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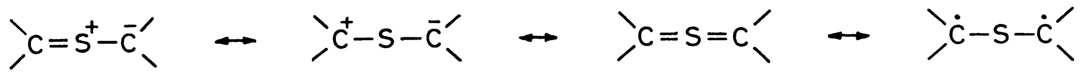
MESOIONIC THIOCARBONYL YLIDES

Shuki ARAKI and Yasuo BUTSUGAN*
Department of Applied Chemistry, Nagoya Institute of
Technology, Gokiso-cho, Showa-ku, Nagoya 466

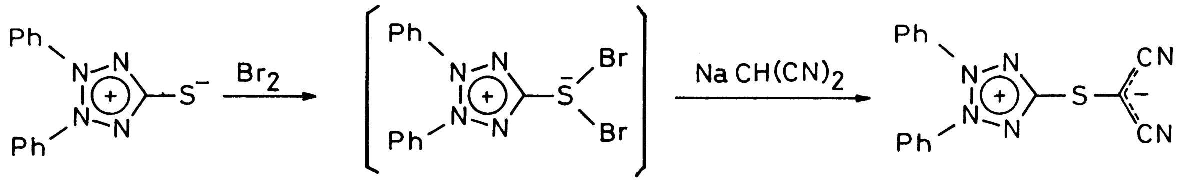
Four kinds of mesoionic thiocarbonyl ylides were synthesized by the treatment of mesoionic thiolate with bromine followed by the reaction with conjugate base of active methylene compounds. The structures were discussed based on the spectroscopic properties.

Thiocarbonyl ylide (1) is an interesting family of compounds which can be represented by a series of resonance forms (1a - d). A number of examples have been synthesized so far and the structures and the reactions have been extensively studied.$^{1)}$ However, mesoionic thiocarbonyl ylides, in which a mesoionic ring system is incorporated, have received little attention. In 1976, Russian chemists synthesized the first example of mesoionic thiocarbonyl ylide by the reaction of 1,3,4-thiadiazolium-3-thiolate with tetracyanoethylene oxide.$^{2)}$ They also achieved the preparation of 1,2,4-triazolium derivatives by another method.$^{3)}$ Here, we describe the general method for the synthesis of mesoionic thiocarbonyl ylides, which involves the treatment of mesoionic thiolates with bromine followed by the reaction with the conjugate base of active methylene compounds. The electronic structures of the synthesized ylides are also discussed.



1a 1b 1c 1d

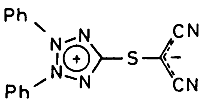
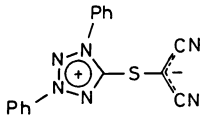
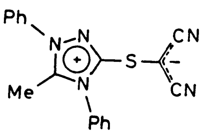
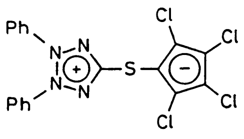
To a solution of 2,3-diphenyltetrazolium-5-thiolate (2)$^{4)}$ in dichloromethane was added an equimolar amount of bromine. Pale yellow crystals precipitated within a few minutes. Although the instability of the compound prevented full characterization, it is considered to be the bromine adduct (3) by analogy with the cases of some activated thiones.5) Further reaction of 3 with sodiomalononitrile gave the desired sulfur ylide (4) in high yield.6) 1,3-Diphenyltetrazolium-5-thiolate (5)7) and 5-methyl-1,4-diphenyl-1,2,4-triazolium-3-thiolate (6)8) also gave the respective dicyanomethylides (7 and 8) by this method in 36 and 90% yields.6) The reaction of 3 with sodium tetrachlorocyclopentadienide gave the dark purple powder of dicyclic ylide (9) in 76% yield.6) The compound (9) represents the first mesoionic thiocarbonyl ylide bearing a cyclopentadienide ring as a counterpart.



2 3 4

The dicyanomethylides (4, 7, and 8) are colorless to pale yellow crystals, stable to air at room temperature, whereas the cyclopentadienylide (9) is an extremely unstable compound and forms an intractable blue substance on contact with atomospheric oxygen. The melting points and the spectral data of 4, 7, 8, and 9 are summarized in Table 1. The 1,3-diphenyltetrazolium derivative (7) decomposes above 120°C to give quantitatively 1,3-diphenyltetrazolium-5-thiolate (5) and tetracyanoethylene. The mass spectra of 4, 8, and 9 reveal the intense molecular ion peak, while the thermally labile 7 does not show the molecular ion but a strong fragment peak of the thiolate (5) [M$^+$ - C(CN)$_2$]. In the IR spectra, the dicyanomethylides (4, 7, and 8) show the intense absorptions of asymmetric and symmetric C≡N stretching vibrations at 2190 - 2180 and 2150 - 2140 cm^{-1}, respectively. The ^{13}C NMR chemical shifts of the sulfur ylides (4, 7, 8, and 9) are listed in Table 2. The dicyanomethylide carbon [$\underline{C}^-$(CN)$_2$] of 4, 7, and 8 resonates at very high field (4.0 - 5.3 ppm) indicating the high electron density on this carbon. These values are shifted to higher field compared with that (9.9 ppm) of the dicyanomethylide of 1,3-dimethylimidazolethione,1c) a non-mesoionic thiocarbonyl ylide. Although the signal of the C-1 carbon in the tetrachlorocyclopentadienide ring of 9 was not observed owing to the rapid decomposition, the C-2(5) and C-3(4) carbons appeared at 105.3 and 100.2 ppm, more than 20 ppm upfield than the corresponding sp^2 carbons of tetrachlorocyclopentadiene (128.0, 125.4 ppm), thus indicating the large contribution of the cyclopentadienide ion character to the resonance hybrid.

Table 1. Melting points and spectral data of the ylides (4, 7, 8, and 9)

Ylide	Mp θ_m/°C	MS (20 eV) m/z	IR (KBr) $\tilde{\nu}$/cm^{-1}	UV (MeCN) λ/nm(log ε)	^{1}H NMR(DMSO-d_6) δ/ppm
 4	170(dec)	318(M^+)	2180,2140, 1486,1356, 1222,1148, 994,774, 766,686	257(4.00), 320(s,3.64)	7.71(m,10H,Ph)
 7	120(dec)	254(M^+-C(CN)$_2$)	2290,2150, 1492,1434, 1278,1234, 766,680	226(4.15), 260(4.10), 294(s,4.07)	8.22(m,2H,Ph), 7.85(m,8H,Ph)
 8	223(dec)	331(M^+)	2190,2150, 1534,1496, 1264,1226, 772,696	——a)	7.70(m,10H,Ph), 2.45(s,3H,Me)
 9	170(dec)	454(M^+, ^{35}Cl)	1484,1360, 1346,1296, 1142,996, 768,758, 684	261(4.11), 508(2.49)	7.68(m,10H,Ph)

a) End absorption only.

The chemical shifts (171.1 and 169.4 ppm) of the tetrazolium ring carbon of 4 and 9 are shielded by more than 10 ppm compared with that for the corresponding carbon of the thiolate (2) (181.6 ppm) and are almost coincident with the value (168.7 ppm) of 2,3-diphenyl-5-methylthiotetrazolium iodide. Similar tendency was also observed for 7 and 8. Thus, the tetrazolium ring carbon of the thiolate (5) resonates at 171.4 ppm, whereas the corresponding carbon of its S-methylated tetrazolium iodide resonates at 164.1 ppm. The triazolium ring carbon of 6 adjacent to the sulfur atom appears at 169.0 ppm and that of its methiodide at 155.8 ppm.

The spectroscopic properties described above clearly indicate that the mesoionic thiocarbonyl ylides (4, 7, 8, and 9) are highly polarized compounds and can be best expressed by the dipolar canonical structure (1b).

Table 2. ^{13}C NMR spectral data of the ylides (4, 7, 8, and 9)[a]

Ylide	Phenyl				C^+-S	C^--S	Others
	ipso	ortho	meta	para			
4	133.2	126.5	130.4	134.0	171.1	4.5	125.2 (CN)
7	134.8 131.3	125.1 121.4	130.9 130.6	133.5 132.9	165.7	5.3	124.0 (CN)
8	135.0 130.6	127.1 125.4	130.6 130.2	131.9 131.3	157.1	4.0	153.9 (Me-C) 125.0 (CN) 11.7 (Me)
9	133.0	126.4	130.1	133.8	169.4	—[b]	105.3 100.2 (C-2 - C-4)

a) In DMSO-d_6.
b) Not observed.

References

1) For reviews: a) R. Huisgen, Angew. Chem., 75, 604 (1963); b) R. M. Kellog, Tetrahedron, 32, 2165 (1976); for stable thiocarbonyl ylides: c) A. J. Arduengo and E. M. Burgess, J. Am. Chem. Soc., 98, 5020, 5021 (1976); d) K. Nakasuji, K. Nishino, I. Murata, H. Ogoshi, and Z. Yoshida, Angew. Chem., 89, 904 (1977) and references cited therein.
2) A. Y. Lazaris and A. N. Egorochkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1191.
3) A. Y. Lazaris, A. I. Kalinin, and A. N. Egorochkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 2717; A. Y. Lazaris and A. N. Egorochkin, Khim. Geterotsikl. Soedin., 1981, 117.
4) R. N. Hanley, W. D. Ollis, C. A. Ramsden, and I. S. Smith, J. Chem. Soc., Perkin Trans. 1, 1979, 744.
5) A. J. Arduengo and E. M. Burgess, J. Am. Chem. Soc., 99, 2376 (1977); U. Chiacchio, A. Corsaro, and F. A. Bottino, Org. Magn. Reson., 22, 724 (1984).
6) Satisfactory elemental analyses (C, H, and N) were obtained for this compound.
7) R. N. Hanley, W. D. Ollis, and C. A. Ramsden, J. Chem. Soc., Perkin Trans. 1, 1979, 741.
8) K. T. Potts, S. K. Roy, and D. P. Jones, J. Org. Chem., 32, 2245 (1967); see also R. Grashey and M. Baumann, Tetrahedron Lett., 1972, 2947.

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