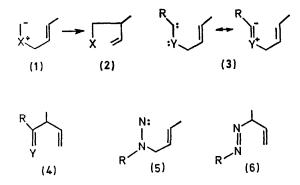
2,3-Sigmatropic Rearrangement of Nucleophilic Carbenes. A New Approach to Stereospecific Synthesis of Carbon–Carbon Bonds

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Summary S-Methyl-S-(3,3-dimethylallyl)carbene, generated by Bamford-Stevens reaction of the corresponding toluene-*p*-sulphonylhydrazone, undergoes a 2,3-sigmatropic rearrangement to a dithiocarboxylic acid ester, thereby providing a new carbon-carbon bond synthesis.

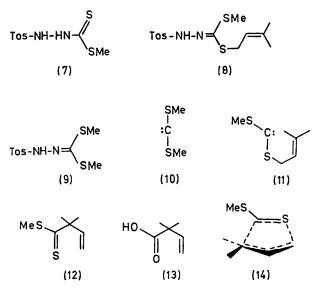
THE 2,3-sigmatropic rearrangement of ylides and related species, e.g. (1) to (2) is now a well established reaction type¹ which is being applied in synthetic work.² This reaction has been demonstrated to proceed with high stereospecifity.³ It appeared to us that a nucleophilic carbene of type (3) would be ideally suited to rearrange to (4) and in doing so would provide a new and stereospecifically defined carboncarbon bond. Added support for this hypothesis came from the observation that allylic diazenes (5) rearranged smoothly to the azo-compounds (6).⁴



We now report the first case of such a transformation where Y = S. Thus the toluene-*p*-sulphonyl-S-methylcarbazate (7), prepared according to the literature⁵ was alkylated with 3,3-dimethylallyl bromide in the presence of potassium hydroxide to the toluene-*p*-sulphonylhydrazone derivative (8), m.p. 73.5-75°.† Schöllkopf and his collaborators have shown⁵ that bis-alkylmercapto-derivatives,

† All new compounds gave satisfactory analytical data.

e.g. (9), undergo a base-induced decomposition to carbenes (10), with loss of nitrogen and the toluene-*p*-sulphinic acid salt.



In our case, the sodium salt of (8) (sodium hydride), was stable at room temperature in THF but on heating under reflux (65°) for 4 h under nitrogen was converted essentially quantitatively into the dithioester (12), presumably by way of the carbene (11). This liquid ester (12) was identified by spectral properties, n.m.r. (CDCl₃) δ 1.55 (s, 6H), 2.58 (s, 3H), 5.3—6.2 (ABC multiplet, 3H), and hydrolysis (methanolic NaOH) to the known acid (13), identical in all respects with an authentic specimen.⁶

This mild procedure then allows the conversion of allylic halides into the corresponding rearranged carboxylic acids, involving a stereochemically suprafacial relationship between the original carbon-sulphur bond and the newly created carbon-carbon bond, as in (14).³ The recently described stereospecific procedure for conversion of allylic alcohols into allylic halides adds further generality to this method.7

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- ¹ J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, Chem. Comm., 1970, 576.
- ² J. E. Baldwin, J. De Bernardis, and J. E. Patrick, *Tetrahedron Letters*, 1970, 570; V. Rautenstrauch, *Chem. Comm.*, 1970, 4; C. W. Ashbrook, J. E. Baldwin, and G. V. Kaiser, J. Amer. Chem. Soc., 1971, 93, 2342; D. A. Evans, G. C. Andrews, and C. L. Sims, ibid., p. 4956.

³ J. E. Baldwin and J. E. Patrick, J. Amer. Chem. Soc., 1971, 93, 3556. These workers demonstrated that the 2,3-sigmatropic process is clearly suprafacial with respect to the allylic unit.

⁴ J. E. Baldwin, J. E. Brown, and G. Höfle, J. Amer. Chem. Soc., 1971, 93, 788.
⁵ U. Schöllkopf and E. Wiskott, Annalen, 1966, 694, 44.
⁶ W. E. Parham and S. H. Groen, J. Org. Chem., 1966, 31, 1694. We thank Dr. J. E. Brown for this sample.

⁷ G. Stork, P. R. Grieco, and M. Gregson, Tetrahedron Letters, 1969, 1393.