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SYNTHESIS OF SATURATED AND UNSATURATED DITHIOESTERS.

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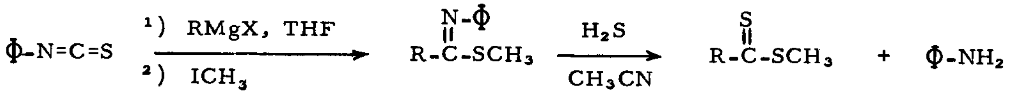
In the course of our studies concerning reactions of Grignard reagents with dithioesters and their synthetic uses, we needed α-and β-olefinic dithioesters. Various preparations of saturated dithioesters were described (1a-e) but such olefinic compounds appear scarcely in the literature (2, 3, 4, 5). We describe here a simple preparative method for dithioesters which is convenient for the synthesis of β-ethylenic dithioesters.

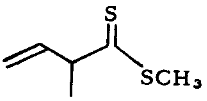
In 1923, Gilman and Kinney (6) isolated a N-phenylthio carboximidate by addition of phenylmagnesium bromide to phenylisothiocyanate and alkylation of the intermediate magnesium salt. Starting from this result and by using various Grignard reagents, we obtained thiocarboximidates in nearly quantitative yields. Treatment of these compounds by hydrogen sulfide gave the corresponding dithioesters.



$$\Phi\text{-N=C=S} \xrightarrow[2)\ ICH_3]{1)\ RMgX,\ THF} R\text{-}\overset{\overset{N\text{-}\Phi}{\|}}{C}\text{-}SCH_3 \xrightarrow[CH_3CN]{H_2S} R\text{-}\overset{\overset{S}{\|}}{C}\text{-}SCH_3 + \Phi\text{-}NH_2$$

		Yields %	Réf.
R= ethyl-	1	68	(1c-d)
R= isobutyl-	2	67	(1d)
R= ter-butyl-	3	59	(1d)
R= allyl-	4	41	
R= crotyl-	5*	77	
R= méthallyl-	6	78	
R= prenyl-	7*	72	(2a-b)

*With allylic Grignard reagents, the carbophilic addition on the thiocarbonyl of phenylisothiocyanate occurs as expected (7) exclusively with "inversion" of the allylic chain (e.g. structures of 5 and 7).



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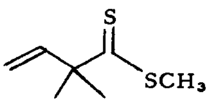

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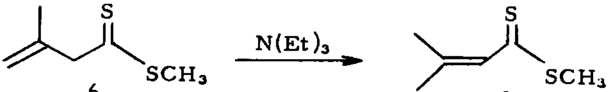

6 $\xrightarrow{N(Et)_3}$ 8

Conjugation of the double bond with the thiocarbonyl was readily obtained by catalytic amounts of triethylamine ; α-ethylenic dithioester 8 was prepared from 6 but from 4 and 5 only dimers (resulting from a Diels Alder reaction) were isolated at room temperature. We are now studying these compounds.

Experimental : Grignard reagents were prepared in tetrahydrofuran (8) according to the usual procedures and for allylic reagents the excess of magnesium was eliminated before use. Phenylisothiocyanate (0.1 mole for about 0.12 mole of Grignard reagent) was slowly added to the solution of organomagnesium compound previously cooled to 0°C (-10°C with allylic reagents). Agitation was maintained at room temperature for 1 hr (with alkyl magnesium bromides the solution was then warmed 1 hr at 50°). Methyl iodide (0.15 mole) was added and the mixture allowed to react at room temperature with agitation for about 16 hrs, then poured in an aqueous solution of ammonium chloride. The thiocarboximidate was extracted with petroleum ether and dried over sodium sulfate. After elimination of the solvent (and also of the duplication products of allylic Grignard reagents) under reduced pressure, the crude thiocarboximidate was dissolved in 200 ml of acetonitrile and the solution, cooled in an ice-salt bath, was saturated with hydrogen sulfide. Gas was passed in rather rapidly at first and then slowly for 8-9 hrs (when R= alkyl the saturated solution was allowed to react about 16 hrs more at 0°C). The yellow mixture, was poured in a 5 % aqueous solution of chlorhydric acid, extracted with petroleum ether, washed with dilute chlorhydric acid and water, and dried over sodium sulfate. Dithioesters were purified by distillation under reduced pressure or by passing through a column of silica (eluent : light petroleum ether).

NMR (CCl_4, $\delta_{TMS} = 0$) for new dithioesters : 4 2.56 (3H, s) ; 3.68 (2H, m∼d, 6 Hz) 4.9-6.3 (3H, m) ; 5 1.40 (3H, d, ∼7 Hz) ; 2.53 (3H, s) ; 3.85 (1H, m) ; 4.85-6.26 (3H, m) ; 6 1.73 (3H, t, ∼1 Hz) ; 2.55 (3H, s) ; 3.67 (2H, ∼s) ; 4.85 (2H, m) ; 8 1.92 (3H, d, ∼0.5 Hz) ; 2.18 (3H, d, ∼0.5 Hz) ; 2.55 (6H, ∼s) ; 6.63 (1H, m).

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8. THF was prefered to ether in which the alkylation step is very slow.