

BIS-(ALKYLTHIO)-CARBENES

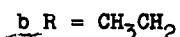
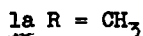
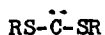
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A RECENT<sup>1</sup> brief report by Schöllkopf and Wiskott describes the synthesis, and for the first time the trapping of a bis-(alkylthio)-carbene (1a). We wish to record results of our experiments with a series of dithiocarbenes (1a, 1b, and 2). Like the German workers, we had chosen thermal decomposition of



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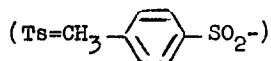
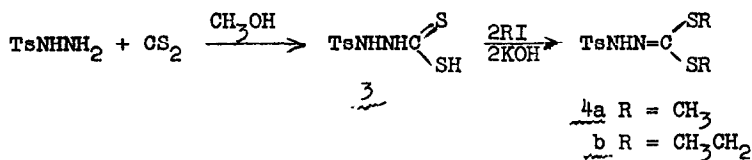
p-toluenesulfonylhydrazone salts as the source of the divalent species, and had prepared the hydrazones 4a and b by twofold alkylation of the carbazinic acid (3) formed from tosylhydrazine and carbon disulfide.<sup>2,3</sup> The cyclic hydrazone 6 was synthesized both by this route (using ethylene bromide as the alkylating

<sup>1</sup> U. Schöllkopf and E. Wiskott, Angew. Chem., 75, 725 (1963).

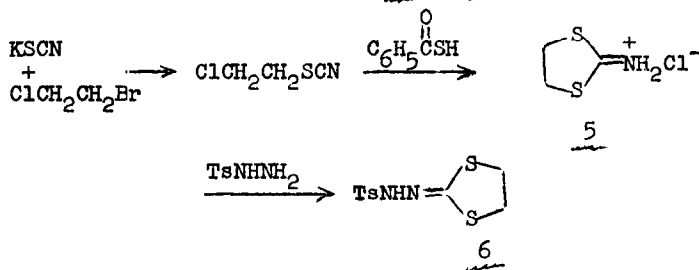
<sup>2</sup> For related reactions, see M. Busch and G. Lingenbrink, Ber. 32, 2620 (1899); J. prakt. Chem. [2] 61, 336 (1900).

<sup>3</sup> Satisfactory microanalyses were obtained on all new compounds.

agent<sup>4</sup> and by transamination with tosylhydrazine of the iminium salt 5 derived from thiolbenzoic acid and  $\beta$ -chloroethyl thiocyanate.

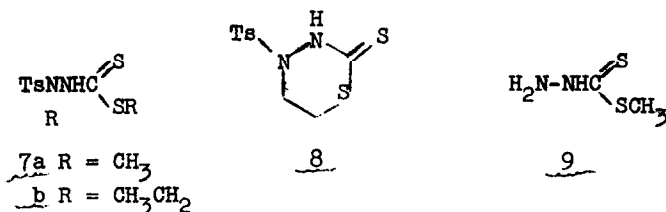


Spectral measurements afforded proof that the dialkylated products were correctly represented by 4 and 6, not their respective isomers 7 and 8. In particular, the



ultraviolet spectra of all three compounds were very similar to one another and markedly different from that of methyl carbazinate (9). Moreover, conversion of 4b

<sup>4</sup> H. L. Wheeler and H. F. Merriam, J. Am. Chem. Soc., 24, 439 (1902).



to its sodium salt in dimethyl sulfoxide resulted in an nmr <sup>(60 Mc.)</sup> shift of  $\sim 13$  cps. upfield for the AB quartet attributable to the aryl protons. A shift of this magnitude, typical for a *p*-toluenesulfonamide salt, <sup>5</sup> would not be expected for the anion of 7 in which the negative charge and the ring protons are well separated. <sup>6</sup>

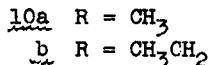
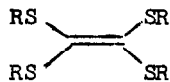
Tetrahydrofuran solutions of the sodium salts of 4a and b (prepared *in situ* with sodium hydride) decomposed smoothly at the reflux temperature giving nitrogen, sodium *p*-toluenesulfinate, and the tetrakis-(alkylthio)-ethylenes 10a (49%) <sup>1</sup> and b (55%) <sup>7</sup>, respectively. Ethylene formation constitutes good evidence for the carbene intermediates 1a and b, whether the mechanism involve simple dimerization or attack of the carbene on starting material (or inter-

<sup>5</sup> D. M. Lemal, G. D. Underbrink and T. W. Rave, unpublished results.

<sup>6</sup> Treatment of 4b with ethyl iodide in basic solution introduced an ethyl group on the sulfonamide nitrogen. The methyl, but not the methylene protons, of this ethyl group were shifted substantially ( $\sim 17$  cps.) upfield relative to those of the S-ethyls. Models showed that these three protons were oriented properly to be shielded by the aromatic ring.

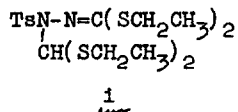
<sup>7</sup> Triethyl orthothioformate invariably accompanied the 10b in low yield. The German workers also found the trimethyl counterpart in their study of 4a decomposition, but the pathway for orthothioester formation is not yet known.

mediate diazo compound).<sup>8</sup>

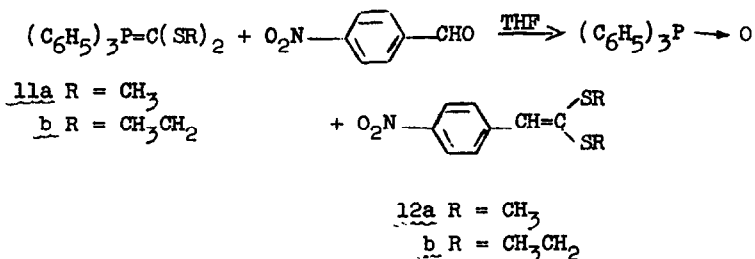


Decomposition of 4b sodium salt in tetrahydrofuran containing a severalfold excess of triphenylphosphine resulted in a brilliant yellow suspension. Excess *p*-nitrobenzaldehyde was added to the cooled mixture, which was stirred a few hours at room temperature, then under reflux. Workup entailed stripping the solvent, separating most of the remaining phosphine by crystallization from methanol, evaporating the mother liquor and chromatographing the residue on alumina. In this fashion 12b was obtained in 71% yield as a viscous yellow-orange oil which was vapor chromatographed for analysis. UV:  $\lambda_{\text{max}}^{\text{EtOH}}$  371 (16,100), 254 (11,500). Nmr (proper relative areas): 1.88 and 2.30 $\tau$  (doublets of AB quartet for aryl protons,  $J = 8.5$  cps.),

<sup>8</sup> Isolation of 1 when 4b sodium salt was pyrolyzed in the presence of excess 4b constituted evidence that the diazo compound was a discrete intermediate in the decomposition (cf. D. M. Lemal and A. J. Fry, *J. Org. Chem.*, in press).



3.12  $\tau$  (vinyl proton), 7.12  $\tau$  (quartet corresponding to methylenes,  $J = 7.5$  cps.), 8.67 and 8.74  $\tau$  (methyl triplets,  $J = 7.5$  cps.). Since no 10b was detected in the reaction mixture, triphenylphosphine is apparently an efficient interceptor of the divalent intermediate 9 1b. Analogous results were obtained with 4a sodium salt; the yield of intensely orange 12a was 64% (m.p. of analytical sample, 40-41°). The good overall yields of ketene thioacetals 12 indicate that ylides of the type 11 10,11 may find considerable synthetic use as Wittig reagents.



<sup>9</sup> It is conceivable, but not likely that the diazo compound instead of the carbene is trapped by triphenylphosphine, giving a phosphazine. In general, phosphazines neither decompose to Wittig reagents (particularly at 65°) nor do they yield Wittig reaction products with carbonyl compounds (cf. H. J. Bestmann and L. Göthlich, Ann., 655, 1 (1962) and earlier papers).

<sup>10</sup> Other carbenes have been trapped by triphenylphosphine (V. Franzen and G. Wittig, Angew. Chem., 72, 417 (1960); G. Wittig and M. Schlosser, Ber., 94, 1376 (1961); A. J. Speziale, G. J. Marco and R. W. Ratts, J. Am. Chem. Soc., 82, 1260 (1960); D. Seyferth, S. O. Grim, T. O. Read ibid., 82, 1510 (1960)).

When 4b sodium salt was decomposed in tetrahydrofuran containing massive amounts of cyclohexene the yield of 10b was nearly as high as in the absence of olefin and no norcaranone thioketal was isolated. Schöllkopf reported a similar observation with 4a but noted that the electron-rich olefins ketene diethylacetal and 1-morpholino-1-phenylethylene were capable of trapping 1a in low yield. Hence the experience of both research groups indicates that a high degree of nucleophilicity is required of a trapping agent for bis-(alkylthio)-carbenes, a fact which implies relatively great internal stabilization in the divalent species.<sup>1</sup>

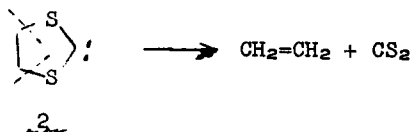
Surprisingly, the sodium salt of the cyclic tosylhydrazone 6 was rather stable. In order to complete its

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<sup>11</sup> Tetrakis-(alkylthio)-ethylenes were first prepared by Hine (ref. 12) from trialkyl orthothioformates and a powerful base. Although carbene intermediates were proposed, we have been unable to intercept them working with lithium diethylamide in diethylamine containing a large excess of triphenylphosphine. Since other work from our Laboratory supports a carbenoid mechanism for this reaction, it appears that orthothioformate anion competes very effectively with triphenylphosphine for the divalent species. The carbenoid intermediate in these experiments may actually be a complex of lithium mercaptide with the bis-(alkylthio)-carbene.

<sup>12</sup> J. Hine, R. Bayer and G. Hammer, J. Am. Chem. Soc., 84, 1751 (1962).

pyrolysis in several hours temperatures of 140-150° were required. With sulfolane the solvent, the major products were carbon disulfide and ethylene, the latter in excellent yield. No tetrathioethylene was detected. Fragmentation of the carbene 2 (free or incipient) would produce the observed result.<sup>13</sup>



Other aspects of the chemistry of sulfur-substituted carbenes are under investigation.

Acknowledgments - The authors wish to thank Mr. Stephen Tobey for helpful discussion and the National Science Foundation, the National Institutes of Health, and the Research Committee of the University of Wisconsin for generous financial support.

<sup>13</sup> For analogous fragmentation reactions in which dialkoxycarbenes are likely intermediates, see E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963); D. M. Lemal, E.P. Gosselink and A. Ault, ibid., in press.