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THE REACTION OF VINYLIC GRIGNARD COMPOUNDS WITH SOME THIOKETONES

M. DAGONNEAU*

Département de Chimie, Université de Caen, 14032 Caen Cedex (France)

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Summary

Vinylic organomagnesium compounds react with thiobenzophenone, thiopinacolone and thiopivalophenone to give first the organomagnesium compound resulting from the addition of the vinyl group on carbon. This compound rearranges, probably by a radical mechanism, to give an *S*-addition compound. Terpenic thioketones (thiocamphor and thiofenchone) do not react.

The reaction of organomagnesium compounds with thioketones has only recently been studied in spite of some early work on diarylthioketones [1—3]. Aliphatic Grignard reagents were the first to be investigated [4—11]. These reagents yield mainly the sulfide resulting from the addition of the organic radical to the sulfur atom of the thiocarbonyl group, but allylic Grignard reagents seem to behave in the same way as with the carbonyl group of ketones: the addition on carbon with rearrangement is observed [12]. These results prompted us to study the reaction of vinylmagnesium halides (bromide or chloride) on thiobenzophenone Ia, thiopivalophenone Ib, thiopinacolone Ic, thiocamphor Id and thiofenchone Ie in THF. Depending on the time of contact of reagents with thioketones Ia and Ic, α-ethylenic thiol II (resulting from the addition of the vinyl group to the carbon of thiocarbonyl) and/or vinylic sulfide III (resulting from the addition to sulfur) were obtained after hydrolysis. With thiopivalophenone Ib, only sulfide IIIb was isolated, after 1 h as well as 1 min reaction time. Inverse addition (Grignard on thioketone) did not change this result. Finally, thiocamphor Id probably completely enethiolized (complete decoloration of the solution) in 4 h and was regenerated on hydrolysis. Thiofenchone Ie

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* Present address: Institut National Supérieur de Chimie Industrielle de Rouen, B.P. 08, 76130 Mont-Saint-Aignan (France).

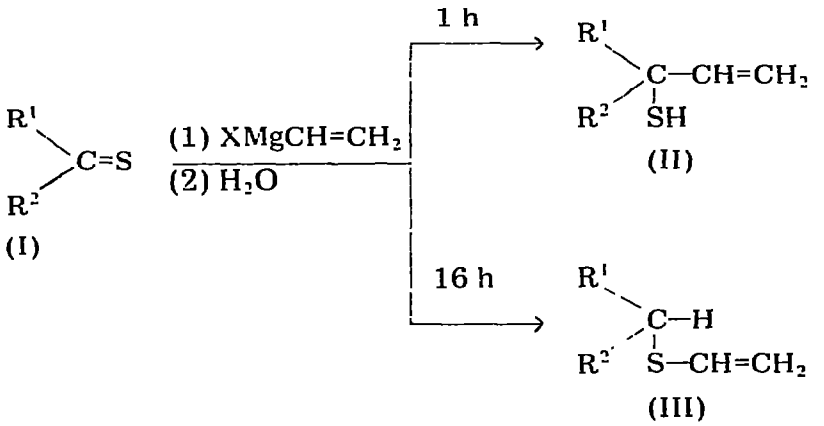
TABLE 1

THE REACTION OF VINYLMAGNESIUM HALIDES WITH THIOKETONES

Thioketone	Time	Products (%)		
		I	II	III
Ia	1 h	—	(30)[a]	—
Ia	16 h	—	—	(11)
Ib	1 min to 16 h	—	—	100
Ic	1 h	—	80[b]	—
Ic	4 h	—	13	46
Id	4 h	100	—	—
Ie	4 days	100	—	—

[a] Thiol IIa and sulfide IIIa decomposed during VPC to produce mainly diphenylmethane. The figures in parentheses show the actual yield of the compounds after column chromatography. [b] This compound has been previously isolated [6].

did not react, even after 4 days. This reminds us of the behavior of terpenic thioketones with non-reducing aliphatic Grignard reagents [7].



The compounds, separated by VPC or chromatographed on a column were identified by their NMR spectra (Table 2). The proportions of the compounds I, II or III present in the mixture after hydrolysis are given in Table 1.

Discussion

With thiobenzophenone Ia and thiopivalophenone Ib we detected by ESR at 20° the presence of a stable free radical in the reaction medium as soon as the reaction had started (Fig. 1). By analogy with our earlier observations on aliphatic Grignard reagents using ESR [13—15] the radicals here are probably diphenylvinylthiomethyl IVa and t-butylphenylvinylthiomethyl IVb, resulting from homolytic cleavage of the corresponding organomagnesium compound. In the earlier work we were able to simulate the ESR spectra of the radicals but here, because the hydrogen atoms of the vinyl group are not equivalent, the resulting spectra are probably too complex to be simulated. The g factors are higher than in the aliphatic series (g = 2.003 [13, 14]) probably because of participation of the non-bonding orbital

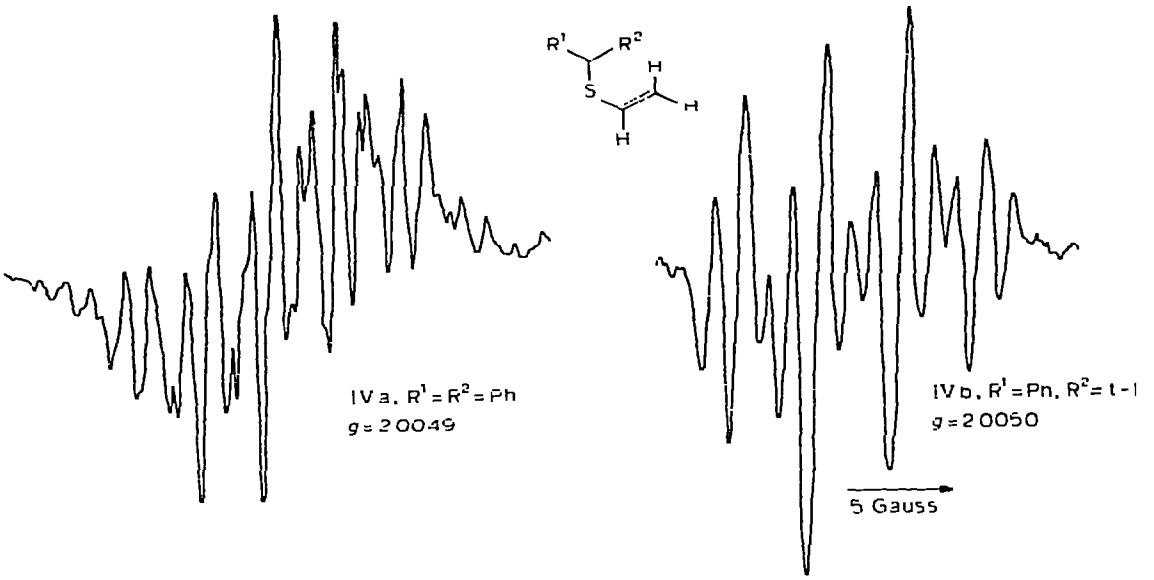
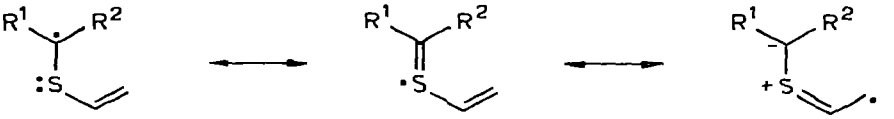


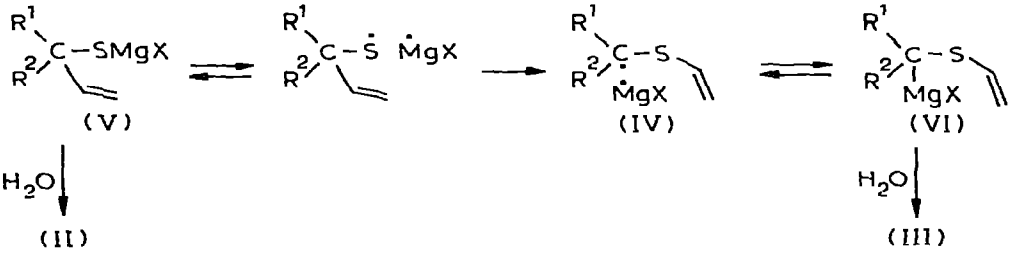
Fig 1.

of the sulfur in conjugation; the form B contributes notably to the stability of the radical, allowing an extension of the delocalization from the vinyl group.



(A) (B) (C)

We compared the presence of the radicals IV to the yield of products II or III whose structure depends on the time of reaction. These observations prompt us to propose a radical mechanism such as the following:



(V) (IV) (VI)

(II) (III)

If the reaction time is short, one obtains the kinetic product (organomagnesium compound V), but after longer reaction times the compound corresponding to the most thermodynamically stable radical is formed (compound VI)*. The transient thiyl radical cannot be detected using ESR at room temperature and

* Such a rearrangement is sometimes observed in the course of the reaction of some aliphatic Grignard reagents with thiobenzophenone [11].

the only paramagnetic species which is observed is the tertiary radical IV*. Possibly one can imagine a rotation of the vinylic group. To test this we treated thiobenzophenone Ia with 1-propenylmagnesium bromide: the NMR spectrum of the product showed that the hydrocarbon chain remains linear**. One can account for the addition of aliphatic Grignard reagents to thioketones using the concept of hard and soft acids and bases (HSAB): hard reagents react more easily with the carbon of the thiocarbonyl group and soft reagents add better to the more polarizable sulfur [8, 11]. It is known that the ionic character of the carbon—metal bond is more accentuated with a sp^2 carbon than with a sp^3 carbon [16]; consequently a vinylic Grignard reagent will be harder than an aliphatic one and the reactions will be charge-controlled. This explains why the kinetic product (the only significant one according to the HSAB theory [17]) is the product of *C*-addition.

Experimental

Microanalyses. All the quoted compounds gave analytical results (C, H, S) corresponding to their formulae (max. disparity ± 0.3%).

NMR. The spectra were recorded on a Varian A 60 D spectrometer. Products were dissolved in CCl_4 and TMS was used as an internal reference.

Thioketones. The preparation of thioketones Ia to Ie has been described in another paper [12].

Vinylic Grignard reagents. They are prepared in THF by Normant's method [18].

TABLE 2

NMR SPECTRA OF VINYLIC THIOLS II AND VINYLIC SULFIDES III[a]

Compound	tertiary H	SH[b]	ABX syst.[c]	R^1	R^2
				C_6H_5	
IIa		s 2.35	AB m 4.6—5.4	m 6.9—7.5	
			X m 5.9—6.8		
IIIa	masked		AB m 4.9—5.4	m 6.8—7.8	
			X m 5.9—6.8		
IIIb	s(w) 3.83		AB m 4.8—5.2	t-Bu	C_6H_5
			X m 5.7—6.3	s 0.98	m 7.1—7.4
IIc		s 1.33	AB m 4.8—5.3		CH_3
			X m 5.9—6.5	s 1.00	s 1.47
IIIc	q 2.77		AB m 4.9—5.3		
			X m 6.1—6.8	s 0.98	d 1.30

[a] Chemical shifts in ppm downfield from TMS (δ = 0); s = singlet, d = doublet, q = quartet, m = multiplet, w = signal widened by long distance couplings [b] This signal disappeared on adding D_2O. [c] To a first approximation

* The tertiary radical IVc corresponding to thiopinacolone Ic, unstable with an α hydrogen, is probably formed but may undergo different reactions (vinyl transfer, hydrogen transfer [14]), and this may explain the relative decrease in the proportions of the compounds II and III when the reaction time is prolonged with this thioketone

** In this case, however, only the *S*-addition compound is isolated (yield 56% after 5 min of reaction) by column chromatography.

Reaction with thioketones. A solution of about 0.01 mol of thioketone in THF was slowly added to 0.05 mol of organometallic compound at 20°. The colour changed from blue to red with thiobenzophenone; the colour faded very rapidly with thiopivalophenone. Thiopinacolone was immediately decoloured and thiocamphor was decoloured in 4 h. The mixture was stirred under a nitrogen atmosphere until the hydrolysis, which was performed with a saturated solution of ammonium chloride, was complete. The oily crude product obtained after work-up was chromatographed on a silica gel column in the case of the derivatives of thiobenzophenone. A second chromatographic run was necessary to reach analytical purity. The other compounds were separated by VPC at 150—200° on a column containing 40% of methylsilicone SE 30 impregnated Chromosorb W AW 45/60. The carrier gas was hydrogen.

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