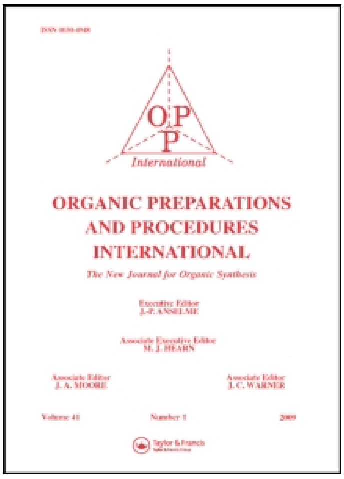

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THE SYNTHESIS OF 3-R-7-CARBOMETHOXYMETHYLENE-7H-1,2,4-TRIAZOLO[3,4-b]-1,3,4-THIADIAZIN-6-ONES

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minum chloride-catalyzed dechlorinative methylation of the "disilane fraction", which is obtained as by-product from the direct synthesis of methylchlorosilanes, with trimethylchlorosilane; see H. Matsumoto, T. Motegi, M. Hasegawa and Y. Nagai, J. Organometal. Chem., 142, 149 (1977).

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THE SYNTHESIS OF 3-R-7-CARBOMETHOXYMETHYLENE-7H-1,2,4-TRIAZOLO[3,4-b]-1,3,4-THIADIAZIN-6-ONES

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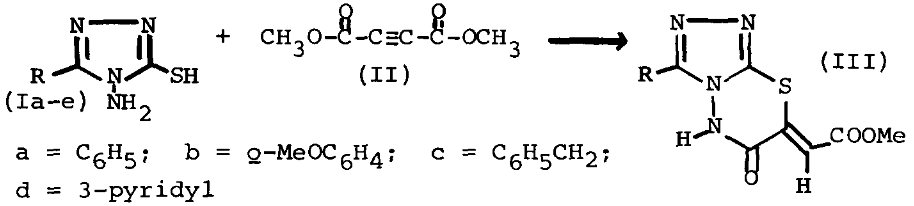
The vicinal amino and mercapto groups of 4-amino-3-mercapto-(4H)-1,2,4-triazoles (Ia-d) constitute useful bridging loci for fusion of hetero rings onto the *s*-triazole. Fused systems have included 1,3,4-thiadiazoles,[1] 1,3,4-thiadiazines,[2,3] and 1,3,4-thiadiazepines.[4] Normally, o-aminothiophenols react rapidly and in high yield with dimethyl acetylenedicarboxylate (II) to give 2-carbomethoxymethylene-3,4-dihydro-3-oxo-2H-benzo-1,4-thiazines.[5] Despite numerous experimental variations, the comparable condensation of I with II has proven difficult and proceeded in modest yield. A recent report on the synthesis of IIIa, with neither yield nor experimental detail, conveys the impression that the reaction is facile.[3] Our results have been to the contrary.



a = C_6H_5; b = o-$MeOC_6H_4$; c = $C_6H_5CH_2$;
d = 3-pyridyl

EXPERIMENTAL

Melting points are uncorrected. PRM spectra were obtained in DMSO-d_6 on a Perkin Elmer-Hitachi R20A spectrometer.

5-R-4-Amino-3-mercapto-(4H)-1,2,4-triazoles (Ia-d).- Compounds Ia-c have been described.[1,6] Compound Id was prepared from nicotinic acid hydrazide in 59% yield by the method described for isonicotinic acid hydrazide,[6] mp. 194-196° from 1:1 ethanol:water.

Anal. Calcd for $C_7H_7N_5S$: C, 43.51; H, 3.65; N, 36.24.
Found: C, 43.25; H, 3.80; N, 36.04.

3-R-7-Carbomethoxymethylene-7H-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazin-6-one. General Procedure for III a-d.- A solution of 30 mmol each of Ia-c and II was prepared in 100 ml of methanol. After the initial exotherm, the solution was refluxed for 2 hrs. and evaporated. The resulting gum was transferred to a watch glass, heated in an oven at 80-90° for 2 days, placed in a desiccator for several days, and triturated with methanol to induce crystallization. The solids were recrystallized from methanol to analytical purity.

If Id and II were treated as above, only inseparable mixtures resulted, a probable consequence of the known condensation of alkynyl esters and pyridine rings.[7] Instead, Id and II were allowed to react at room temperature for 2 weeks to yield IIId. Products displayed sharp vinyl singlets at δ 6.75 ± 0.15 ppm and ester methoxyls at δ 3.75 ± 0.05.

IIIa, 18% yield, mp. 254-256°, lit. mp. 251°[3]

<u>Anal</u>. Calcd for $C_{13}H_{10}N_4O_3S$: C, 51.66; H, 3.33
Found: C, 51.49; H, 3.60

IIIb, 63% yield, mp. 253-254°

<u>Anal</u>. Calcd for $C_{14}H_{12}N_4O_4S$: C, 50.61; H, 3.62
Found: C, 50.71; H, 3.69

IIIc, 28% yield, mp. 262-265°

<u>Anal</u>. Calcd for $C_{14}H_{12}N_4O_3S$: C, 53.16; H, 3.82
Found: C, 53.14; H, 4.04

IIId, 27% yield, mp. 247-249°

<u>Anal</u>. Calcd for $C_{12}H_9N_5O_3S$: C, 47.53; H, 2.99
Found: C, 47.41; H, 3.21

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REDUCTION OF 5-HYDROXYMETHYL-1-AZA-3,7-DIOXABICYCLO[3.3.0]OCTANE AND OF 2-PHENYL-4,4-DIMETHYLOXAZOLIDINE WITH FORMIC ACID

Submitted by
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Amino alcohols which have an amino group or a monosubstituted amino group and an alcohol group attached to adjacent carbon react with aldehydes to give oxazolidines. Amino polyhydric alcohols with similar structures react with two moles of aldehydes to yield substituted 1-aza-3,7-dioxabicyclo[3.3.0]octanes. These heterocyclic compounds are useful for the preparation of monoalkyl or dialkylamino alcohols; reduction has been accomplished by hydrogenation using 1% palladium on charcoal as a catalyst at 100^{o} and 1000 psi.[1]

The same type of reduction has been found to occur when 5-