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Addition Reaction of Sulfonyl Isocyanates to Benzocyclopropene

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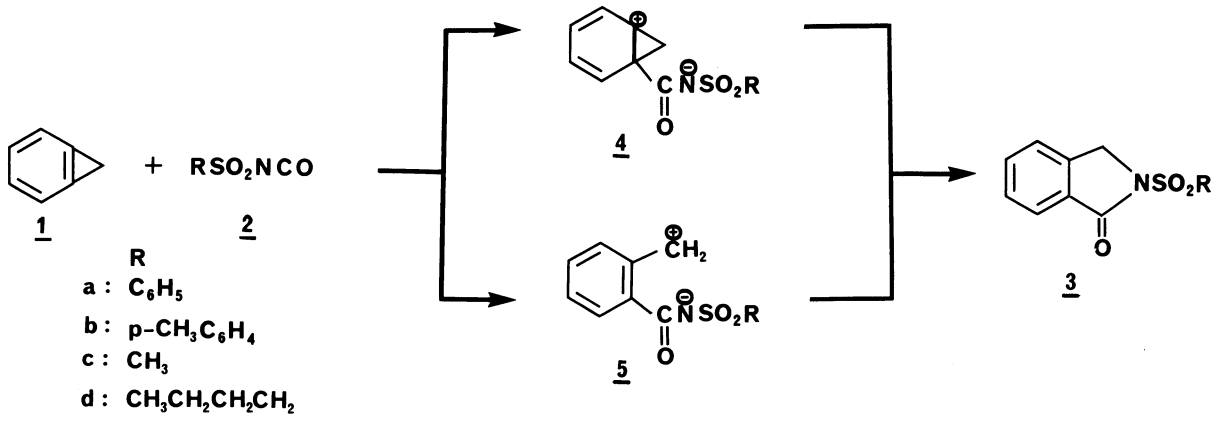
Benzocyclopropene reacted with methane- and n-butanesulfonyl isocyanates at room temperature, and arenesulfonyl isocyanates at 60 °C to afford the corresponding N-sulfonylphthalimidines.

Benzocyclopropene behaves as an electron-rich dienophile toward electron-demanding dienes in cycloadditions,[1] and recently was found to react with dihalocarbenes.[2] According to MO calculations, benzocyclopropene having a higher HOMO is expected to be more susceptible to electrophiles than benzene.[3] We have studied the title reaction to see if the highly strained hydrocarbon can be attacked by isocyanates, well-dokumented species to react with electron-rich alkenes,[4] in a manner of electrophilic aromatic substitution.[5]

The reaction of benzocyclopropene 1 with methyl- and phenyl isocyanates were sluggish, and we could not detect any cycloaddition product. However, 1 reacted with sulfonyl isocyanates to give N-sulfonylphthalimidines. The solution of 1 (1 mmol) and p-toluenesulfonyl isocyanate 2b (1 mmol) in 5 ml chloroform was warmed at 60 °C for 40 h. The subsequent TLC afforded N-toluenesulfonylphthalimidine 3b and phthalimidine in 39 and 4% yields, respectively.[6] With benzenesulfonyl isocyanate 2a in benzene at 60 °C for 30 h, 1 gave N-benzenesulfonyl derivative 3a and phthalimidine in 36 and 4% yields, respectively. Similarly, addition of methane- 2c and butanesulfonyl isocyanate 2d to 1 in chloroform at ambient temperature for 3 d produced 3c and 3d in 21 and 26% yields, respectively. The structures of 3a-d were determined by the elemental analyses and the spectral properties.[7] The higher shift of carbonyl absorptions of 3 around 1720 cm^{-1} from that of phthalimidine at 1680 cm^{-1} noted the presence of an electronegative substituent at the nitrogen. ^1H NMR showed the reasonable chemical shifts between 4.85 and 4.90 ppm for the methylene protons of the phthalimidine skeleton.[8]

The smooth reaction of 1 with strongly electrophilic sulfonyl isocyanates reflects well the electron-donating nature of 1. According to ab initio calculations, the HOMO is located at the bridge bond.[3] The title reaction can be rationalized by an electrophilic attack of the sulfonyl isocyanate on the π-system at C1 to give 4 followed by ring opening of the cyclopropyl cation and subsequent re-closing to 3. However, considering the fragile three-membered ring, it is also possible that first the electrophilic attack occurs at the σ-bond followed by ring cleavage to 5 with a relief of the strain energy of ca. 290 kJ/mol. The real operative mechanism, the FMO-controlled aromatic substitution at the fused ring or a process initiated by the energetically profitable ring rupture, is still open.



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2) S. Kagabu and K. Saito, Tetrahedron Lett., 29, 675 (1988).

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4) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," ed by G. A. Olah, Interscience Publishers, New York (1967).

5) Some examples of the reaction with electrophiles such as acids, halogens, or metal-ion mediated alcohols have been reported; See Ref. 1.

6) Phthalimidine is obviously arisen from the dissociation of 3b. 3b decomposed slowly in the open air and rapidly in alkaline solution.

7) The elemental analysis data are in accord with the proposed structures. 3a: mp 193.5 °C; IR (KBr, cm^{-1}) 1722, 1360, 1182, 1175, 1100; ^1H NMR ($CDCl_3$, δ) 4.92 (s, 2H), 7.4-7.7 (m, 6H), 7.82 (d, J=8.1 Hz, 1H), 8.16 (d, J=7.7 Hz, 2H); CIMS (isobutane, rel int) m/z 274 (M^++1, 76), 134 (79), 57 ($C_4H_9^+$, 100); 3b: mp 218 °C; IR (KBr, cm^{-1}) 1718, 1358, 1166, 1090; ^1H NMR ($CDCl_3$, δ) 2.41 (s, 3H), 4.91 (s, 2H), 7.33 (d, J=8.4 Hz, 2H), 7.4-7.5 (m, 2H), 7.63 (t, J=7.0 Hz, 1H), 7.86 (d, J=8.1 Hz, 1H), 8.03 (d, J=8.4 Hz, 2H); CIMS (isobutane, rel int) m/z 288 (M^++1, 81), 134 (67), 57 ($C_4H_9^+$, 100); 3c: mp 162 °C; IR (KBr, cm^{-1}) 1720, 1340, 1142, 1130, 1092; ^1H NMR ($CDCl_3$, δ) 3.42 (s, 3H), 4.89 (s, 2H), 7.2-7.6 (m, 2H), 7.71 (t, J=7.3 Hz, 1H), 7.92 (d, J=7.7 Hz, 1H); CIMS (isobutane, rel int) m/z 212 (M^++1, 78), 134 (79), 57 ($C_4H_9^+$+1, 100); 3d: mp 102.5 °C; IR (KBr, cm^{-1}) 1720, 1340, 1320, 1155, 1105; ^1H NMR ($CDCl_3$, δ) 0.94 (t, J=7.3 Hz, 3H), 1.48 (m, 2H), 1.83 (m, 2H), 3.61 (t, J=8.1 Hz, 2H), 4.88 (s, 2H), 7.5-7.6 (m, 2H), 7.70 (t, J=7.3 Hz, 1H), 7.92 (d, J=7.3 Hz, 1H); CIMS (isobutane, rel int) m/z 254 (M^++1, 49), 134 (79), 57 ($C_4H_9^+$+1, 100).

8) The structure of 2-oxindole, a possible alternative regioisomer, is unlikely, judging from the chemical shift of 3.50 in $CDCl_3$ for the methylene protons.

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