

REACTIONS OF ALLYLIC GRIGNARD REAGENTS WITH DITHIOESTERS.

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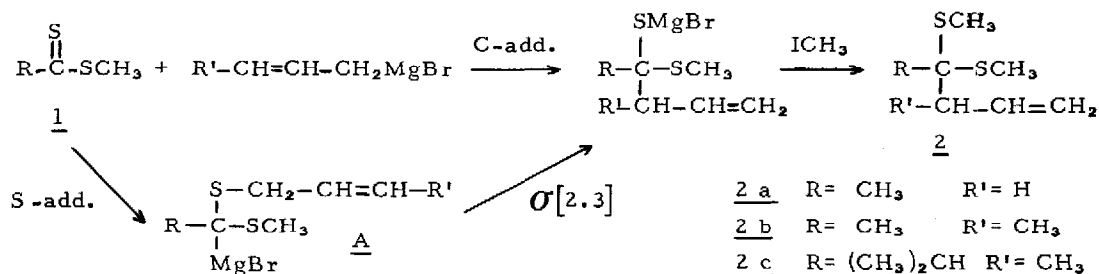
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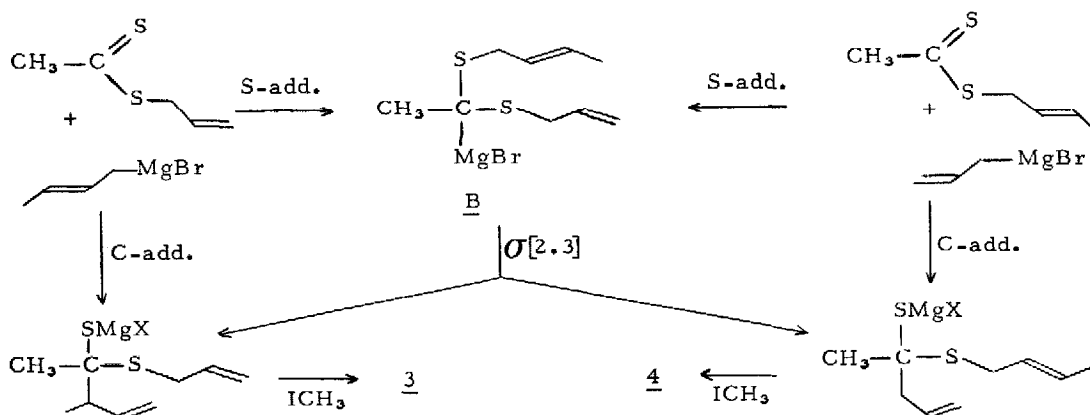
In a previous paper, we have shown that a clean thiophilic addition is obtained by réactions of alkyl magnesium bromides with S-alkyl dithioesters at -17° in tetrahydrofuran (1). Concerning reactions of allylic organometallics with the thiocarbonyl group, only thioketones were studied and carbophilic additions were observed (2, 3). We describe here some results about the reactions of allylic Grignard reagents with dithioesters; the observed additions reveal that these reactions proceed through a direct carbophilic process.

The reactions could be carried out at -60° in tetrahydrofuran. We obtained exclusively, after methylation, the dithioacetals 2 (a, b, c) of β -unsaturated ketones, products of carbophilic addition with "inversion" of the allylic chain (with 2-butenyl magnesium bromide we obtained products bearing a 1-methyl allyl substituent).

It is known that 2-butenyl magnesium bromide or 3-methyl 2-butenyl magnesium bromide reacts with unhindered carbonyl compounds to afford products with branched allylic chain (4, 5, 6). Besides, in a previous study (7) we have shown that thiophilic addition of an alkyl magnesium bromide (in tetrahydrofuran at low temperature) to substituted S-allylic dithioesters is followed by a [2.3] sigmatropic shift involving the S-allylic chain and leading to dithioacetals of β -unsaturated ketones. So, two interpretations can be given for the formation of the products 2 (a, b, c): a direct carbophilic addition, involving the most substituted carbon atom of the allylic magnesium bromide by a mechanism which may be similar to the one suggested for the reactions with carbonyl compounds (8), or an initial thiophilic addition, involving therefore the less substituted carbon atom of the allylic reagent, followed by a [2.3] sigmatropic rearrangement of the intermediate carbanion A.



In an attempt to clarify this problem we investigated the reactions of allylic Grignard reagents with S-allylic dithioesters. We ran the reaction of crotyl magnesium bromide with the S-allyl dithioacetate and, under the same experimental conditions, the reaction of allyl magnesium bromide with the S-crotyl dithioacetate. Considering an initial thiophilic addition, we expect, from both reactions, the formation of the same intermediate carbanion B which should undergo a [2.3] sigmatropic rearrangement involving either one, or the other, or both S-allylic groups. So, both reactions should give, after methylation, the same mixture of the dithioacetals 3 and 4 (or the same dithioacetal 3 or 4). On the other hand, a direct carbophilic path should yield 3 for the first reaction and 4 for the second reaction. This last situation is observed experimentally and this result rules out the thiophilic path.



A very recent result (9) seems to support this conclusion : addition of 2-butenyl magnesium bromide to the thioketone $t\text{-Bu}(\text{C}=\text{S})\text{COOEt}$ bearing an electronwithdrawing substituent, affords a product of C-addition with a linear allylic chain. This may be interpreted by an initial thiophilic addition of the branched allylic chain followed by a [2.3] sigmatropic shift.

Structures of compounds 2 (a, b, c), 3 and 4 were established from their microanalysis, their N.M.R. and mass spectra. They will be discussed in a full paper relating to the addition of allylic, benzylic, propargylic and vinylic Grignard reagents to dithioesters.

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