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The Reaction of Acyl-substituted Sulfonium and Pyridinium Ylides with Diphenylthiirene Dioxide

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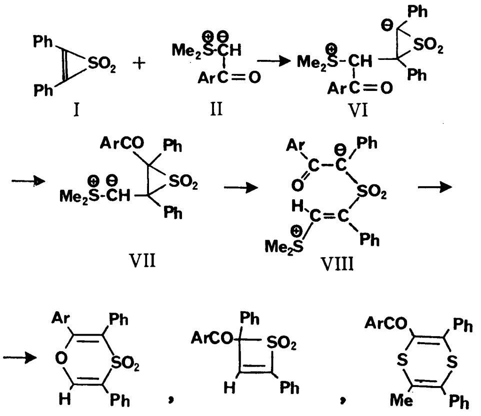
In contrast to the preceding paper,[1] which dealt with the reaction of sulfonium ylides with cyclopropenone, the present paper will report studies of the reactions of diphenylthiirene dioxide (I) as an electrophile with acyl-substituted sulfonium and pyridinium ylides.

Reaction with Sulfonium Phenacylides. The reaction of I with an equimolar quantity of dimethylsulfonium *p*-methylphenacylide (IIa) in benzene at reflux gave four crystalline products; the major one (67%) was a sulfur dioxide-elimination product, tolan, while the three minor products were identified as an oxathiin dioxide, IIIa (15%), a thiete dioxide, IVa (13%), and a dithiin, Va (12%). These products were identified from their spectral properties and from the results of elementary analyses. Thus, in the mass-spectrum fragmentation of IIIa, the elements of SO_2+CHO were lost from the molecular ion (*m/e* 374) to give a significant peak at *m/e* 281, probably because of a cyclopropenium ion. Meanwhile, the mass spectrum of IVa displayed a characteristic toluyl ion (*m/e* 119).

The formation of IIIa and IVa could be formulated by assuming the following sequences: (1) the benzoyl-migration in the VI adduct, giving intermediary ylides, VII;[2] (2) the subsequent isomerization to VIII, and finally (3) the ring closure of VIII with the elimination of dimethyl sulfide (Scheme 1). Remarkably, the carbon-to-carbon bond of the episulfone VII is preferentially broken instead of extruding sulfur dioxide.[3] The reaction pathway leading to Va is open to future research.

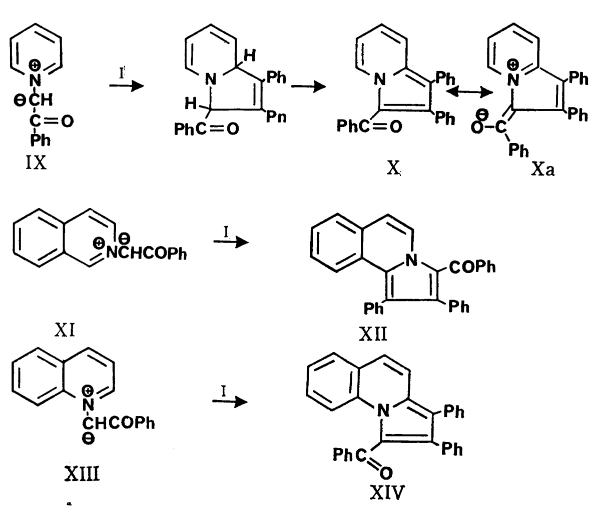
Analogously, the reaction of dimethylsulfonium phenacylide IIb with I afforded three crystalline products upon careful chromatography on silica gel. The spectroscopic and elementary analyses of the major product (36%) supported the structure IIIb; the very small amounts of the two minor products could be formulated as IVb (<5%) and Vb (6%) after a comparison of their spectra with those of IVa and Va respectively.

Reaction with Pyridinium and Related N-*Ylides.* 1,3-Dipolar cycloadditions of pyridinium and related heteroaromatic ylides with diethyl acetylenedicarboxylate, ethyl propiolate, and so on have been reported to give indolizine derivatives.[4] Diphenylthiirene dioxide (I) was found to behave similarly to *N*-ylides. Thus, pyridinium phenacylide (IX) reacted with an equimolar amount of I in benzene at room temperature to yield a yellow, crystalline solid, X (46%). The UV spectrum indicated the presence of cyclic conjugation systems.[4] The results of elementary analysis and the mass spectrum were in good accordance with the empirical formula of $C_{27}H_{19}NO$. The IR spectrum showed intense absorption bands at 1595, 1385, and 1210 cm^{-1}, which revealed the contribution of a charge-separated structure, *e.g.*, Xa, to the resonance hybrid. The structure of X was further confirmed by com-



Ar=*p*-MeC$_6$H$_4$ (Series a), Ph (Series b)

Scheme 1. Reaction of I with sulfonium acylmethylides



Scheme 2. Reaction of I with pyridinium acylmethylides

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1) Y. Hayasi and H. Nozaki, *Tetrahedron*, **27**, 3080 (1971). See also T. Eicher, E. von Angerer, and A. M. Hansen, *Ann. Chem.*, **746**, 102 (1971).

2) a) H. Nozaki, Y. Hayasi, M. Takaku, and K. Kondo, *Tetrahedron*. **24**, 6563 (1968); b) M. Higo and T. Mukaiyama, *Tetrahedron Lett.*, **1970**, 2565.

3) For the C-C bond cleavage reaction of episulfone, see L. A. Paquette and S. Maiorane, *Chem. Commun.*, **1971**, 313.

4) a) T. Sasaki, K. Kanematsu, Y. Yukimoto, and S. Ochiai, *J. Org. Chem.*, **36**, 813 (1971), and references cited therein; b) J. E. Douglass and J. M. Wesolosky, *ibid.*, **36**, 1165 (1971); c) N. Basketter and A. O. Plunkette, *Chem. Commun.*, **1971**, 1578.

parison with an authentic sample, independently prepared from 1,2-diphenylindolizine by reaction with benzoyl chloride following the general method of Borrows.[5] It should be added that the attempted reaction of IX with tolan (1: 1) at room temperature for 22 hr in benzene failed to afford the adduct X. A similar pattern was repeated using isoquinolinium (XI) and quinolinium (XIII) phenacylides to furnish two 3-benzoylindolizine derivatives XII and XIV respectively.

Experimental

All the melting points are uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyoto University. The NMR spectra were taken with JEOL C-60H and JNM-MH-60 spectrometers, and the chemical shifts are reported in δ values relative to TMS as the internal standard, unless otherwise stated. The abbreviations s and m refer to singlet and multiplet respectively. The UV absorption spectra were measured in 95% EtOH on a Shimadzu MPS-50L spectrometer, and the mass spectra, on a Hitachi RMU-6E instrument by the direct-injection method.

Reaction of Dimethylsulfonium p-*Methylphenacylide (IIa) with Diphenylthiirene Dioxide (I).* A solution of IIa (2.7 g, 13.6 mmol) and I (3.0 g, 12.4 mmol) in benzene (150 ml) was stirred at room temperature for 2 hr. The reaction mixture was then heated at reflux for 9 hr. The chromatographic separation of the crude products on a silica gel column (benzene and chloroform) gave tolan (1.5 g, 67%), IIIa (0.7 g, 15%), IVa (0.6 g, 13%), and Va (0.6 g, 12%).

3,5-Diphenyl-2-*p*-tolyl-1,4-oxathiin dioxide (IIIa): mp 183.5—185°C (PhH); $\lambda_{\max}^{\text{EtOH}}$ 233 (log ε 4.30), 238 (4.33) nm; IR (KBr) 1645, 1605, 1290, 1220, 1140 cm^{-1}; NMR ($CDCl_3$) 2.31 (s, 3), 7.2—7.8 (m, 15) ppm; MS *m/e* 376 (9), 375 (27), 374 (100, P), 311 (26), 310 (95), 282 (9), 281 (32), 193 (37), 192 (64), 191 (72), 190 (18), 184 (27), 165 (31), 119 (17), 91 (14), 89 (17), 77 (11).

Found: C, 74.0; H, 4.8%. Calcd for $C_{23}H_{18}O_3S$: C, 73.8; H, 4.9%.

2,4-Diphenyl-2-*p*-toluylthiete dioxide (IVa): mp 230—231°C (PhH); $\lambda_{\max}^{\text{EtOH}}$ 218 (4.35), 268 (4.35) nm; IR (KBr) 1680, 1610, 1280, 1150 cm^{-1}; NMR (DMSO-d_6) 2.5 (s, 3), 7.4—8.1 (m, 15) ppm; MS *m/e* 376 (1), 375 (4), 374 (13, P), 342 (5), 236 (6), 311 (22), 310 (77, P-SO_2), 205 (12), 191 (25), 189 (13), 165 (6), 120 (33), 119 (100), 105 (19), 91 (54), 77 (13), 64 (16).

Found: C, 74.0; H, 4.9%. Calcd for $C_{23}H_{18}O_3S$: C, 73.8; H, 4.9%.

2-Methyl-3,5-diphenyl-6-*p*-toluyl-1,4-dithiin (Va): mp 145—145.5°C (PhH); IR (KBr) 1655, 1605, 1280 cm^{-1}; NMR ($CDCl_3$) 2.30 (s, 3), 2.47 (s, 3), 7.2—8.2 (m, 14), ppm; MS *m/e* 402 (7), 401 (31), 400 (100, P), 285 (6), 367 (12), 309 (10), 295 (11), 262 (4), 234 (8), 220 (7), 154 (4), 121 (6), 119 (14), 91 (17).

Found: C, 74.5; H, 5.0; S, 15.5%. Calcd for $C_{25}H_{20}OS_2$: C, 75.0; H, 5.0; S, 16.0%.

Reaction of IIb with I. A solution of IIb (3.3 g, 18.2 mmol) and I (4.0 g, 16.5 mmol) in benzene (200 ml) was stirred at room temperature for 24 hr and then at reflux for 3 hr. After concentration, the residual oil was chromatographed on a silica gel column (benzene) to afford IIIb (2.4 g, 36%), IVb (0.3 g, 5%), and Vb (0.4 g, 6%).

2,3,5-Triphenyl-1,4-oxathiin dioxide (IIIb): mp 206—207°C (PhH); $\lambda_{\max}^{\text{EtOH}}$ 228 (4.35), 240 (4.32), 266 (4.12) nm; IR (KBr) 1650, 1283, 1220, 1135 cm^{-1}; NMR ($CDCl_3$) 6.9—7.8 (m) ppm; MS *m/e* 362 (3), 361 (7), 360 (23, P), 296 (40, P$-SO_2$), 268 (11), 267 (21), 178 (100), 177 (11), 176 (9), 152 (7), 149 (7), 105 (11), 102 (6),

Found: C, 73.2; H, 4.7%. Calcd for $C_{22}H_{16}O_3S$: C, 73.3; H, 4.5%.

4-Benzoyl-2,4-diphenylthiete dioxide (IVb); mp 142—143°C (PhH); IR (KBr) 1665, 1300, 1150 cm^{-1}; NMR ($CDCl_3$) 7.2—7.8 (m) ppm; MS *m/e* 362 (1), 361 (3), 360 (9, P), 297 (8), 296 (24, P$-SO_2$), 191 (14), 189 (7), 165 (10), 105 (100), 77 (19).

2-Benzoyl-3,5-diphenyl-6-methyl-1,4-dithiin (Vb): mp 111—112°C (PhH); $\lambda_{\max}^{\text{EtOH}}$ 244 (4.53), 286 (4.25) nm; IR (KBr) 1638, 1420, 1226, 1012 cm^{-1}; NMR ($CDCl_3$) 2.43 (s, 3), 6.8—7.5 (m, 15) ppm; MS *m/e* 388 (14), 387 (33), 386 (100, P), 372 (11), 371 (19), 353 (11), 309 (16), 295 (6), 262 (7), 234 (14), 221 (6), 193 (8), 154 (6), 145 (5), 121 (13), 105 (32), 77 (38).

Found: C, 74.6: H, 4.6; S, 16.5%. Calcd for $C_{24}H_{18}OS_2$: C, 74.6; H, 4.7; S, 16.5%.

Reaction of IX with I. A solution of IX (2.0 g, 10 mmol) and I (2.4 g, 10 mmol) in benzene (150 ml) was stirred at room temperature for 10 hr. After the solvent had then been removed *in vacuo*, the residual solids were chromatographed on a silica gel column (benzene) to give the unchanged I and yellow crystals (X, 1.7 g, 46%): mp 166—167°C (EtOH); $\lambda_{\max}^{\text{EtOH}}$ 251 (4.56), 286 (sh, 4.25), 400 (4.17) nm; IR (KBr) 1595, 1572, 1385, 1210 cm^{-1}; NMR ($CDCl_3$) 6.8—7.8 (m) ppm; MS *m/e* 375 (5), 374 (32), 373 (100, P), 344 (7), 296 (20), 268 (13), 267 (32), 239 (4), 186 (5), 177 (9), 133 (4), 105 (11), 77 (14).

Found: C, 86.6; H, 5.5; N, 3.6%. Calcd for $C_{27}H_{19}NO$: C, 86.8; H, 5.1; N, 3.8%.

1,2-Diphenylindolizine. A solution of 2-benzylpyridine (5.0 g, 30 mmol) and phenacyl bromide (5.9 g, 30 mmol) in ether was stirred at room temperature for 10 days. The resulting precipitates were filtered and then washed with ether to afford 1-phenacyl-2-benzylpyridinium bromide (quantitatively); mp 174—176°C (decomp.). The pyridinium bromide (0.6 g, 1.7 mmol) was dissolved in water (6 ml), $NaHCO_3$ (0.5 g) was added, and the mixture was brought to a boil. The resulting thick magma was recrystallized from ethanol to afford 1,2-diphenylindolizine (0.40 g, 94%); mp 112—113°C (EtOH).

Found: C, 89.0; H, 5.5; N, 5.4%. Calcd for $C_{20}H_{15}N$: C, 89.2; H, 5.6; N, 5.2%.

3-Benzoyl-1,2-diphenylindolizine (X). A mixture of 1,2-diphenylindolizine (0.40 g, 1.6 mmol) and benzoyl chloride (1.2 ml) was heated at 40°C for 24 hr. The cooled reaction mixture was triturated with petroleum ether (bp 30—50°C), and the resulting green solid was filtered off. Recrystallization from ethanol gave X (0.24 g, 35%); mp 166—167°C. Both specimens showed no depression upon a mixed-mp determination, and the IR spectra were completely superimposable.

Found: C, 86.7; H, 4.9; N, 3.9%. Calcd for $C_{27}H_{19}NO$: C, 86.8; H, 5.1; N, 3.8%.

Reaction of Isoquinolinium Phenacylide (XI) with I. A solution of isoquinolinium phenacylide (XI, 1.86 g, 7.5 mmol) and I (1.80 g, 7.4 mmol) in acetonitrile (300 ml) was heated at reflux for 39 hr. Chromatography (silica gel, benzene) afforded yellow crystals of 3-benzoyl-1,2-diphenylpyrrolo-[2,1-*a*]isoquinoline (XII, 1.95 g, 61%); mp 196—199.5°C (PhH); $\lambda_{\max}^{\text{EtOH}}$ 270 (4.57), 296 (4.19), 336 (3.94), 398 (4.23)

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[5] E. T. Borrows, D. O. Holland, and J. Kenyon, *J. Chem. Soc.*, **1946**, 1069.

nm; IR (KBr) 1605, 1592, 1365, 1198 cm^{-1}; NMR ($CDCl_3$) 6.75—7.8 (m) ppm; MS *m/e* 425 (6), 424 (36), 423 (100, P), 394 (4), 346 (19), 318 (10), 317 (20), 211 (9), 105 (10), 77 (7).

Found: C, 88.1; H, 5.1; N, 3.0%. Calcd for $C_{31}H_{21}NO$: C, 87.9; H, 5.0; N, 3.3%.

Reaction of Quinolinium Phenacylide (XIII) with I. A solution of quinolinium phenacylide (XIII, 0.93 g, 3.7 mmol) and I (0.90 g, 3.7 mmol) in benzene (150 ml) was stirred at room temperature for 2 days. Subsequent chromatography (silica gel, benzene) afforded yellow crystals of 1-benzoyl-2,3-diphenylpyrrolo[1,2-a]quinoline (XIV, 0.12 g, 8%): mp 218—219°C (PhH); λ_{max}^{EtOH} 266 (4.59), 292 (sh, 4.15), 332 (3.92), 380 (4.11), 394 (4.18) nm; IR (KBr) 1600, 1350, 1198, 890 cm^{-1}; NMR (CCl_4) 6.6—7.7 (m) ppm; MS *m/e* 424 (35), 423 (100, P), 394 (4), 346 (18), 318 (8), 316 (10), 211 (9), 105 (8), 77 (8).

Found: C, 87.9; H, 5.2; N, 3.0%. Calcd for $C_{31}H_{21}NO$: C, 87.9; H, 5.0; N, 3.3%.