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REACTION OF METHYL 2,3-DIHYDRO-3-METHYL-2-METHYLENE-BENZOTHIAZOLE-α-DITHIOCARBOXYLATE WITH DIMETHYL ACETYLENEDICARBOXYLATE.

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Treatment of methyl 2,3-dihydro-3-methyl-2-methylenebenzothiazole-α-dithiocarboxylate with dimethyl acetylenedicarboxylate in dimethylformamide resulted in a Diels-Alder cycloaddition which were followed by desulfurization. This product is a spiro-compound 2,3-dimethoxycarbonyl-4-methylthio-2,4-cyclopentadiene-1-spiro-2-(2,3-dihydro-3-methylbenzothiazole).

In our previous papers, we reported that Diels-Alder reactions of methyl 3-indoledithiocarboxylates[1)] and methyl 1,2-dihydro-1-methyl-2-methylenepyridine-α-dithiocarboxylate[2)] which were thought to have an enaminodithiocarboxylate, with dimethyl acetylenedicarboxylate afforded Diels-Alder reaction products, 4a-substituted-5-methyl-1-methylthio-3,4-dimethoxycarbonyl-4aH-thiapyrano[4,3-b]indole and 4-(3-formylprop-2-enylidene)-5-methylthio-2,3-dimethoxycarbonyl-4H-thiapyrone, respectively.

In our present paper, we report Diels-Alder reactions of methyl 2,3-dihydro-3-alkyl-2-methylenebenzothiazole-α-dithiocarboxylate and methyl 2,3-dihydro-3-methyl-2-methylenethiazoline-α-dithiocarboxylate with dimethyl acetylenedicarboxylate.

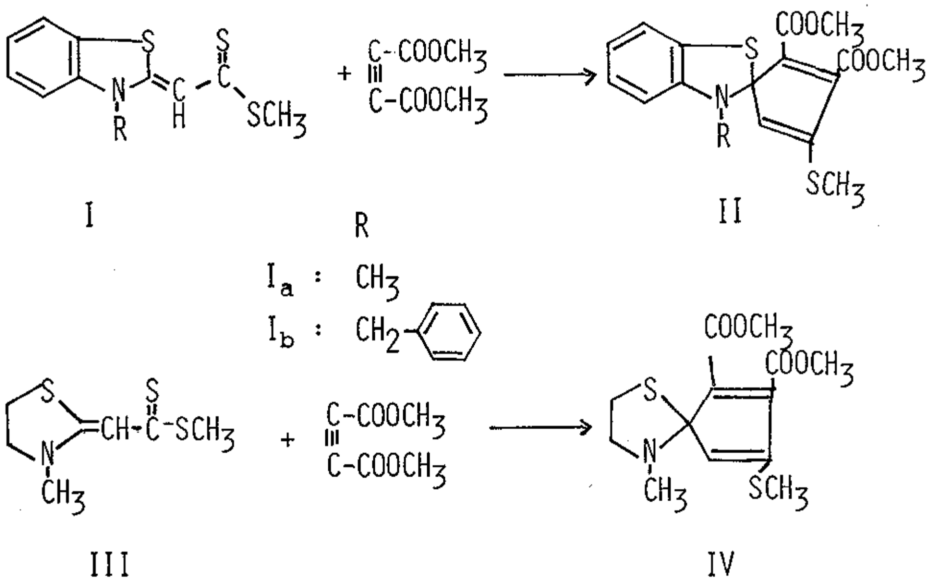

Chart I

A mixture of Ia and dimethyl acetylenedicarboxylate in dimethylformamide was heated on a steam bath for 3-4 hours. After cooling at room temperature, the precipitates were collected by filtration and recrystallized from acetone to give yellow needles of mp 209°, in good yield. This product was not obtained using dioxane as solvent or without solvent.

Sulfur was obtained simultaneously from the mother liquor. Elemental analysis of this product corresponded to $C_{17}H_{17}O_4S_2N$ (R: CH_3)=363.31 (Calcd; C, 56.20; H, 4.72; N, 3.86. Found; C, 56.34; H, 4.76; N, 3.72). The molecular weight of this compound was also supported by mass spectroscopy (M^+: 363). The nuclear magnetic resonance (NMR) spectrum (in pyridine) of this compound displayed four sharp singlets due to methyl protons at 2.40ppm (3H, singlet, SCH_3), 3.31ppm (3H, singlet, OCH_3), 3.36ppm (3H, singlet, OCH_3) and3.73ppm (3H, singlet, NCH_3). The infrared (IR) spectrum of this compound showed the carbonyl band of the ester groups at 1735 cm^{-1} and 1655 cm^{-1}. The ultraviolet (UV) spectrum revealed maxima at 230nm[a], 251nm, 296nm and 455nm. From these spectral data and elemental analysis, this compound was found to be 2,3-dimethoxycarbonyl-4-methylthio-2,4-cyclopentadiene-1-spiro-2-(2,3-dihydro-3-methylbenzothiazole).

In a similar manner, treatment of other compounds(Ib, III) with dimethyl acetylenedicarboxylate, as shown in Chart I, gave corresponding compounds(IIb and IV) in good yield.

IIb): mp 184-185°, Anal. Calcd. for $C_{23}H_{21}O_4S_2N$; C, 62.86; H, 4.82; N, 3.19. Found; C, 63.14; H, 4.94; N, 3.19. M^+: 439. IR (KBr) ν cm^{-1}; 1740, 1655 (C=O). UV λ_{max}^{EtOH} nm[a]; 250, 294, 440. NMR (in pyridine) δ ppm; 2.20 (3H, singlet, SCH_3), 3.41 (3H, singlet, OCH_3), 3.71 (3H, singlet, OCH_3).

IV): mp 185-186°, Anal. Calcd. for $C_{13}H_{17}O_4S_2N$; C, 49.52; H, 5.44; N, 4.44. Found: C, 49.62; H, 5.51; N, 4.62. M^+: 315. IR (KBr) ν cm^{-1}; 1740, 1660 (C=O). UV λ_{max}^{EtOH} nm[a]; 295, 400. NMR (in pyridine) δ ppm; 2.35 (3H, singlet, SCH_3), 2.82 (3H, singlet, NCH_3), 3.56 (3H, singlet, OCH_3), 3.67 (3H, singlet, OCH_3).

In conclusion it is of interest to note that desulfurization occured in a Diels-Alder reaction containing thiocarbonyl diene system. Similar desulfurization have been reported by McKinnon[3)] and Reinhoudt[4)].

A possible mechanism for this reaction is outlined in Chart II.

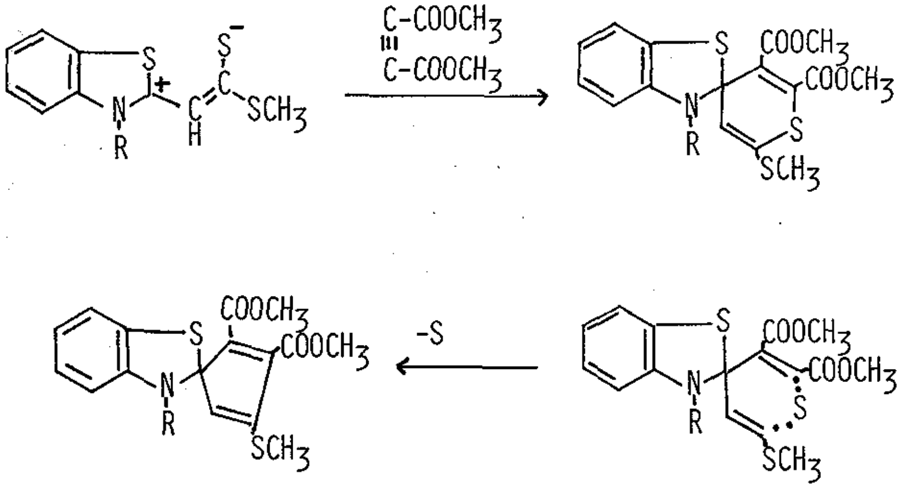

Chart II

We have now a plan to study the reaction of other enaminodithiocarboxylates of a heterocyclic compound with dimethyl acetylenedicarboxylate or other dienophiles.

We hope to present more definite information in this direction in future communications.

REFERENCES

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a) Concentration is unknown because of insufficient solubility.

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