMU-6E spectrometer.

Materials. Tris(*p*-*t*-butylphenylthio)cyclopropenium perchlorate (**1c**) was prepared by a modification of the method of Yoshida and Tawara.[4] **1c**, mp 180 °C (from ether); UV max (CH_3CN) 232 (ε 32300) and 290 nm (19900); IR (KBr) 3010, 2970, 1242, and 824 cm^{-1}; NMR (acetone-d_6) δ 7.85 (m, 6H), 7.65 (m, 6H), and 1.75 (s, 36H, *t*-Bu); MS *m/e* 534 (M^+). Found: C, 62.66; H, 6.17%. Calcd for $C_{33}H_{39}S_3O_4Cl$: C, 62.78; H, 6.24%. The ylides were synthesized according to the reported procedures[5] and identified by elemental analyses as well as by comparison of IR and melting points. The solvents were purified before use.[6]

*Reactions of Tris(ethylthio)-(**1a**), Tris(*t*-butylthio)-(**1b**), and Tris(*p*-*t*-butylphenylthio)cyclopropenium Perchlorate (**1c**) with N-Benzoyliminopyridinium Ylide (**2a**).* A mixture of **1a** (7 mmol) and **2a** (5.1 mmol) in freshly distilled DMSO (30 ml) was stirred at 80 °C for 8 h under nitrogen atmosphere. After the reaction mixture had been allowed to stand overnight, the solvent was removed under reduced pressure. Urea (**4a**), dark brown oil, was obtained in 60% yield by column chromatography (silica gel) of the residue. The reactions of **1b** and **1c** with **2a** under the same conditions afforded the corresponding ureas (**4b**), pale yellow powder, and (**4c**), pale yellow needles, in 75 and 89% yields, respectively.

*Urea (**4a**).* IR (neat) 2930, 1795, 1635 (N–CO–N), and 790 cm^{-1}. UV max (EtOH) 319.5 nm (ε 22400). NMR (CCl_4) δ 1.50 (t, 12H, J=7.4 Hz) and 3.12 (q, 8H, J=7.4 Hz). MS *m/e* 372 (M^+). Found: C, 48.15; H, 5.82; N, 7.57%. Calcd for $C_{15}H_{20}N_2OS_4$: C, 48.35; H, 5.42; N, 7.52%.

*Urea (**4b**).* Mp 113—114.5 °C (from MeOH–H_2O). IR (KBr) 2960, 1800, 1630 (N–CO–N), 1360, 1090, and 770 cm^{-1}. UV max (EtOH) 327 nm (ε 34100). NMR (CCl_4) δ 1.50 (s, 36H, *t*-Bu). MS *m/e* 484 (M^+). Found: C, 56.74;

H, 7.77; N, 5.54%. Calcd for $C_{23}H_{36}N_2OS_4$: C, 56.97; H, 7.50; N, 5.78%.

Urea (4c). Mp 120—121 °C (from chloroform–ether). IR (KBr) 2900, 1805, 1640 (N–CO–N), 1470, 820, and 760 cm^{-1}. UV max (CH_3CN) 247 (ε 18600) and 238 nm (10200). NMR (CD_3CN) δ 1.31 (s, 36H, *t*-Bu) and 7.26—7.35 (m, 16H). MS *m/e* 788 (M^+). Found: C, 71.86; H, 6.43; N, 3.87%. Calcd for $C_{47}H_{52}N_2OS_4$: C, 71.52; H, 6.65; N, 3.55%.

Reactions of 1a, 1b, and 1c with N-*(Ethoxycarbonyl)iminopyridinium Ylide (2b).* By application of the same procedure as that for urea (**4a**), **1c** (2 mmol) was treated with **2b** (6 mmol) in dry THF (30 ml). The reaction mixture was worked up to give a crude oil, which was extracted with benzene. The solvent was then removed. The residue was extracted with ether to give **4c** in 89% yield. The reactions of **1a** and **1b** with **2b** were carried out by a similar procedure to give **4a** and **4b** in 39 and 31% yields, respectively.

Reactions of 1a, 1b, and 1c with S,S-*Dimethyl*-N-*(ethoxycarbonyl)sulfimide (3b).* By a procedure similar to that described above, **1b** (2 mmol) was treated with **3b** (8 mmol) in dry THF (30 ml) at room temperature for 8 h under nitrogen atmosphere. The reaction mixture was worked up to give a hygroscopic residue. The residue was crystallized from MeOH–H_2O to give **4b** in 43% yield. The reactions of **1a** and **1c** with **3b** were carried out in the same manner to give **4a** and **4c** in 42 and 73% yields, respectively.

Reactions of 1a, 1b, and 1c with S,S-*Dimethyl*-N-*acetylsulfimide (3a).* A mixture of **1c** (2.8 mmol) and **3a** (8.4 mmol) in chloroform (30 ml) was kept at room temperature for 8 h under nitrogen atmosphere with stirring. The reaction mixture was allowed to stand overnight and then the solvent was removed. The residual materials were dissolved in acetonitrile and the solution was extracted with petroleum ether. After removal of petroleum ether, the residue was recrystallized from chloroform–ether to afford **4c** in 84% yield. However, **1a** and **1b** did not react with **3a** and were recovered quantitatively.

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