

HOMOLYTIC CLEAVAGE OF ORGANO-MAGNESIUM COMPOUNDS - III (1, 2)

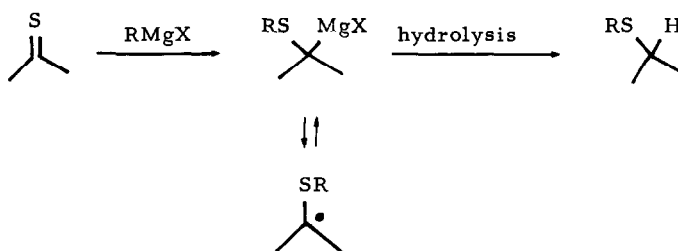
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(Received in UK 20 July 1973; accepted for publication 3 August 1973)

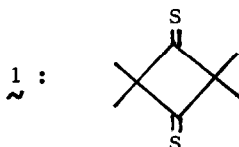
In the course of our investigation of thioketones, we studied their behaviour with organo-magnesium compounds. "Thiophilic" addition of R in RMgX is now well established with thiobenzophenone (3, 4, 5), thiopivalophenone (6), thiopinacolone (7), thiocamphor and thiofenchone (8) and unsaturated thioketones (9).

We have already reported that the resulting organo-magnesium compounds could be cleaved to give a free radical, detected with an EPR spectrometer in some cases (1, 2).



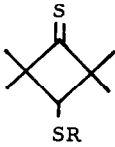
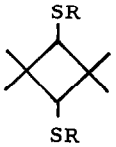

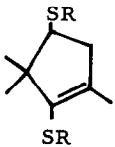
This observation prompted us to study the behaviour of such a radical included in a molecule containing another reactive site and particularly to investigate if a new bond could be formed via internal elimination.

Therefore we have studied the reaction of tetramethyl cyclobutanedithione-1,3 ¹ with some alkyl-magnesium halides in THF or ether during varied time intervals.

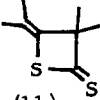


After hydrolysis VPC allowed us to isolate four main products, identified by NMR spectra and analysis :

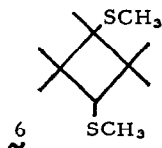
- alkylthio-3 tetramethyl cyclobutanethione 2, red coloured (10)
 (nmr (CCl₄): C3 hydrogen at 3.4 ppm, singlet)
- bis (alkylthio)-1,3 tetramethyl cyclobutane 3
 (C1 and C3 hydrogens at 2.8 ppm, singlet)
- bis (alkylthio)-1,3 tetramethyl bicyclo[1.1.0] butane 4
 (Me singlets at 1.67 and 1.90 ppm)
- bis (alkylthio)-2,4 tetramethyl-1,3,3 cyclopentene 5
 (C3 Me at 0.94 and 1.15 ppm; C1 Me at 1.87 ppm).

RMgX	Reaction time (hours)				
		<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Solvent : THF					
MeMgBr	1.5	-	-	50	20
	20	-	-	65	30
EtMgBr	1.5	70	25 (cis)	-	-
	20	-	40 (15 trans, 25 cis)	15	10
<u>t</u> -BuMgBr	1.5	45	-	-	-
	20	55	-	-	-
Solvent : ether					
MeMgBr	1	20	-	40	20
	20	2	-	40	20
MeMgI	20	65	-	20	9

* Ratio [organometallic] / [dithione] ~ 5.

** The yields are lower because of the formation of the thiolactone  (11).
 This compound is usually formed by alkaline treatment of the dithione 1 (11).

*** With CH₃MgBr and CH₃MgI in 20 h. we obtained also 36 and 4 %, respectively, of a compound 6 resulting from a double addition on one of the thiocarbonyls (12).



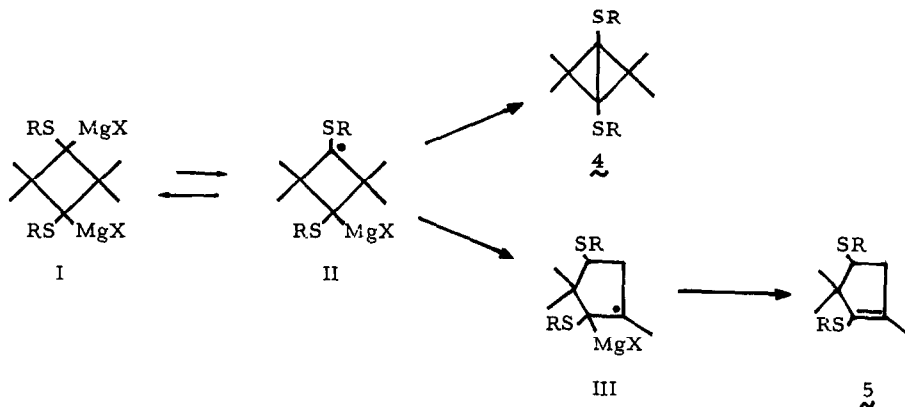
nmr : C3 hydrogen at 2.92 ppm, singlet ;
 C1 and C2 MeS at 2.13 ppm, singlet ;
 C1 Me at 1.97 ppm, singlet.

Formation of compounds 2 and 3 is normal in the light of earlier reported results : first a rapid "thiophilic" addition proceeds, then a second one that may be sterically hindered in the presence of a bulky group such as tert-Butyle. As already shown, these reactions are appreciably slower in ether than in THF.

More interesting is the formation of two new "anomalous" compounds : bicyclobutane 4 and cyclopentene 5 . They are always obtained together, mostly from organo-magnesium compounds having few hydrogen atoms : Me \gg Et and not for t-Bu .

These facts suggest to us a radical mechanism, in accordance with earlier results and the observation in the reaction mixture of a labile EPR spectrum with fine structure. The first step involves a homolytic cleavage of one carbon-metal bond of the product I . The radical II may then follow two reaction paths :

- internal elimination of MgX^\bullet would lead to a bicyclo compound 4 .
- hydrogen transfer and expansion of the cyclobutane ring would lead to a compound III in which MgX^\bullet could then be eliminated .



It can be seen, after these results, that the radical formed via the homolytic cleavage of C-Mg bond in compounds of the type II can react with another site of the molecule. We are now investigating some new types of such reactions which can lead to unusual compounds.

- References -

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- 8 - M. DAGONNEAU, D. PAQUER and J. VIALLE, Bull. Soc. chim. Fr., 1973, p. 1699.
- 9 - P. METZNER and J. VIALLE, Bull. Soc. chim. Fr., 1973, p. 1703.
- 10 - After completion of the reaction, the mixture is discoloured but sometimes the red colour characteristic of the thiocarbonyl group appears on hydrolysis (compound 2): this shows that the C=S group is first complexed with the GRIGNARD reagent before the reaction proceeds further.
- 11 - E.U. ELAM and H.E. DAVIS, J. org. Chem., 1967, 32, 1562 .
- 12 - Such a double addition has been observed with thiopinacolone (7), thiopivalophenone (6) and thiobenzophenone (13).
- 13 - M. DAGONNEAU and J. VIALLE, unpublished results.