

Paramagnetic products formed in the reactions of organometallic compounds

XV.* Influence of solvents on diaryl ketyl radicals

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Ketyl radicals $\text{PhCO}^{\cdot-}\text{—R}$ arise as products of the reactions of benzenecarboxylic acid (PhCOOH) with phenylmagnesium bromides (RMgBr) in the presence of nickel in diethyl ether provided the ratio $\text{RMgX}:\text{PhCOOH} \doteq 4$. An addition of solvents, such as Pr_2O , $n\text{-Bu}_2\text{O}$, *tert*- BuOMe , benzene, toluene, hexane, cyclohexane to diethyl ether has no influence on the course of reaction and the values of splitting constants of the investigated radicals. The presence of dimethoxyethane, dioxan, and hexamethylphosphortriamide manifests itself by a change in splitting constants and the stability of radicals increases from one to several days. Moreover, a greater excess of RMgBr ($\text{RMgBr}:\text{PhCOOH} \doteq 8$) is necessary for generation of the radicals. A new type of intermediates — aroyl radicals may be observed in tetrahydrofuran.

В реакциях бензолкарбоксильной кислоты (PhCOOH) с фенилмагни-бромидами (RMgBr) в присутствии никеля в диэтилэфире возникают кетил радикалы $\text{PhCO}^{\cdot-}\text{—R}$, если соотношение $\text{RMgX}:\text{PhCOOH} \doteq 4$. Прибавление таких растворителей, как Pr_2O , $n\text{-Bu}_2\text{O}$, *трет*- BuOMe , бензол, толуол, гексан, циклогексан к диэтилэфире не влияет на протекание реакций и на значения констант расщепления изучаемых радикалов. Присутствие диметоксиэтана, диоксана и гексаметилфосфортриамида вызывает изменение констант расщепления, увеличение стабильности с одного до нескольких дней и для образования радикалов необходимо больше RMgBr ($\text{RMgBr}:\text{PhCOOH} \doteq 8$). В тетрагидрофуране наблюдается новый тип промежуточного продукта — ароил радикалы.

The influence of solvents on reactivity of organomagnesium compounds was described in several papers [2—21]. It is very intricate and depends on the type of substrate, basicity of individual components, solvation, steric factors, and polarity of medium. For this reason, we are not able to arrange an absolute series of solvents and draw general valid conclusions.

*For Part XIV see Ref. [1].

The solvents affect the relative yields of individual products in reactions of the Grignard reagents with ketones as well as the overall reaction rate. According to the influence on the course of the reaction of pinacolone with *n*-propylmagnesium bromide, the investigated solvents were divided into two groups [5, 11—17]. The first group comprises the solvents in which the reactions proceed in the same way as in diethyl ether, *i.e.* diisopropyl ether, di-*n*-butyl ether, anisole, and most amines. The solvents having similar influence on the course of reaction as tetrahydrofuran, *i.e.* dimethoxymethane, diethoxyethane, and hexamethylphosphortriamide belong to the second group. The reaction of phenyl isopropyl ketone with the Grignard reagents in diethyl ether is an addition reaction whereas it is a reduction in hexamethylphosphortriamide [20, 21]. The reaction of fluorenone with $(C_6H_5CH_2)_2Mg$ gave a stable signal in tetrahydrofuran, dimethoxyethane, and hexamethylphosphortriamide the stability of which, however, considerably decreased in diethyl ether and triethylamine.

In this study, we investigated the influence of solvents on the formation, stability, and values of splitting constants of the radicals arising in the reaction of benzenecarboxylic acid with phenylmagnesium bromide and 4-*tert*-Bu-phenylmagnesium bromide in the presence of nickel.

Experimental

The experiments were carried out in argon atmosphere. The purification of solvents may be characterized by the following generalized procedure: First of all, the solvents were dried over $MgSO_4$ or $CaCl_2$, then further dried over sodium and finally dried by molecular sieves or addition of the Grignard reagent or organometal and distilled or subjected to fractional distillation in argon atmosphere.

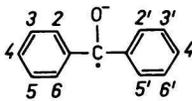
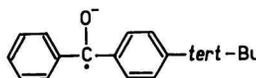
Benzenecarboxylic acid was obtained from Lachema, Brno. The Grignard reagents and their 2 M solutions were prepared by the standard method in diethyl ether in argon atmosphere. We used the experimental technique described in preceding papers [22—24]. The ketyl radicals were generated immediately in the e.s.r. cells at laboratory temperature in argon atmosphere. We always added diethyl ether and particular solvent to 0.1 cm³ of the 0.5 M solution of benzenecarboxylic acid in this solvent so that a 0.14 M solution of acid was obtained. The volume percentage of this solvent with respect to diethyl ether changed in the range from 80 to 10%. Subsequently, we added 0.04 cm³ of the 0.1 M benzene solution of nickel acetylacetonate and 0.15 cm³ of the 2 M solution of the Grignard reagent in diethyl ether. All spectra were taken at laboratory temperature with a spectrometer Varian E-3 and simulated by means of a computer Varian Spectra System 100.

Results and discussion

The reaction of benzenecarboxylic acid with phenyl- or 4-*tert*-Bu-phenylmagnesium bromide in the presence of nickel gives rise to the corresponding aryl-aryl

Table 1

Influence of solvents on the splitting constants of protons of the ketyl radicals arising in the reaction of benzenecarboxylic acid with phenylmagnesium bromide and 4-*tert*-Bu-phenylmagnesium bromide

Structure	Solvent	Splitting constants (mT)									
		a_2	a_3	a_4	a_5	a_6	$a_{2'}$	$a_{3'}$	$a_{4'}$	$a_{5'}$	$a_{6'}$
	DME	0.318	0.117	0.359	0.117	0.305	0.318	0.117	0.359	0.117	0.305
	HMPA	0.290	0.102	0.358	0.102	0.290	0.290	0.102	0.358	0.102	0.290
	Et ₂ O	0.255	0.125	0.282	0.125	0.255	0.228	0.125	—	0.125	0.228
	Toluene	0.253	0.130	0.285	0.130	0.253	0.235	0.130	—	0.130	0.235
	Dioxan	0.327	0.117	0.367	0.117	0.327	0.305	0.117	—	0.117	0.305
	DME	0.325	0.118	0.375	0.118	0.325	0.300	0.118	—	0.118	0.300
	HMPA	0.306	0.103	0.383	0.103	0.306	0.271	0.103	—	0.103	0.271

ketyl radicals. The solvent used has influence on their generation, stability, and values of splitting constants. We investigated these reactions in mixtures of diethyl ether with the following solvents: diisopropyl ether (*i*-Pr₂O), di-*n*-butyl ether (*n*-Bu₂O), methyl *tert*-butyl ether (*tert*-BuOMe), hexane, cyclohexane, benzene, toluene, triethylamine, tetrahydrofuran (THF), dimethoxyethane (DME), dioxan, and hexamethylphosphortriamide (HMPA). The portion of the investigated solvent varied from 10 to 80 volume % with respect to diethyl ether. The spectra of the ketyl radicals obtained in particular solvents are presented in Fig. 1 while the corresponding splitting constants are quoted in Table 1. On the basis of the

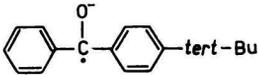
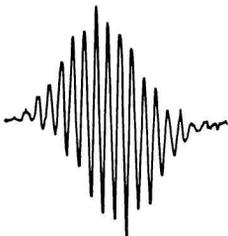
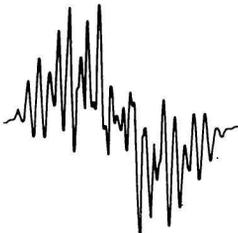
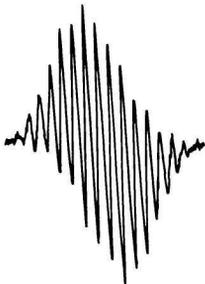
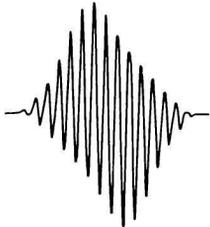
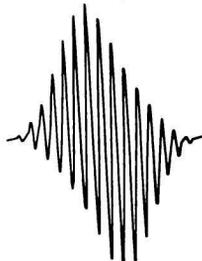
				
		in diethyl ether	in dioxan	in toluene
experimental				
	simulated			
		a_H 0.282 $2 \times a_H$ 0.255 $2 \times a_H$ 0.228 $4 \times a_H$ 0.125 pp 0.040	a_H 0.367 $2 \times a_H$ 0.327 $2 \times a_H$ 0.305 $4 \times a_H$ 0.117 pp 0.045	a_H 0.285 $2 \times a_H$ 0.253 $2 \times a_H$ 0.235 $4 \times a_H$ 0.130 pp 0.040

Fig. 1a

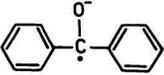
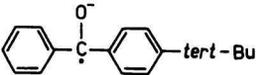
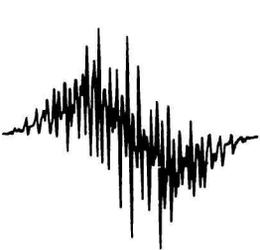
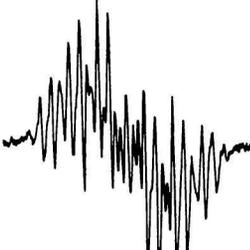
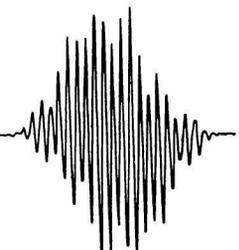
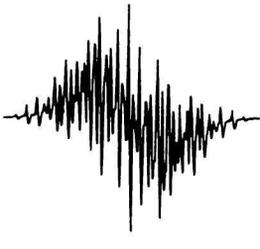
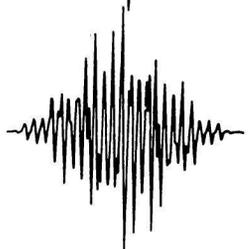
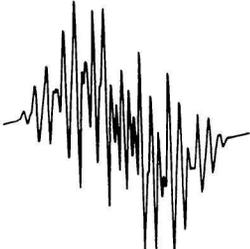
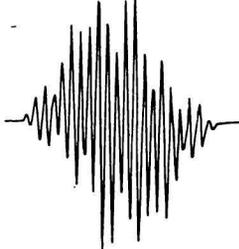
	Fig. 1b 		Fig. 1c 	
	in dimethoxyethane	in hexamethylphosphotriamide	in dimethoxyethane	in hexamethylphosphotriamide
experimental				
simulated				
	$2 \times a_H$ 0.359 $2 \times a_H$ 0.318 $2 \times a_H$ 0.305 $4 \times a_H$ 0.117 pp 0.017	$2 \times a_H$ 0.358 $4 \times a_H$ 0.290 $4 \times a_H$ 0.102 pp 0.027	a_H 0.375 $2 \times a_H$ 0.325 $2 \times a_H$ 0.300 $4 \times a_H$ 0.118 pp 0.028	a_H 0.383 $2 \times a_H$ 0.306 $2 \times a_H$ 0.271 $4 \times a_H$ 0.103 pp 0.040

Fig. 1. Experimental and simulated e.s.r. spectra of the radicals observed in the reaction of benzenecarboxylic acid with phenyl- and 4-*tert*-Bu-phenylmagnesium bromide in a mixture of particular solvents with diethyl ether.

a_H — the splitting constants of protons in mT; pp — the peak-to-peak distances of simulated spectra in mT.

obtained spectra, we may divide the investigated solvents into two groups. First group: *i*-Pr₂O, *n*-Bu₂O, *tert*-BuOMe, hexane, cyclohexane, benzene, toluene, triethylamine. Second group: DME, dioxan, HMPA.

We did not observe any defined spectra of the aryl-aryl ketyl radicals in tetrahydrofuran under given conditions. After standing for one night, we, however, obtained the spectra of the aryl radicals the formation of which has been discussed in more detail in paper [25].

The first group contains those solvents the addition of which did not produce any observable changes in the values of splitting constants of the investigated radicals. If the proportion of these solvents is changed, the concentration of radicals remains in the scope of the error of measurement constant and identical with the concentration of radicals measured in diethyl ether ($\sim 10^{-4}$ mol dm⁻³). An exception is represented by triethylamine in the presence of which a precipitate is formed and the concentration of radicals is lower. The stability of the ketyl radicals in these solvents at laboratory temperature is like in diethyl ether, *i.e.* 1 or 2 days. The similar behaviour of radicals in the presence of different solvents comprised in the first group is caused by the predominating influence of diethyl ether. As it was not possible to prepare the solutions of the Grignard reagents of required concentration in the above solvents, it was necessary to start from their ethereal solutions. Though the final concentration of the investigated solvent in the reaction mixture is high (up to 80%), the significant factor for solvation is always represented by diethyl ether because of its relatively small volume and great polarity. Owing to these facts, we did not observe any changes in the values of splitting constants in the presence of the solvent classified in the first group.

The second group is represented by the solvents which have influence on the values of splitting constants of the investigated aryl-aryl ketyl radicals (Table 1). Radicals are to be observed only at lower concentrations of these solvents (up to 60 volume %) while a precipitate appears at higher excess. These radicals are stable in the presence of these solvents for a few days and in the case of HMPA for a week.

In comparison with diethyl ether and the solvents of the first group, dioxan, dimethoxyethane, and hexamethylphosphortriamide raise the values of splitting constants in *ortho* and *para* position and reduce them in *meta* position. This fact may be explained by the increased solvation of magnesium which functions as a counter-ion to ketyl radical. That involves an increase in negative charge on the carbonyl carbon atom which manifests itself by an increase in spin density in *ortho* and *para* position. The solvation of anion radical itself has also influence on the distribution of spin density. These effects are complex and can be attributed to different properties of solvent such as its basicity, ability to coordinate, steric properties, *etc.* which frequently have an opposite influence and for this reason, it is difficult to find out a correlation between individual properties of solvents and the change in splitting constants of the investigated radicals.

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