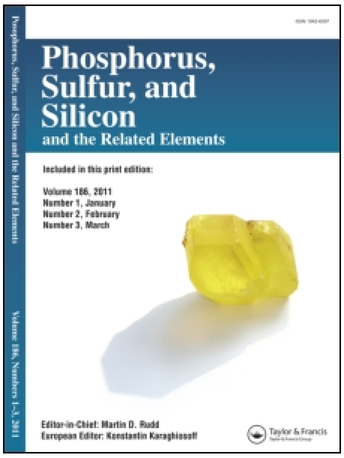

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ALTERNATIVE PATHWAYS IN CYCLOADDITIONS OF α-(ALKYLTHIO)ACRYLIC ACID DERIVATIVES TO ALKENES AND ALKYNES

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Abstract In a multistep reaction, the title compounds form hydrothiophenes or polysubstituted butadienes, respectively, when warmed in dioxane solution for periods of several hours to a few days.

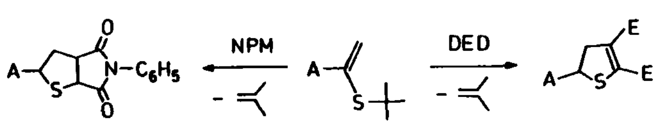
INTRODUCTION

The "captodative"[1] character of α-(alkylthio)acrylic acid esters or nitriles[2)] and their tendency to undergo [2+2]-cycloadditions with other alkenes and reversible [2+2] dimerizations at ambient temperature is well documented[1-3]. On prolonged warming (100 °C) of either the neat α-(alkylthio)-acrylic acid derivative or a mixture of the olefinic reactants, either in absence of solvent or in solution, additional reactions ensue.

RESULTS

In refluxing dioxane under argon within five days, α-(tert-butylthio)acrylonitrile (**1a**) with N-phenyl maleic imide (NPM) or dimethyl ethyne dicarboxylate (DED), respectively, gave 77% **2a** and 84% **3a**, respectively, with elimination of isobutene in either case[4]. Both reactions each involve at least two discrete steps. For the reaction of **1a** with DED, $\Delta H^{\ddagger} = 62$ kJ mole^{-1} and $\Delta S^{\ddagger} = -155$ J mole^{-1}K^{1} have been determined. Analogous reactions of **1a** have been carried out with dimethyl maleate and fumarate, fumaric acid, methyl methylacrylate and crotonate, phenylvinylsulfone, norbornene, styrene, phenylethyne, propiolic acid, and 4-phenyl-3-butyne-2-one[5].

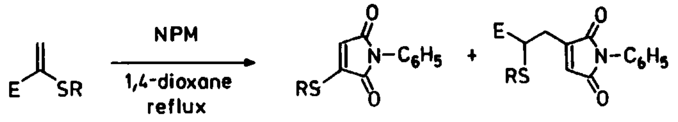
Addition of NPM to **1b** (24h, dioxane, reflux) gave 46% of **2b** as a (5,7:1) mixture of syn (m.p. 146 °C) and anti (m.p. 95 °C) isomers[5]. From **1b** and DED (dioxane, 80 °C, 3 days) **3b** was obtained in 45% yield together with a complex mixture of minor by-products including butadienes analogous to those described below.



2a,b **1a,b** **3a,b** (E = COOCH$_3$)

a: A = CN; **b**: A = COOCH$_3$

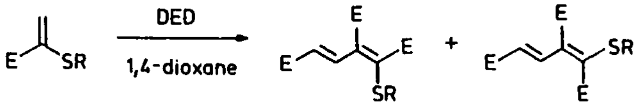
Reaction of NPM with esters **1c,d** gave some methyl acrylate, which was distilled off together with the solvent, and the alkylthio substituted imides **4c,d** as major and the propionic acid derivatives **5c,d** as minor products. An adduct analogous to **5** has been obtained previously by Gundermann from maleic anhydride and methyl α-(methylthio)acrylate[6].



R = i-Pr:	1c	24 h	4a (77%), m.p. 126°C	5a (12%)
R = Et:	1d	2 h	4b (34%), m.p. 131°C	5b (11%)

E = $COOCH_3$

Butadienes 6a,b and 7, however, are the sole products from 1c,d and DED. A 2-(E)-configuration was assigned to 6a,b under the assumption that during ring opening of the presumed precursor the 2,3-double bond retains its configuration[7]. A 3-(E) geometry was assigned to 6a,b and 7 on the basis of a rather uniform value (16± 0.2 Hz) for $^3J_{AB}$.



R = i-Pr:	1c	17 h, 40°C	6a (46%)	–
R = Et:	1d	24 h, 50°C	6b (60%)	7 (6%)

E = $COOCH_3$

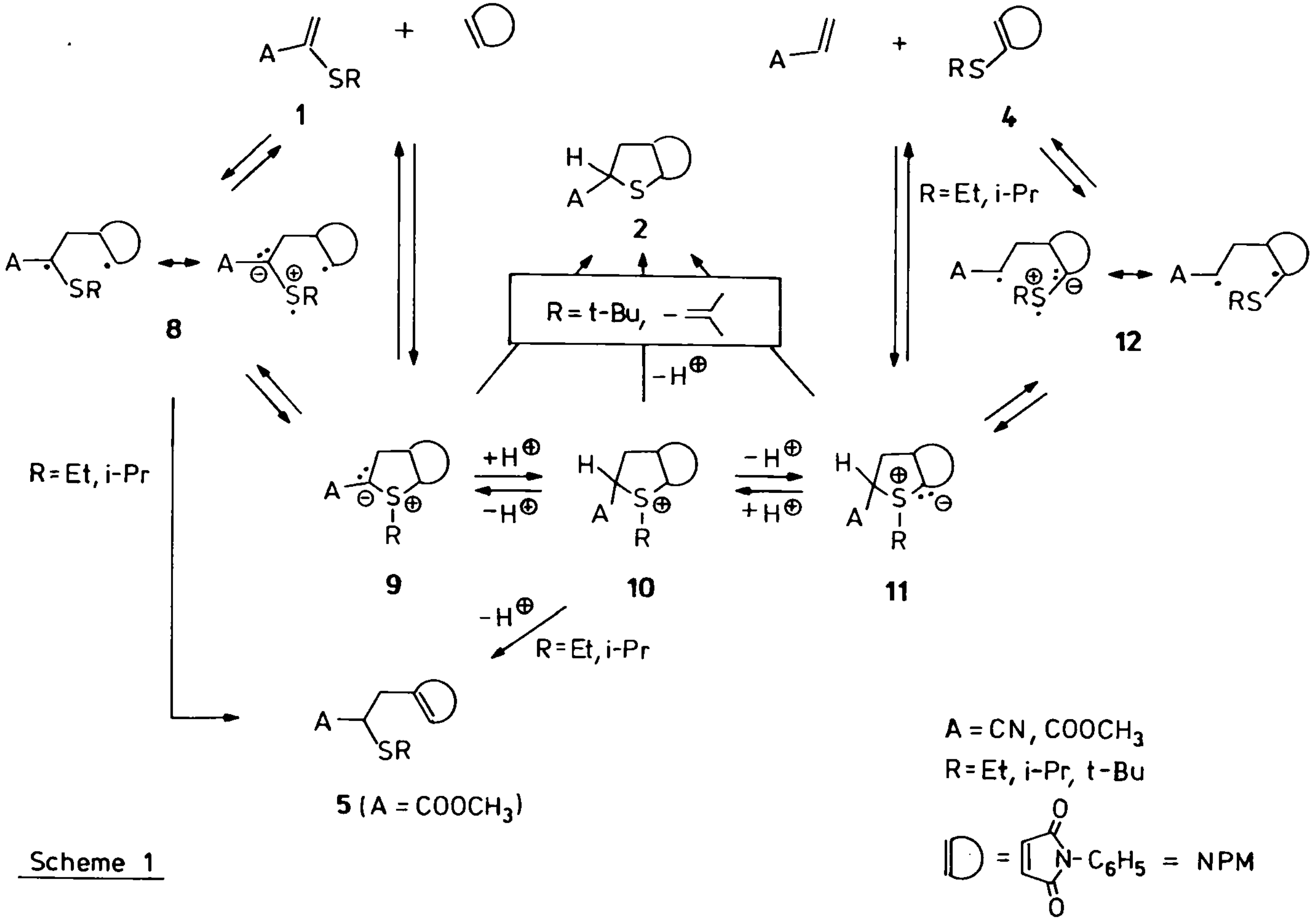
DISCUSSION

Imides 4a,b may be envisaged as products from intermolecular alkylthio group transfer from 1c,d to NPM. In the butadienes 6a,b and 7, the former C-2 of DED ends up to be connected with C-3 of the acrylate, and the alkylthio group has been transferred from the former acrylate C-2 to the former C-3 of DED. This constitutes a formally intramolecular version of the aforementioned intermolecular group transfer.

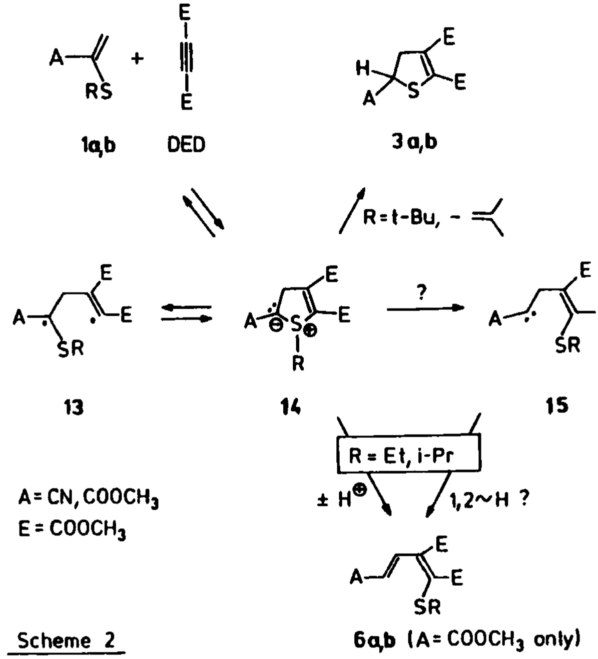
The formation of all products reported here is best rationalized by the hypotheses outlined in schemes 1 and 2, which, for clarity, are reduced to the reactions of 1 with NPM and DED, but apply accordingly to the additions of other alkenes or alkynes.

Scheme 1: The starting materials, being in equilibrium with the 1,4-diradical 8, may form the sulfonium ylid 9 either via 8 or directly. The presumed ylid 9 may be seen in equilibrium with 10 and 11. When R = t-butyl, elimination of isobutene is favourable from all three species. For R = isopropyl or ethyl, ylid 11 prefers to be cleaved into the group transfer products, as ylid 9 may return to the starting materials. By-products 5 may arise either from an intramolecular disproportionation within 8 or via ß-elimination like ring opening of 10.

Scheme 2: Likewise, cycloaddition of 1a,b to DED may give (either via 13 or directly) the monounsaturated ylide 14. The latter either undergoes loss of isobutene (for R = t-butyl) or protonation at the carbanionic center followed by deprotonation at the ß-carbon concomitant with ring opening[8] to give the butadienes 6,7. Opening of 14 to the carbene 15 and a 1,2-H-shift to form 6,7 would be another attractive alternative. It should be noted that the activation parameters reported above are in accord with either a rate limiting 3+2 cycloaddition of 1a and DED to form 14 (A = CN, R = t-Bu) or with a slow formation of the latter from a diradical precursor.


1
4
2
8
12
R = t-Bu, $-\!\!=\!\!\!<$
$-H^{\oplus}$
$+H^{\oplus}$
$-H^{\oplus}$
$-H^{\oplus}$
$+H^{\oplus}$
R=Et, i-Pr
9
10
11
$-H^{\oplus}$
R=Et, i-Pr
R=Et, i-Pr
5 (A = COOCH$_3$)
A = CN, COOCH$_3$
R=Et, i-Pr, t-Bu
= N-C$_6$H$_5$ = NPM

Scheme 1



Scheme 2

Clearly, ylids 9, 11, and 17 play a key role in both hypotheses. Arguments in favour of these intermediates are: (a) Hydrothiophenes as 2 and 3 as well as the group transfer products 4, 6 and 7 are not easily rationalized when cyclic intermediates are excluded from the discussion. (b) When α-(benzylthioacrylonitrile is reacted with DED, trimethyl 5-benzyl-4,5-dihydrothiophene 2,3,5-tricarboxylate is formed in good yield. This product may well arise by 1,2-migration[9] of the benzyl group within a caged radical pair generated from the corresponding cyclic ylid. Bicyclic sulfonium ylids have also been suggested as intermediates in the reactions of cyclic vinylsulfides with DED[10].

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