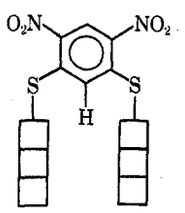
adjacent ring and experiences its diamagnetic shielding.[3]

The experimental nmr shieldings have been computed as the differences between the chemical shifts of each compound and that of compound III.

A theoretical shielding of about 1.0 ppm is calculated[1] for the aromatic proton lying below the adjacent ring (form VIII) in diphenyl sulfide. The agreement is better for compound V (Δ = 0.79 ppm) than IV (Δ = 0.58 ppm) indicating that, if the adjacent ring carries ortho substituents, form VIII receives further stabilization.

In compounds VI and VII the protons under consideration lie between two adjacent phenyl rings, and, if a conformation of type IX is present, the shielding experienced should be nearly doubled with respect to compounds IV and V.

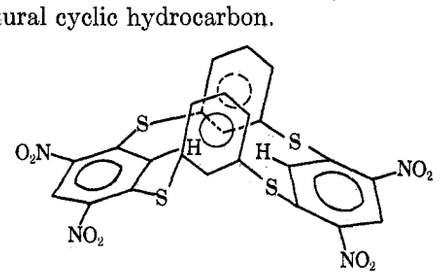


IX

The actual shieldings (Δ = 1.01 and 1.40 ppm, respectively) confirm that conformation IX is preferred in these cases, the preference being stronger for compound VII.

The lower shieldings observed for the cyclic sulfides I and II have a steric origin, we believe. In these molecules, as shown by inspection of molecular models, the cyclic structure puts steric restraints to the existence of conformations of type VIII and IX, and the inner protons are forced somewhat outside the area of maximum shielding.

Compound I is thought to exist in a form (X) for which a sensible shielding is still predictable. A similar conformation has been found in solid state[4] for an isostructural cyclic hydrocarbon.

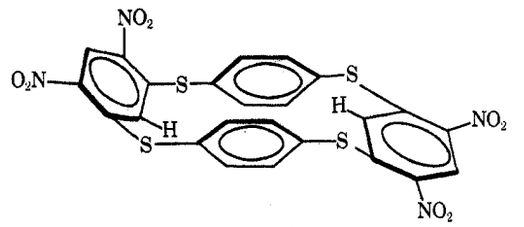


X

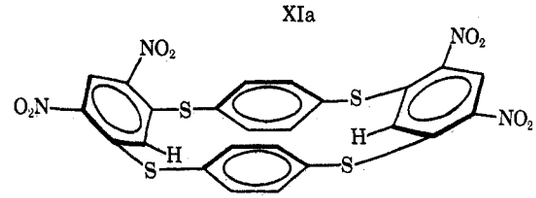
Molecular models show two structures (XIa and XIb) as equally plausible in the case of compound II.

In both forms the inner protons appear little shielded, in agreement with the experimental findings. Our results therefore show that, due to the presence of the nitro groups, a strong conjugation develops between the sulfur atom and the aromatic ring bearing the nitro groups in compounds IV–VII. The conjugation energy is strong enough to cause the internal rotation to become thermodynamically (but not kinetically) restricted, so that forms VIII and IX become preferred.

Steric factors, however, come into action for cyclic sulfides I and II, which prevent these molecules from assuming conformations of the former type.



XIa



XIb

(3) G. Montaudo, P. Finocchiaro, E. Trivellone, F. Bottino, and P. Maravigna, *Tetrahedron*, **27**, 2125 (1971).

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Experimental Section

Compound I was obtained by refluxing for 1 hr very dilute ethanol solutions (20:1) of 1,3-benzenedithiol (1.7 g) with NaOH (0.9 g) and 1,3-dichloro-4,6-dinitrobenzene (2.8 g). The yellow precipitate formed was filtered, washed, and dried (yield 65%). Recrystallization from nitrobenzene afforded a product which did not melt up to 350°. *Anal.* Calcd for $C_{24}H_{12}N_4O_8S_4$ (mol wt 612): C, 47.06; H, 1.96; N, 9.16; S, 20.90. Found: C, 47.18; H, 2.20; N, 9.22; S, 21.02. Mass spectrum *m/e* 612 (M^+); nmr (DMSO-d_6, 80°) 9.02 (1 H), 7.69 (4 H), 6.71 ppm (1 H).

Compound II was obtained as above by refluxing 1,4-benzenedithiol (1.7 g), NaOH (0.9 g), and 1,3-dichloro-4,6-dinitrobenzene (2.8 g, yield 70%). The product obtained was infusible up to 350°.

Anal. Calcd for $C_{24}H_{12}N_4O_8S_4$ (mol wt 612): C, 47.06; H, 1.96; S, 20.90. Found: C, 47.24; H, 2.30; N, 9.31; S, 20.93. Mass spectrum *m/e* 612 (M^+); nmr (DMSO-d_6, 80°) 9.04 (1 H), 7.66 (4 H), 7.20 ppm (1 H).

Compounds III, IV, and V were prepared according to the literature.[5] Compound VII was obtained by refluxing 1,3-dichloro-4,6-dinitrobenzene, NaOH, and 1,3,5-trimethyl-2-benzenethiol in ethanol, similarly to the preparation described[6] for compound VI. Data for VII follow.

Anal. Calcd for $C_{24}H_{24}N_2O_4S_2$ (mol wt 468.5): C, 61.52; H, 5.16; N, 5.98; S, 13.69. Found: C, 61.71; H, 6.01; S, 13.90. Nmr ($CDCl_3$, 70°) 9.25 (1 H), 6.73 (4 H), 6.11 (1 H), 2.50 (6 H), 2.07 ppm (12 H); mp 300° (dioxane).

All the nmr measurements were performed with a Varian HA-100 spectrometer (100 MHz).

Registry No.—I, 32730-77-1; II, 32827-45-5; VII, 32827-46-6.

(5) N. M. Cullinane, C. G. Davies, and C. G. I. Davies, *J. Chem. Soc.*, 1435 (1936); G. Leandri and A. Tundo, *Ann. Chim. (Rome)*, **44**, 261 (1954).

(6) A. Livingstone and J. D. London, *J. Chem. Soc.*, 246 (1937).

A Convenient Synthesis of α-Keto Esters

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Corey and Seebach[2,3] have described a very convenient method of synthesis of aldehyde and ketone

(1) From the Ph.D. dissertation of Armando A. Hartmann, University of Notre Dame, Notre Dame, Ind., 1971.

(2) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075 (1965).

(3) D. Seebach, *Synthesis*, **1**, 17 (1969).

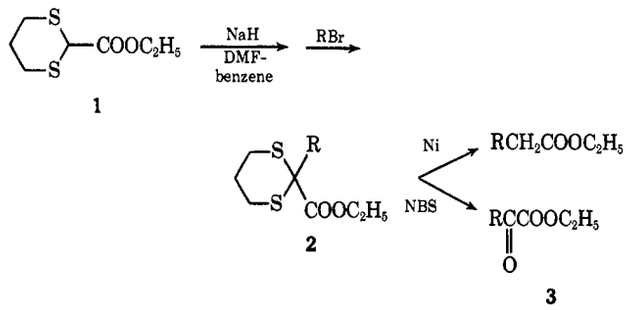
TABLE I

ETHYL 2-ALKYL-1,3-DITHIANE-2-CARBOXYLATES (2)

Alkyl group[a]	Registry no.	Yield, %	Bp, °C (mm)	$n^{20}D$	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Benzyl	4882-96-6	85	145 (0.05)[b]	1.5651	59.54	6.42	59.82	6.84
n-Butyl	32557-27-0	94	90–95 (0.1)	1.5140	53.18	8.12	53.36	8.07
Isopropyl	32557-28-1	75	85–95 (0.1)	1.5205	51.24	7.74	51.19	7.70
sec-Butyl	32557-29-2	90	90–95 (0.1)	1.5208	53.18	8.12	53.23	8.11

[a] Introduced as alkyl bromide except for benzyl, which was introduced as benzyl chloride. [b] Lit.[3] bp 144° (0.01 mm).

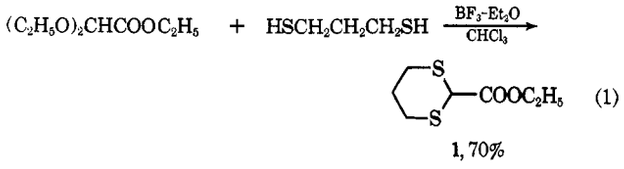
derivatives by alkylation of the lithium salts of 1,3-dithianes. When we attempted to synthesize the ester **1** by reaction of 2-lithio-1,3-dithiane with 1 mol of



ethyl chloroformate, we obtained, instead, 0.5 mol of the disubstituted product, 2,2-biscarbethoxy-1,3-dithiane, and 0.5 mol of recovered dithiane. Clearly, **1** is a strong enough acid to be converted completely into its lithium derivative by 2-lithio-1,3-dithiane.

It became apparent that the high acidity of **1** could be utilized in a rather facile alkylation in which sodium hydride in dimethylformamide (DMF)–benzene[4] is used to convert **1** into its sodium salt which is then alkylated with a primary or secondary halide in the usual way in yields of 75–95%. Desulfurization of the resulting alkylated ester **2** by means of Raney nickel provides an alternative to the malonic ester synthesis of alkylated acetic acids, with the variation that the product is obtained in the form of the ester rather than as the acid. Perhaps more significant is the conversion of **2** in good yield to the corresponding α-keto ester **3** by means of *N*-bromosuccinimide as previously described by Seebach.[3]

The significance of this α-keto ester synthesis is enhanced by the fact that the common starting material **1** has been found to be very easily available from ethyl diethoxyacetate prepared from dichloroacetic acid[5] and 1,3-propanedithiol (eq 1).



(1)

Although the present α-keto ester synthesis is quite similar to that previously described[2,3] in which the starting material is 1,3-dithiane or (if available) the appropriate 2-alkyl-1,3-dithiane, it has the advantage that a common, readily available precursor (**1**) is used for all α-keto esters and that it is not necessary to use alkyllithium reagents in the synthesis.

Experimental Section

Ethyl 1,3-Dithiane-2-carboxylate (1).—1,3-Propanedithiol, 10.8 g (0.1 mol), and 17.6 g (0.1 mol) of ethyl diethoxyacetate[5] dissolved in 20 ml of chloroform were added dropwise to a refluxing solution of 28.2 g (0.2 mol) of BF_3 etherate in 60 ml of chloroform over a period of 15 min. The solution was boiled for 0.5 hr, cooled, and washed successively with 80 ml of water, 80 ml of 20% aqueous potassium carbonate, and twice more with 80-ml portions of water. After drying over $MgSO_4$ the solution was filtered and concentrated at reduced pressure and the product was distilled, bp 75–77° (0.2 mm), yield 13.4 g (70%), $n^{20}D$ 1.5379, infrared and nmr spectrum in accordance with structure **1** [lit.[3] bp 96° (0.4 mm), $n^{25}D$ 1.5385].

General Procedure for Alkylation.—A solution of 0.1 mol (19.2 g) of **1** and 0.11 mol of the desired alkyl halide in 40 ml of DMF was added slowly to a well-stirred suspension of 0.1 mol (2.4 g) of sodium hydride in 120 ml of dry benzene cooled to 5°. The mixture was stirred in an ice bath for 1 hr and then at room temperature for 12 hr. The benzene layer was extracted three times with 200-ml portions of water, dried over $MgSO_4$, filtered, and concentrated. The crude product is suitable for desulfurization or conversion to the α-keto ester; however, the products tabulated in Table I were purified by distillation at reduced pressure, and all had the expected infrared and nmr spectra.

α-Keto Esters.—The procedure of Seebach[3] was followed. The following esters were thus obtained: ethyl phenylpyruvate, 76%, bp 145° (12 mm) [lit. bp 152° (15 mm)]; ethyl α-ketocaproate, 60%, bp 80–92° (12 mm), $n^{20}D$ 1.4187 [lit.[6] bp 74–96° (10 mm), $n^{20}D$ 1.4178]; ethyl α-ketoisovalerate, 85%, bp 63–70° (12 mm), 2,4-dinitrophenylhydrazone mp 171–172° [lit.[7] bp 72° (16 mm); lit.[8] 2,4-dinitrophenylhydrazone mp 171.5–172°]; ethyl α-ketoisocaproate, 62%, bp 76–78° (12 mm), $n^{20}D$ 1.4192 [lit.[6] bp 76–77° (10 mm), $n^{20}D$ 1.4175]. The infrared and nmr spectra of the four keto esters were compatible with the assigned structures.

Ethyl Hydrocinnamate.—To 24 g (0.1 mol) of nickel chloride hexahydrate dissolved in 80 ml of ethanol was added 7.5 g (0.2 mol) of sodium borohydride in small portions with stirring and the resulting suspension was stirred for an additional 0.5 hr. Then 2.8 g (0.01 mol) of 2-benzyl-2-carbethoxy-1,3-dithiane was added and the mixture was refluxed with stirring for 48 hr, filtered, concentrated, and distilled at reduced pressure. Ethyl hydrocinnamate boiled at 112° (12 mm), $n^{20}D$ 1.4936 [lit. bp 123° (14 mm), $n^{17}D$ 1.4941], yield 1 g (56%).

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