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REACTIONS OF (2-BROMOALKYL)TRIPHENYLSILANES WITH MAGNESIUM AND GRIGNARD REAGENTS

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SUMMARY

The reactions of (2-bromoalkyl)triphenylsilanes with magnesium and Grignard reagents were investigated in several solvents. Product analysis indicates that these reactions follow homolytic and other pathways. Both the solvent and the Grignard reagent play an important part in directing the course of the reaction.

We reported recently the results of some preliminary investigations on the reactions of (2-bromoethyl)triphenylsilane (I) with magnesium and Grignard reagents[1]. We have now examined these reactions in greater detail and have extended our investigations to the related reactions of the secondary halide (2-bromopropyl)triphenylsilane (II). In our original investigation we found that (I) reacted with a number of Grignard reagents to give good yields of ethyltriphenylsilane (III) after work up of the reaction mixture, and we concluded from this observation that halogen–metal exchange had occurred and that the carbanion $Ph_3SiCH_2CH_2^-$ possessed some additional stability not available to alkyl carbanions. However, in recent years evidence has been accumulating that radical intermediates are formed in many reactions of organometallic compounds with halogen derivatives[2], and in consequence we have also examined certain of these reactions to determine the relative importance of the radical and ionic pathways in product formation.

The results of these studies are presented in Tables 1 and 2.

Although not quantitative, the product yields were reproducible. The residual material which was not separated and identified would appear from spectroscopic analysis to be a mixture of products derived from reaction of the various intermediates with the solvent.

We established, by work up of the reactions with deuterium oxide, that the Grignard of (I) is stable in both tetrahydrofuran and diethyl ether; this observation helped us in some cases to distinguish between radical and organometallic pathways. The n-propyltriphenylsilane (IV) derived from the reaction of (II) with magnesium incorporated no deuterium indicating that either the Grignard of (II) is unstable under the conditions of the reaction or that a second electron transfer does not take place in this system in which the radical would be expected to be more stable than the carbanion.

TABLE 1

PRODUCT YIELDS FROM THE REACTIONS OF (I) WITH RMgX

R	*Quenching reagent*	*Product yields (%)*				
		$Ph_3SiCH_2CH_3$	*$Ph_3SiCH_2CH_2D$*	*$(Ph_3SiCH_2CH_2)_2$*	*$Ph_3SiCH_2CH_2R$*	*Others*
In ether						
Pr	H_2O	68		8	4	Ph_3SiR (2)
Pr	D_2O	40	30	10	5	Ph_3SiR (2)
Bu	H_2O	51		10	7	$CH_3(CH_2)_2CH_3$ (24); $CH_3CH_2CH{=}CH_2$ (11); $CH_3(CH_2)_6CH_3$ (42)
Bu-2-*d*$_2$	H_2O	34		19	4	$Ph_3SiCH_2CH_2Br$ (4); $CH_3(CH_2)_2CH_3$ (28); $CH_3CH_2CH{=}CH_2$ (3)
t-Bu	D_2O		51		4	$Ph_3SiCH_2CH_2Br$ (38)
Ph	H_2O	8		4	40	Ph_3SiOH (17); Ph_3SiR (8)
Ph	H_2O^a	0		5	50	
In tetrahydrofuran						
Pr	H_2O	52		16	2	$Ph_3SiCH{=}CH_2$ (4)
Pr	H_2O^a	14		16	2	$Ph_3SiCH{=}CH_2$ (2); "polystyrene"
Pr	D_2O	30	20	16	3	$Ph_3SiCH{=}CH_2$ (5)
Bu	H_2O	55		11	3	$Ph_3SiCH{=}CH_2$ (7); $CH_3(CH_2)_2CH_3$ (63); $CH_3CH_2CH{=}CH_2$ (33)
Ph	H_2O	40		13	5	$Ph_3SiCH_2CH_2Br$ (12) Ph–Ph (52)
Ph	D_2O	36	4	16	4	$Ph_3SiCH_2CH_2Br$ (9)
In benzene						
Pr	H_2O	40		15	9	$Ph_3SiCH{=}CH_2$ (27)
Pr	D_2O		40	16	10	$Ph_3SiCH{=}CH_2$ (25)
Bu	H_2O	46		11	4	$Ph_3SiCH{=}CH_2$ (28)
3-Butenyl	H_2O	66		1	3	$Ph_3SiCH{=}CH_2$ (12)
Allyl	H_2O				94	
Ph	H_2O	4			90	
Ph	H_2O^a				95	

[a] Reaction in presence of styrene.

TABLE 2

PRODUCT YIELDS FROM THE REACTIONS OF (II) WITH PhMgBr

Solvents	*Quenching reagent*	*Product yields (%)*			
		$Ph_3Si(CH_2)_2Me$	*$(Ph_3SiCH_2CHMe)_2$*	*$Ph_3SiCH_2CHMePh$*	*Others*
Ether	H_2O	<1	3	79	Ph_3SiOH (12); Ph_3SiPh (12); $Ph_3SiCH_2CH{=}CH_2$ (1)
Tetrahydrofuran	H_2O	22	24	13	Ph_3SiOH (4); Ph_3SiPh (6); $Ph_3SiCH_2CH{=}CH_2$ (9) $Ph_3SiCH_2CHMeOH$ (5); $Ph_3SiCH{=}CHMe$ (6); Ph–Ph (50)
Benzene	H_2O			88	Ph_3SiOH (8)

In the reaction of (I) and (II) with phenylmagnesium bromide in ether, Wurtz coupling is the principal process, the coupling reaction is unaffected by the addition of styrene and is probably not homolytic, which is consistent with the recent observation[3] that the coupling of alkyl halides with phenylmagnesium bromide and phenyllithium is a concerted reaction. However at variance with this proposal is the finding that (II) gives greater yields of coupling products than (I) and it would be expected that substitution at the reaction site would retard a concerted process. The hydrocarbons (III) and (IV) are the major products from the reaction of (I) and (II) with alkyl Grignard reagents. Neither (III) nor (IV) is formed by true halogen–metal exchange, the exchanged halide could not be detected even in systems in which high yields of (III) and (IV) were found. The hydrocarbon products are derived both from the organometallic intermediates and by hydrogen abstraction from the medium by the intermediate radical. The 2-triphenylsilylethyl radical probably abstracts hydrogen from both the alkyl radical of the Grignard and from the solvent, since, although there is no (2-deuterioethyl)triphenylsilane formed in the reaction of (I) with (2,2-dideuteriobutyl)magnesium bromide a lower yield of (III) is obtained from the reaction of (I) with the heavy compound.

The reactions of (I) with several alkyl Grignards were quenched with deuterium oxide in order to determine the extent of organometallic involvement in the production of (III). From the reactions with n-propyl- and tert-butylmagnesium bromides in ether there was obtained (III) approximately 40% and 100%, respectively, deuteriated in one position. These results indicate, as would be expected, that the carbanion/radical ratio and the extent of electron transfer depends on the electron-donating ability of Grignard reagent. Somewhat surprisingly Bach[4] found in the reactions of benzyl halides with alkyl Grignards that functional exchange follows the opposite order, ethyl > isopropyl > tert-butyl and he concluded that the exchange reaction was highly sensitive to steric hindrance.

The dimerisation reaction is probably homolytic, no dimer is found in the reaction of (I) with tert-butylmagnesium bromide, in which system only carbanion intermediates are detected by deuteriation, whereas approximately 10% dimer is isolated from the reaction of (I) with n-butylmagnesium bromide which is partly radical. However, if this reaction is homolytic, it must be a cage process, since styrene addition has no effect on dimer formation.

In tetrahydrofuran Wurtz coupling is only a minor reaction and in the reactions of both (I) and (II) with Grignard reagents dimerisation and exchange are the major reactions. Deuteriation studies show that in the reaction of (I) with phenylmagnesium bromide the product (III) arises entirely from the radical intermediate, whereas with the n-propyl Grignard only about 70% of the hydrocarbon is derived from this source. The latter result is confirmed by the observation that the yield of (III) is reduced from 50% to 14% in the presence of styrene as a radical scavenger. (The expected yield of (III) is 15% based on the yield of deuteriated product).

Almost quantitative yields of the Wurtz coupled products are isolated from the reactions of (I) and (II) with phenyl- and allylmagnesium bromides in benzene. Addition of styrene has no effect on the yield of coupled products. In the reactions of (I) and (II) with alkyl Grignards formation of the hydrocarbons (III) and (IV) is again the major reaction. In benzene it would not be expected that the 2-triphenylsilylethyl radical would abstract hydrogen from the solvent and we have established by working up the reaction mixtures with deuterium oxide that in this medium the hydrocarbon (III) is not formed by hydrogen abstraction by the intermediate radical from the alkyl group of the Grignard reagent.

In only a few cases did we investigate the products derived solely from the Grignard reagent. High yields of biphenyl were isolated from the reactions of both (I) and (II) with phenylmagnesium bromide in tetrahydrofuran. We considered the possibility that the halogen–metal exchange had occurred and that the exchanged halide was subsequently consumed in the coupling reaction:

$$\mathrm{PhMgBr + PhBr \rightarrow Ph{-}Ph + MgBr_2}$$

This was found not to be the case, negligible yields of biphenyl occurred in the preparation of the phenylmagnesium bromide, and in the reaction of phenylmagnesium bromide with bromobenzene in the presence and absence of magnesium bromide, suggesting that the biphenyl probably resulted from the coupling of phenyl radicals.

The yields of alkene and alkane from the reaction of n-butylmagnesium bromide with (I) in the three solvents were measured. In benzene the difference in the yields of butane and butene is approximately equal to the yield of vinyltriphenylsilane suggesting that the alkane is derived from both disproportionation and cross-disproportionation reactions. In tetrahydrofuran a much lower yield of vinyltriphenylsilane is found, and the excess of alkane over alkene must arise by hydrogen abstaction from the solvent by alkyl radicals. In ether poor yields of both butene and butane are found, the main product formed from the alkyl radicals is octane, the explanation for the difference in behaviour of the alkyl radicals in the two ethereal solvents is not immediately obvious.

EXPERIMENTAL

(2-Bromopropyl)triphenylsilane (II)

Dry hydrogen bromide was bubbled through a 20% solution of triphenylallylsilane in carbon tetrachloride. Evaporation of the solvent followed by recrystallisation from ligroin gave the product in 70% yield, m.p. 89–91°. (Found: C, 65.76; H, 5.48; Br, 20.5. $C_{21}H_{21}BrSi$ calcd.: C, 66.13; H, 5.55; Br, 20.9%.) NMR: τ 2.5 (15H)m; τ 5.6 (1H)m; τ 7.7 (2H)m; τ 8.4 (3H)d.

Reactions of compounds (I) and (II) with magnesium and Grignard reagents

These reactions were carried out and the products separated as described previously[1]. The major products were identified by spectral and chemical analysis, the minor products by GLC and spectral analysis. The following data are for major products not described in the previous publication; 1,4-bis(triphenylsilyl)-2,3-dimethylbutane, m.p. 128–130°. (Found: C, 83.10; H, 6.95. $C_{42}H_{42}Si_2$ calcd.: C, 83.66; H, 7.02%.) NMR ($CDCl_3$ soln.): τ 2.6 (30H); τ 8.2 (2H); τ 8.7 (4H); τ 9.3 (6H). (2-Phenylpropyl)triphenylsilane, m.p. 92–94°. (Found: C, 85.57; H, 7.03. $C_{27}H_{26}Si$ calcd.: C, 85.66; H, 6.92%.)

Gas analysis

The gases were analysed qualitatively by GLC using a squalene column with helium as carrier gas, the quantitative determinations were carried out by conventional gas analysis techniques.

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REFERENCES

1 A. J. Bourne, A. W. P. Jarvie and A. Holt, *J. Chem. Soc. C*, (1970) 1740.
2 G. A. Russel and D. W. Lawson, *J. Amer. Chem. Soc.*, 91 (1969) 3967; H. R. Ward, *ibid.*, 89 (1967) 5517; H. R. Ward and R. G. Lawler, *ibid.*, 89 (1967) 5518; A. R. Lepley, *Chem. Commun.*, (1969) 64; A. R. Lepley and R. L. Landau, *J. Amer. Chem. Soc.*, 91 (1969) 748.
3 R. M. Magid, *J. Org. Chem.*, 36 (1971) 2099.
4 F. L. Bach, *Thesis*, New York University, 1963.