

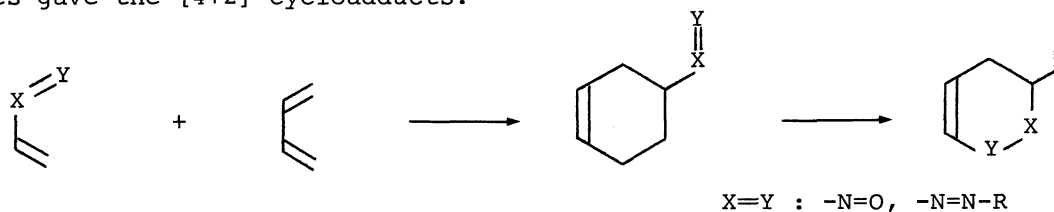
CYCLOADDITIONS OF 2-ARYLMETHYLENE-1-TETRALINTHIONES WITH ISOPRENE
AND (E,E)-1,4-DIPHENYL-1,3-BUTADIENE¹⁾

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2-Arylmethylene-1-tetralinthione reacted with isoprene and (E,E)-1,4-diphenyl-1,3-butadiene to give the 3,4-dihydro-2H-thiopyran derivatives. In these reactions, the thiones and dienes are formally acting as 4 π - and 2 π -electron components, respectively.

Making a comparison of the dienic properties between heterodienes and usual dienes is an interesting problem, however, little attention has been paid to such attempt by carrying out the cycloaddition reaction between these dienes. For example, Gilchrist et al.²⁾ reported that the reactions of nitroso- or azo-alkenes with various dienes gave the [4+2] cycloadducts.



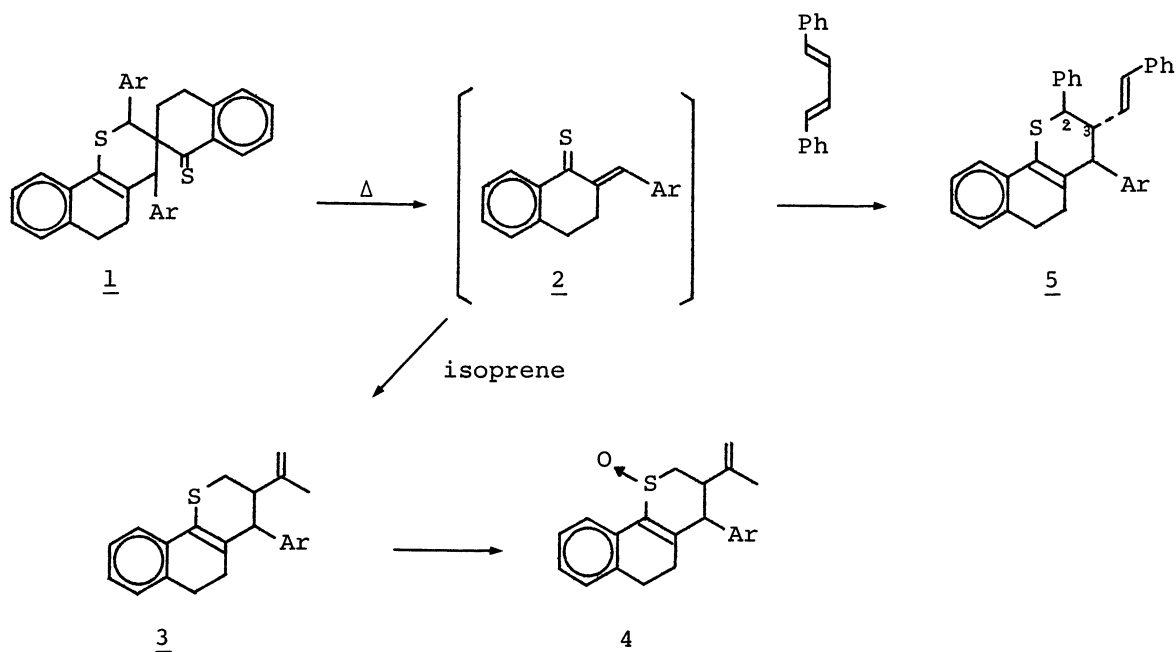
Also, α,β -unsaturated ketones usually participate as 2 π -electron component in their cycloaddition reactions with 1,3-dienes except in the case of o-quinone methides.³⁾

As a result of the studies on the cycloaddition reactions of α,β -unsaturated thiones, it has been found that the thiones can participate in [4+2] cycloaddition reactions as reactive 4 π -electron component toward various double bond compounds.⁴⁾ Accordingly, we have been interested in the reaction of the thiones with acyclic dienes.

A solution of 2-benzylidene-1-tetralinthione dimer^{4b)} (1.0g) and isoprene (0.32g) in dry benzene (5 cm³) was refluxed for 6h under nitrogen atmosphere. The reaction mixture turned from deep blue to slightly green. The product (3a) was identified by its conversion into the sulfoxide (4a) by an oxidation with mCPBA, because 3a could

not be purified by distillation or crystallization. The product (4a) exhibited absorption at 1020 cm^{-1} ($\text{S}=\text{O}$) in the IR spectrum. The ^{13}C -NMR spectrum (CDCl_3 , 25 MHz) exhibited signals at δ 20.8 (q), 27.5 (t), 29.4 (t), 38.3 (d, C-3), 48.8 (t, C-2), and 52.9 (d, C-4).⁵⁾ The mass spectrum displayed ion peaks at m/e 334 (M^+), 317 (60), 271 (45), 250 (13), 249 (33), and 218 (100). These data are consistent with the proposed structure.⁶⁾

In this cycloaddition reaction, 2a and isoprene are formally acting as 4π - and 2π -electron components, respectively. To confirm this interesting results, the reaction of 1a with (E,E)-1,4-diphenyl-1,3-butadiene was examined. The mass spectrum of the product (5a) showed ion peaks at m/e 456 (M^+), 249 (32), and 206 (100). The ^1H -NMR spectrum (CDCl_3 , 100 MHz) showed signals at δ 2.08-2.78 (4H, m), 3.36 (1H, ddd, $J=11.4, 10.0,$ and 4.3 Hz), 3.74 (1H, d, $J=4.3$ Hz), 4.42 (1H, d, $J=11.4$ Hz), 5.34 (1H, dd, $J=15.7$ and 10.0 Hz), 6.26 (1H, d, $J=15.7$ Hz), and 7.00-7.60 (19H, m). In the ^{13}C -NMR spectrum (CDCl_3 , 25 MHz), 5a showed signals at δ 44.4 (d, C-2), 47.8 (d, C-3), and 53.8 (d, C-4) and the ^{13}C assignments are made from comparison of the chemical shifts with those of analogous thiopyran compounds^{4c,4d)} and 4. Whereas, the C-{H} heteronuclear decoupling spectrum (irradiated at δ 4.42) showed signals at δ 44.4 (s), 47.8 (d), and 53.8 (d). These data indicate that the doublets of ^1H -NMR



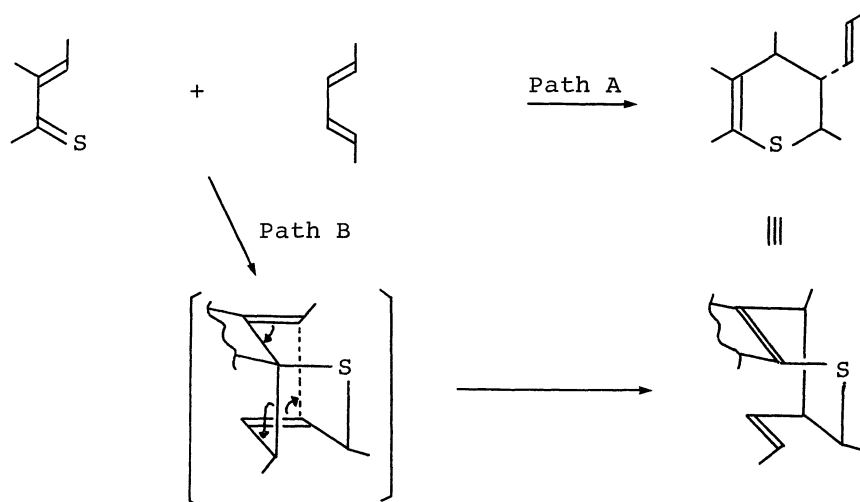
a: $\text{Ar}=\text{C}_6\text{H}_5$, b: $\text{Ar}=\text{p-CH}_3\text{O-C}_6\text{H}_4$, c: $\text{Ar}=\text{p-Cl-C}_6\text{H}_4$

spectrum at δ 4.42 and 3.74 are due to the C-2 and C-4 protons, respectively.

Compd	Yield(%)	mp(°C)	Reaction time (h)	Anal. C %	Found (Calcd) H %
<u>4a</u>	16	228.0-230.0	6	78.65(79.00)	6.83(6.63)
<u>4b</u>	7	188.0-190.0	2	75.59(75.59)	6.63(6.64)
<u>4c</u>	53	202.0-204.0	6	71.32(71.63)	5.74(5.74)
<u>5a</u>	36	175.0-177.0	5	86.85(86.80)	6.18(6.18)
<u>5b</u>	40	93.0-95.0	5.5	83.67(83.91)	6.26(6.22)
<u>5c</u>	60	117.5-119.5	5	-	-

Therefore, the value of the coupling constants between the C-2 and C-3 protons ($J=11.4$ Hz) suggests that 5a has the 2,3-trans configuration.⁷⁾ There are two ways in which such adducts could be formed. A concerted Diels-Alder cycloaddition of the α,β -unsaturated thiones, acting as 4π -electron systems, and the dienes, acting as 2π -electron systems, could give these products (path A). The addition of the C=S bond in α,β -unsaturated thiones to the dienes followed by a [3,3] sigmatropic rearrangement of the adducts would be another possible pathway (path B).

As a guide to the consideration on these reaction mechanisms, we compared the frontier orbital energies and orbital coefficients of thiochalcone^{4c)} and butadiene.⁸⁾ The relative orbital energies indicate that the major interaction is likely to be that between the HOMO of butadiene and the LUMO of thiochalcone. The interaction between sulfur atom of thiochalcone and C-1 of butadiene which gives the observed product regioselectively in both paths appears to be predominant on the basis of the



orbital coefficients. Combination of the orbital coefficients also suggest that Path B, involving addition of the diene to the C=S bond, would be more favorable than Path A, but we have no other experimental data to support such a proposal at present.

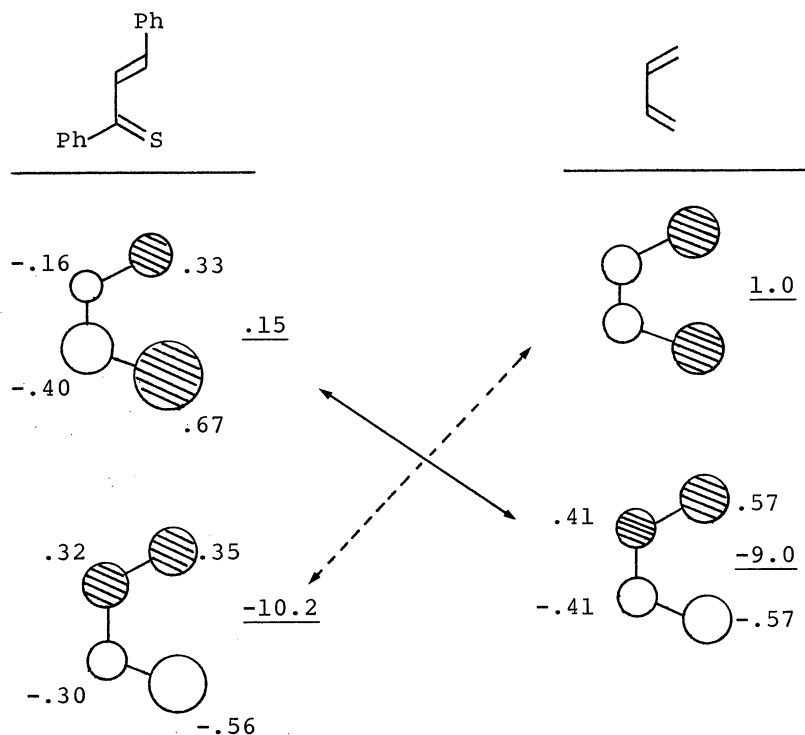


Figure Frontier orbital energies (eV) and coefficients

References and Notes

- 1) Chemistry of α,β -Unsaturated Thione Dimers 4.
- 2) R. Faragher and T. L. Gilchrist, *Chem. Commun.*, 1976, 581; *idem*, *J. Chem. Soc., Perkin Trans. I*, 1979, 249.
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- 5) These assignments are consistent with the result of off-resonance decoupled spectrum.
- 6) The configuration of 4a could not be determined by the NMR spectrum.
- 7) We wish to thank a referee for this point about the configuration.
- 8) K. N. Houk, "Pericyclic Reactions", A. P. Marchand and R. E. Lehr, Ed., Vol. II, Academic Press, New York, p 181, 1977.

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