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REACTION OF DITHIOACETATE WITH TRIALKYL PHOSPHITE

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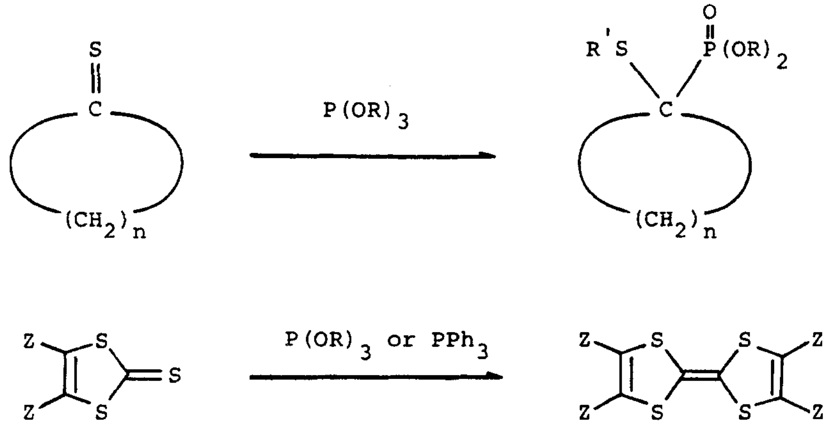
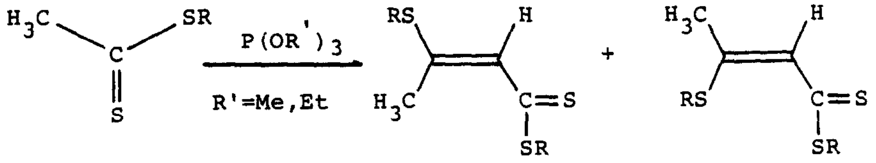
Remarkable developments of the chemistry of thiocarbonyl compounds have brought exciting results (e.g. the successful synthesis of Chlorophyll,[1] the stereospecific syntheses of olefins[2] and the preparation of tetrathiafulvalenes[3-9]) in synthetic field. Especially, the reactions of thiocarbonyl compounds with trivalent phosphorus compounds have been the focus of interest in the past several years. In our previous publications[3,4,10,11] we reported the regiospecific reactions of cycloalkanethiones with trialkyl phosphites leading to sulfur-containing cycloalkane phosphonic acid esters[10,11] and the syntheses of substituted tetrathiafulvalenes by the reactions of 1,3-dithiole-2-thiones with trivalent phosphorus compounds.[3,4]



In this paper, we wish to report the reaction of dithioacetate (I) with trialkyl phosphites, in which the nucleophilicity of phosphites (carbophilicity and/or thiophilicity) was not significant, but the function as base was important.

A mixture of methyl dithioacetate (Ia) and excess trimethyl phosphite was heated to reflux temperature with stirring under argon atmosphere. The reaction was monitored by thin layer chromatograph technique, and heating was continued for 8 hr. During this period, the color of the reaction mixture turned to dark red from light yellow. The reaction mixture was diluted with petroleum ether and was directly subjected to chromatograph on silica eluting with petroleum ether. The first red purple fraction and the second pink fraction upon evaporation gave red liquid (IIa) and red crystal (IIIa), respectively.



I a: R=Me
b: R=Et
II
III

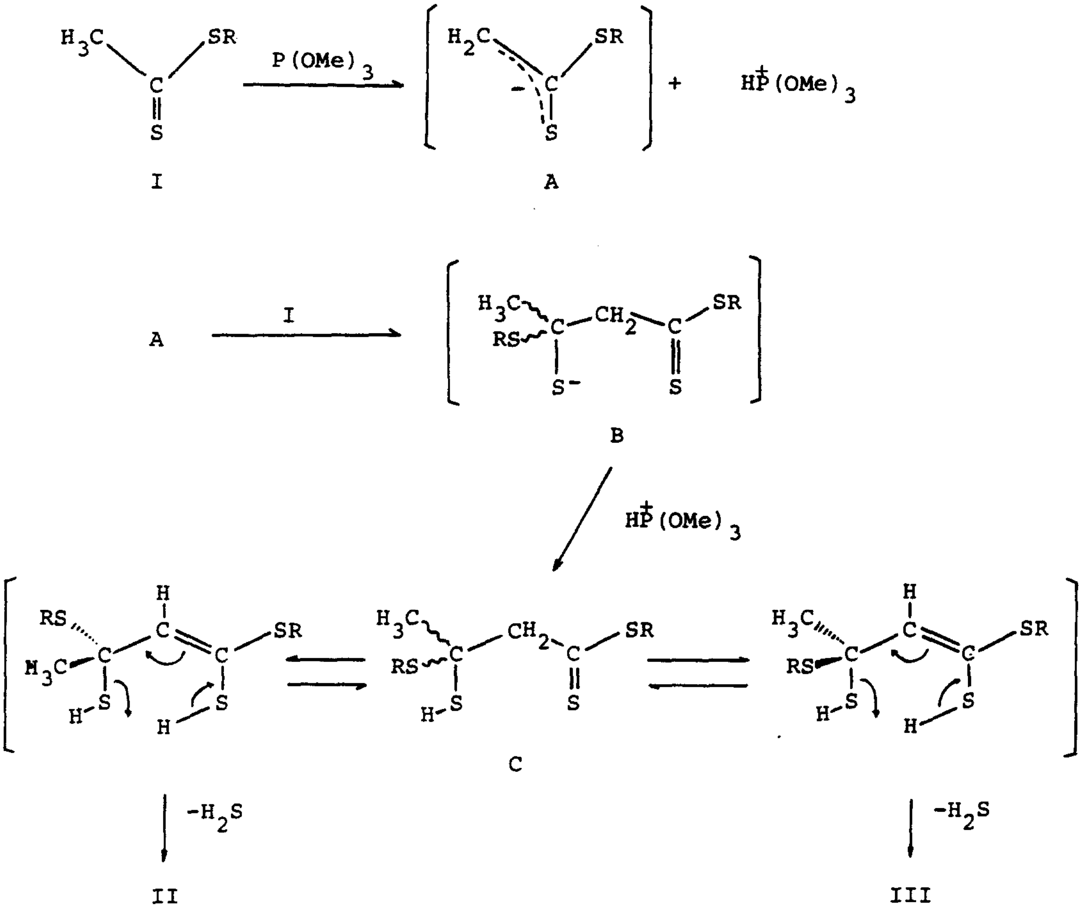
The structures of IIa and IIIa were determined by their analytical and spectral data: IIa; yield 15.0 %; ir (neat) 1555, 1228 cm^{-1}; pmr (CCl_4) δ 2.40 (s, 3H, SCH_3), 2.55 (s, 3H, CH_3), 2.61 (s, 3H, CS_2CH_3), 6.52 (s, 1H, C=C-H); mass m/e 178(M^+), 163, 131: IIIa; mp 56-57°C; yield 13.9 %; ir (KBr) 1515, 1239, 1120 cm^{-1}; pmr (CCl_4) δ 2.28 (s, 3H, CH_3), 2.39 (s, 3H, SCH_3), 2.60 (s, 3H, CS_2CH_3), 7.00 (s, 1H, C=C-H); mass m/e 178(M^+), 163, 131. The analytical data and mass spectra showed that both IIa and IIIa have the same formula $C_6H_{10}S_3$, indicating that IIa and IIIa are isomers to each other. In the cmr spectrum of IIa, the carbon of the thiocarbonyl group ($\underline{C}$=S) resonated at δ 214.0 ppm and those of the carbon-carbon double bond at 157.0 ($\underline{C}$=C-H) and 129.0 (C=$\underline{C}$-H) ppm, which clearly demonstrate the presence of the enethione moiety (C=C-C=S). Comparing the chemical shifts of the methyl protons attached to the carbon-carbon double bond, that of IIa appeared at lower field (δ 2.40) than that of IIIa (δ 2.28). Taking the magnetic anisotropy of thiocarbonyl group into accounts, the lower chemical shift of methyl protons of IIa indicates that the methyl and the thiocarbonyl groups are situated in the same side of the carbon-carbon double bond. That is to say, the stereochemistry of IIa and IIIa is assigned to (E)-form and (Z)-form, respectively.

The reaction of ethyldithioacetate (Ib) with trimethyl phosphite similarly afforded two red liquids, IIb and IIIb, whose structures were determined in a similar manner as above: IIb; yield 12.3 %; ir (neat) 1550, 1220 cm^{-1}; pmr (CCl_4) δ 1.32 (t, 3H, J=7.5Hz, $SCH_2C\underline{H}_3$), 1.38 (t, 3H, J=7.1Hz, $CS_2CH_2C\underline{H}_3$), 2.48 (s, 3H, CH_3), 2.87 (q, 2H, J=7.5Hz, $SC\underline{H}_2CH_3$), 3.19 (q, 2H, J=7.1Hz, $CS_2C\underline{H}_2CH_3$), 6.51 (s, 1H, C=C-H); mass m/e 206(M^+), 177: IIIb; yield 13.9 %; ir (neat) 1520, 1235, 1109 cm^{-1}; pmr (CCl_4) δ 1.31 (t, 3H, J=7.3 Hz, $SCH_2C\underline{H}_3$), 1.35 (t, 3H, J=7.1 Hz, $CS_2CH_2C\underline{H}_3$), 2.28 (s, 3H, CH_3), 2.89 (q, 2H, J=7.3 Hz,

$SC\underline{H}_2CH_3$), 3.22 (q, 2H, J=7.1Hz, $CS_2C\underline{H}_2CH_3$), 6.93 (s, 1H, C=C-H); mass m/e 206(M^+), 177.

These products, II and III, can be considered as thio-Claisen type condensation products of dithioacetate by elimination of hydrogen sulfide. Generally, in the reactions of thiocarbonyl compounds with trialkyl phosphites, phosphites are known to behave as nucleophilic reagents (carbophile and/or thiophile). However, in the reaction of dithioacetate with phosphite, phosphite does not behave as nucleophile, but as base.[12] That is to say, as seen in the following reaction scheme, phosphite should abstract the α-proton of dithioacetate and the resulting anion (A) would react with another dithioacetate to form anion (B). The anion B and $H\overset{+}{P}(OMe)_3$ would afford the dimer (C), followed by dehydrogen sulfide[14] via cyclic concerted mechanism to result in the formation of II and III.[15]

Scheme



The use of trialkyl phosphites other than trimethyl phosphite also yielded the same products, II and III, but did not enhance the yields.

We are continuing to investigate versatile aspects of the reactions of thiocarbonyl compounds with trialkyl phosphites.

References and Footnotes

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11) S. Yoneda, T. Kawase and Z. Yoshida, J. Org. Chem., 43, in press (1978).
12) It is reported that Ia gave a mixture of IIa and IIIa in 18% yield in the presence of sodium methoxide as base,[13] but the yield is better when trimethyl phosphite was used as mild base.
13) S. Scheithauer and R. Mayer, Chem. Ber., 100, 1413 (1967).
14) The phosphites may participate in this dehydrogen sulfide reaction as catalyst, but details are now under investigation.
15) In the reaction scheme, the formation of II and III is interpreted in the terms of dehydrogen sulfide from R- and S- dimers. However, the pmr spectrum of II (or III) changed to that of a mixture of II and III (1:1) at room temperature after 1 day. Therefore, the mechanism, in which only one product would be formed and converted to the mixture of II and III, could not be excluded.