

EXCLUSIVE THIOPHILIC ADDITION OF
ORGANO-MAGNESIUM COMPOUNDS TO A THIOKETONE

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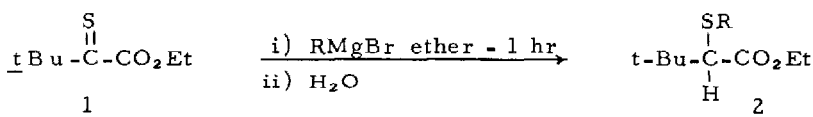
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The reaction of Grignard reagents with aliphatic and aromatic thioketones is now well documented (1-4 and ref. included). Thiophilic addition is frequently reported, thus confirming the prevision of a possible reverse polarity of the thiocarbonyl compared to the carbonyl's polarity. However other various reactions can be observed simultaneously : carbophilic addition, reduction, double addition and formation of enesulphides.

Previous work deals with thioketones bearing electronreleasing substituents. No study reports the reaction of organometallic compounds with thioketones bearing an electronwithdrawing substituent that would increase the positive character of the sulphur atom. To our knowledge, only two thioketones bearing an α -carbonyl group have been synthesized : monothiobenzyl (5,6) and recently ethyl 2-phenyl 2-thioxo ethanoate (7) that could, however, not be isolated analytically pure because of their instability. We focused our attention on non enethiolizable thioketone 1, *t*-BuCSCO₂Et, whose instability should be lowered through replacement of a phenyl group by an aliphatic group. We succeeded in preparing and isolating the deep violet compound 1 after treatment of the corresponding ketone with hydrogen sulphide in acid medium at room temperature (8).

Addition of the thioketone 1 to a solution of alkyl-magnesium bromide (RMgBr ; R= Me, Et, *t*Bu) in ether at room temperature gives, after hydrolysis and distillation, a pure colourless liquid (yield 50-70 %) identified as the compound 2 (RMN (CCl₄) : δ_{CH} = 2,96 - 3,02 ppm - IR (CCl₄) $\nu_{\text{C=O}}$ = 1730 cm⁻¹), resulting from thiophilic addition.

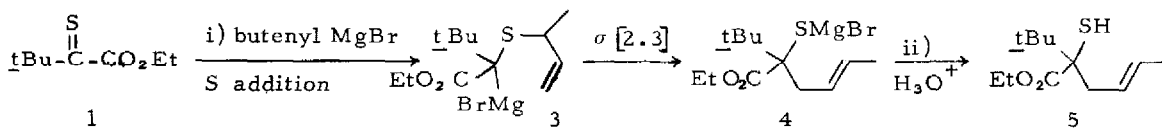


Reaction course is unchanged with tetrahydrofuran as a solvent, in contrast with previous observations (2). Compound 2 is still obtained by reacting methyl-magnesium iodide in ether, however known to afford C-addition. We must also note that the ester function remains unattacked, even with a tenfold excess of Grignard reagent. Such an exclusive thiophilic addition has never been reported for thioketones.

+ It prompted us to investigate the behaviour of thione 1 towards organo magnesium
This work is part of the thesis A.V. will submit in the near future.

compounds known to lead to C-addition : allylic reagents (9). Thus, by reacting various thioketones with 2-buten 1-yl magnesium bromide, Dagonneau obtained thiols, bearing a methylallyl group. It is actually known that butenyl Grignard reagents afford branched compounds and not linear ones. Treatment of the thioketone 1 with 2-buten 1-yl magnesium bromide produces the thiol 5 (RMN ; $\delta_{\text{SH}} = 2,02$ ppm, $\delta_{\text{Me-c=c}} = 1,68$ ppm), bearing a crotyl group and not a methyl allyl group. Formation of the mercaptan 5, from apparent carbophilic addition, may be interpreted as follows (10) :

- thiophilic addition to a methyl allyl sulphide 3
- [2.3] sigmatropic rearrangement of the corresponding carbanion giving the compound 4, with a crotyl substituent. Such a rearrangement was previously reported (11, 12).
- hydrolysis to the crotyl thiol 5.



Such a structure reversal seems previously unreported. This interpretation is supported by a very recent study about the addition of allylic Grignard reagents to dithioesters : with butenyl magnesium bromide methyl allyl products are formed by a direct carbophilic addition (13). Crotyl group of compound 5 has a trans stereochemistry (IR : CH bend at 960 cm^{-1}) in agreement with other iso electronic sigmatropic rearrangements of compounds having a methyl allyl group that are known to lead to the same geometry.

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- 8 - Ethyl 2,2-dimethyl 3-thioxy butanoate 1 :
UV (cyclohexane) $\lambda_{\text{max}} = 539\text{ nm}$ ($\epsilon = 11$). IR (CCl_4) $\nu_{\text{C=O}} = 1727\text{ cm}^{-1}$.
Analysis. Calc. : C, 55,17 ; H, 8,05 ; S, 18,40
Found : C, 55,21 ; H, 8,25 ; S, 18,27.
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- 10 - A different mechanism of addition of butenyl magnesium compound, leading to linear products, has been considered for sterically hindered ketones. We ruled it out here, in the light of previous results showing that hindered thioketones do not behave differently from unhindered ones (9).
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