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A NOVEL REARRANGEMENT OF TRANSIENT 1,3-DIPOLES CONTAINING SULPHUR

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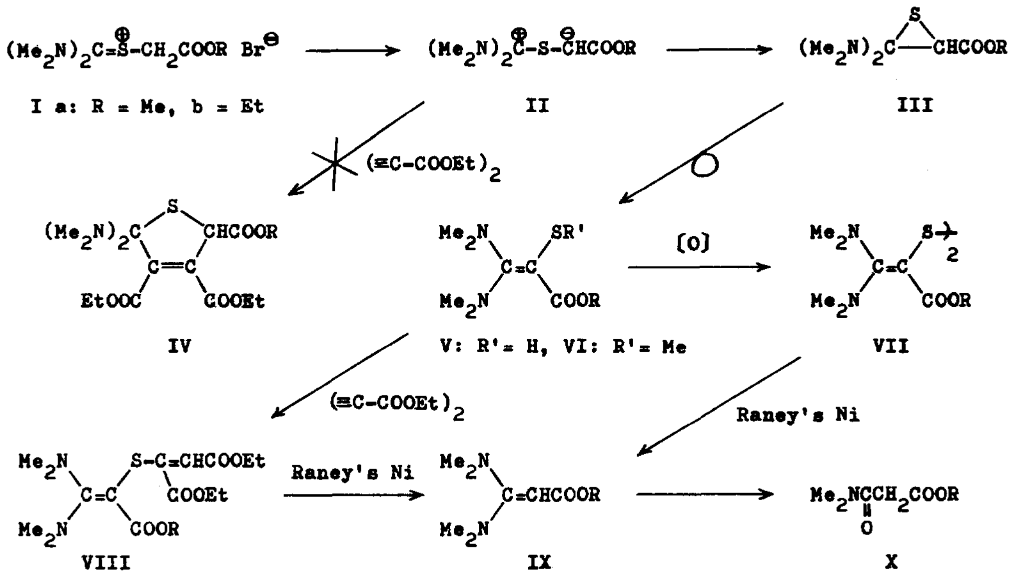
Huisgen's work (1) on 1,3-dipolar cycloaddition has recently been extended to 1,3-dipoles containing central sulphur atom (2). As summarized below, attempts of obtaining novel 1,3-dipoles II by proton abstraction of salts I has resulted in an unexpected rearrangement, which proceeds through II and III to afford products arising from reactive vinylic thiols V.



Salt Ia, m. 116-117°, and Ib, m. 130-131°, were readily prepared from $(Me_2N)_2C=S$ and Me- or Et-OCOCH$_2$Br in 94 and 92% yields, respectively. A mixture of Ia and excess $(\equiv C\text{-}COOEt)_2$ in THF was treated with Et$_3$N at room temp under N$_2$ for 12 hr to afford VIIIa (70%), m. 79-80°. Similarly Ib gave VIIIb (73%), m. 91-92°. Isomeric structure IVa and IVb were excluded as follows. The mass spectrum of VIIIa consisted of peaks at m/e 374

(M), 203 ($(Me_2N)_2C{=}C(COOMe)S^+$ and $EtOOCCH{=}C(COOEt)S^+$) and 171 ($(Me_2N)_2C{=}\overset{+}{C}{-}COOMe$ and $EtOOCCH{=}\overset{+}{C}{-}COOEt$), whereas that of VIIIb at 388 (M), 217 ($(Me_2N)_2C{=}C(COOEt)S^+$), 203 ($EtOOCCH{=}C(COOEt)S^+$), 185 ($(Me_2N)_2C{=}\overset{+}{C}{-}COOEt$) and 171 ($EtOOCCH{=}\overset{+}{C}{-}COOEt$). Desulphurization of VIIIa with Raney's Ni afforded IXa (40%), b. 87-88°/4, and diethyl succinate (68%), whereas that of VIIIb gave IXb (56%), b. 76.5-77°/1, and diethyl succinate (82%). Hydrolysis of IXb gave Xb, which was alternatively prepared from $ClCOCH_2COOEt$.

In the absence of $(\equiv C{-}COOEt)_2$, Ia yielded VIIa (41%), m. 163-164°, upon treatment with equimolar NaH. The mass spectrum of VIIa consisted of peaks: m/e 406 (M, exact mass 406.171, calc. 406.171), 235 ($(Me_2N)_2C{=}C(COOMe)S{-}S^+$) and 203 ($(Me_2N)_2C{=}C(COOMe)S^+$, exact mass 203.086, calc. 203.085). Other spectral data were consistent with the structure and desulphurization gave IXa (68%). Treatment of Ib afforded VIIb (83%), m. 142-143°, whose spectral data had a closed resemblance to VIIa. Desulphurization of VIIb gave IXb (76%). When a solution of Ib in carefully degassed THF was treated with 2 mol. of NaH and then with MeI, there was obtained VIb (17%), m. 31-32°, along with VIIb (12%). The source of oxidant in the formation of VII has not been established yet.

The spectral data of ß,ß-diaminoacrylates merit some discussions. Carbonyl wave numbers were observed for VIb at 1645, VIIa at 1640, VIIb at 1633, VIIIa at 1661, VIIIb at 1660 (KBr), IXa at 1675 and IXb at 1675 cm^{-1} (neat). NMR spectra ($CDCl_3$) of VIIa, VIIb, VIIIa and VIIIb exhibited N-methyl signals as singlets at δ 2.95, 2.96, 2.88 and 2.86, whereas those of others showed splitting of N-methyl signals: VIb at 2.78, 2.88, IXa at 2.81, 2.88, IXb at 2.79, 2.87. These data are explained on the basis of extensive delocalization of olefinic π electrons and low energy barrier for rotation around the bond. This problem will be the subject of the full paper, where reactions of this novel class of enediamines will also be discussed.

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