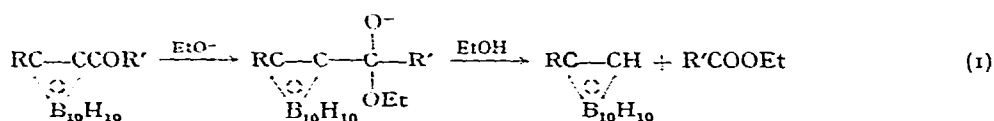# ACTION OF ORGANOMAGNESIUM AND ORGANOLITHIUM COMPOUNDS ON BARENIC KETONES

L. I. ZAKHARKIN AND A. I. L'VOV
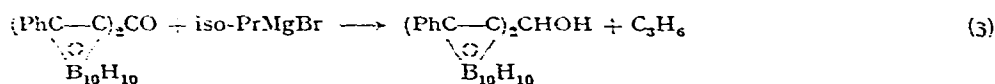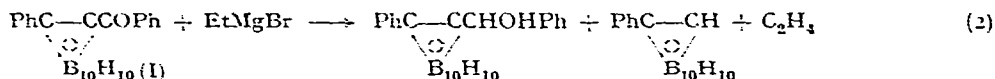
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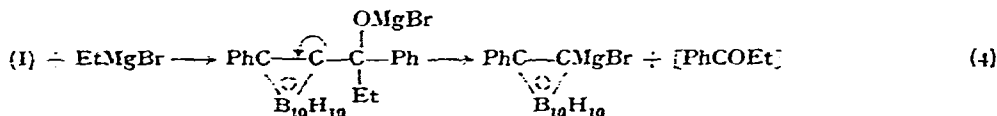
(Received August 20th, 1965)

The barenic ketones in which carbonyl group is bonded directly to the carbon atom of barenic nucleus are little investigated at present. We have recently described[1,2] the synthesis of such ketones by the reaction of the lithium derivatives of barenes with acyl chlorides. It was also found[1] that these ketones suffer the cleavage of carbon–carbon bond under the action of bases as follows:

$$RC\text{---}CCOR' \xrightarrow{\text{EtO}^-} RC\text{---}C\text{---}\overset{O^-}{\underset{\underset{OEt}{|}}{C}}\text{---}R' \xrightarrow{\text{EtOH}} RC\text{---}CH + R'COOEt \qquad (1)$$
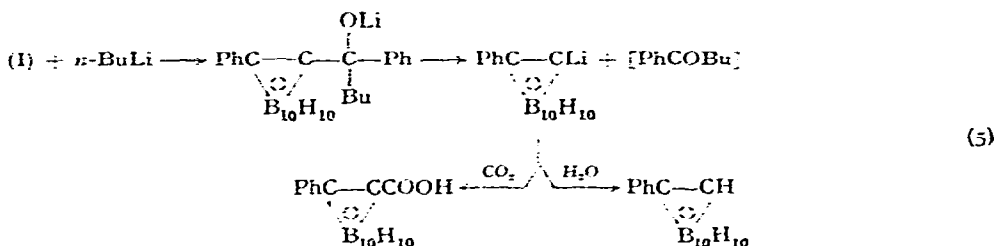
with B$_{10}$H$_{10}$ groups as shown.

We wanted now to prepare still unknown barenic tertiary alcohols by the action of Grignard reagents and organolithium compounds on the barenic ketones. However, it appeared that the interaction of barenic ketones with Grignard reagents and organolithium compounds proceeds abnormal and does not give tertiary alcohols. It was found that mainly the reduction of carbonyl group and in some extent the cleavage of carbon–carbon bond take place in the reaction of Grignard reagents containing a hydrogen atom in β-position, for example C$_2$H$_5$MgBr or iso-C$_3$H$_7$MgBr, with such barenic ketones as 1-phenyl-2-benzoylbarene, 1-methyl-2-p-toluoylbarene and bis-(phenylbarenyl) ketone:

$$PhC\text{---}CCOPh + EtMgBr \longrightarrow PhC\text{---}CCHOHPh + PhC\text{---}CH + C_2H_4 \qquad (2)$$
$$B_{10}H_{10} \text{ (I)} \qquad\qquad B_{10}H_{10} \qquad\qquad B_{10}H_{10}$$

$$(PhC\text{---}C)_2CO + iso\text{-}PrMgBr \longrightarrow (PhC\text{---}C)_2CHOH + C_3H_6 \qquad (3)$$
$$B_{10}H_{10} \qquad\qquad\qquad B_{10}H_{10}$$

The reduction of ketones proceeds in this case undoubtedly owing to a β-hydrogen atom of the Grignard reagent. It seems that the cleavage of carbon–carbon bond is the result of the intermediate formation of magnesium tertiary alkoxide which breaks down then into phenylbarenylmagnesium bromide and phenyl alkyl ketone as follows:

$$(I) + EtMgBr \longrightarrow PhC\overset{\overset{OMgBr}{\underset{B_{10}H_{10}}{|}}}{\underset{Et}{C}}\!-\!\overset{|}{\underset{}{C}}\!-\!Ph \longrightarrow PhC\!-\!\underset{B_{10}H_{10}}{CMgBr} + [PhCOEt] \qquad (4)$$

The formed phenyl alkyl ketone reacts further with the excess of Grignard reagent to give corresponding tertiary alcohol. In the reaction of n-butyl lithium with barenic ketones the cleavage of carbon–carbon bond takes place mainly in contrast to the action of Grignard reagents on barenic ketones. The reduction of carbonyl group proceeds in this case in negligible extent:

$$(I) + n\text{-BuLi} \longrightarrow PhC\overset{\overset{OLi}{\underset{B_{10}H_{10}}{|}}}{\underset{Bu}{C}}\!-\!\overset{|}{\underset{}{C}}\!-\!Ph \longrightarrow PhC\!-\!\underset{B_{10}H_{10}}{CLi} + [PhCOBu]$$

$$\underset{B_{10}H_{10}}{PhC\!-\!CCOOH} \xleftarrow{\;CO_2\;}\;\;\xrightarrow{\;H_2O\;} \underset{B_{10}H_{10}}{PhC\!-\!CH} \qquad (5)$$
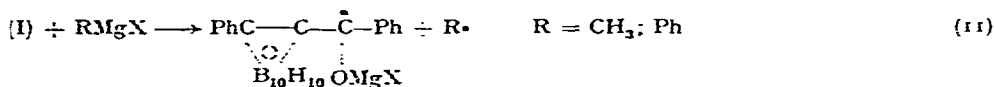
By the treatment of reaction mixture with water or with carbon dioxide respectively phenylbarene or phenylbarenyl carboxylic acid are formed. The cleavage of carbon–carbon bond takes place in (I) under the action of butyllithium even at $-50°$. Parallel with the cleavage of carbon–carbon bond the reduction of carbonyl group proceeds also. However, the corresponding barenic tertiary alcohol is not formed either under these conditions. The obtained results point to the small stability of barenic tertiary alkoxides. This is undoubtedly conditioned by the strong electron-withdrawing character of barenic nucleus and by considerable steric hindrances. Thus owing to the steric hindrances above barenic ketones do not give with 2,4-dinitrophenylhydrazine corresponding hydrazones. The small stability of the barenic tertiary alkoxides permits to explain the absence of barenic tertiary alcohols in the reaction of lithium derivatives of barenes with acyl chlorides and also our unsuccessful attempts to prepare the barenic tertiary alcohols by the action of magnesium and lithium derivatives of barenes on ketones. This permits also to understand the somewhat unexpected transformation found by us in present work. Thus, it was found that by the action of phenylmagnesium bromide on phenylbarenylcarbonyl chloride together with (I) bis(phenylbarenyl) ketone is formed:

$$\underset{B_{10}H_{10}}{PhC\!-\!CCOCl} + PhMgBr \longrightarrow (I) + \underset{B_{10}H_{10}}{(PhC\!-\!C)_2CO} \qquad (6)$$
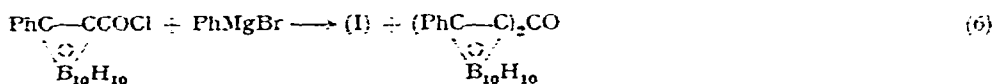
It is evident that the formation of bis(phenylbarenyl) ketone proceeds in the reaction of phenylbarenylcarbonyl chloride with phenylbarenylmagnesium bromide which is obtained intermediately by the splitting of magnesium tertiary alkoxide similar to the above scheme (eqn. 4). The other interesting reaction proceeding through the splitting of intermediate tertiary alkoxide is the interaction of 1-phenyl-2-(p-

chlorobenzoyl)barene with 1-methylbarenyllithium which gives rise (after the treatment with water) to the mixture of phenylbarene, methylbarene, 1-phenyl-2-(p-chlorobenzoyl)barene and 1-methyl-2-benzoylbarene:

$$PhC\text{—}CCOC_6H_4Cl + CH_3C\text{—}CLi \rightleftarrows \begin{bmatrix} & C_6H_4Cl \\ & | \\ PhC\text{—}C\text{--}C\text{--}C\text{—}CCH_3 \\ \diagdown O \diagup & | & \diagdown O \diagup \\ B_{10}H_{10} & OLi & B_{10}H_{10} \end{bmatrix} \rightleftarrows$$

$$\rightleftarrows PhC\text{—}CLi + CH_3C\text{—}CCOC_6H_4Cl \qquad (7)$$

Formally, in this reaction the exchange of the acyl group on lithium takes place. The intermediate formation of tertiary alkoxides in the reaction of metallo-barenes with ketones is confirmed by the preparation of barenetetrahydrofurane derivatives from the lithium, sodium and potassium derivatives of 1-bromomethylbarene with ketones[3].

Similar to barenic ketones the reaction of methyl phenylbarenylcarboxylate and methyl vinylbarenylcarboxylate with butyllithium gives rise to the cleavage of carbon–carbon bond probably as follows:

$$PhC\text{—}CCOOCH_3 + n\text{-}BuLi \longrightarrow PhC\text{—}C\text{--}C\text{--}OCH_3 \longrightarrow PhC\text{—}CLi + [BuCOOCH_3]$$

$$PhC\text{—}CCOOH \xleftarrow{CO_2} \cdot \xrightarrow{HO_2} PhC\text{—}CH \qquad (8)$$

By the action of Grignard reagents on barenic esters also in some extent the fission of carbon–carbon bond proceeds. The interaction of methylmagnesium iodide and phenylmagnesium bromide proceeds abnormal to result in the cleavage of carbon–carbon bond and the reduction of carbonyl group.

$$(I) + PhMgBr \longrightarrow PhC\text{—}CCHOHPh + PhC\text{—}CH + Ph_3COH + Ph_2 \qquad (9)$$

$$(PhC\text{—}C)_2CO + CH_3MgI \longrightarrow (PhC\text{—}C)_2CHOH + PhC\text{—}CH + CH_4 + C_2H_6 \qquad (10)$$

In the reaction of bis(phenylbarenyl) ketone with CH_3MgI the secondary alcohol is obtained in 81 % yield. The cleavage of carbon–carbon bond proceeds in these cases similar to above reactions. The reduction of carbonyl group in barenic

ketones under the action of methylmagnesium iodide and phenylmagnesium bromide which do not contain in β-position the hydrogen atom capable to shift as hydride ion and the formation in this reaction methane, ethane and biphenyl point to the free radical-course of this process. It is known that the radical reduction takes place in some cases under the action of Grignard reagents on aromatic ketones to give pinacols. It was recently shown[4] that ketyl is formed in the reaction of Grignard reagent with benzophenone. It is possible that in the reaction of barenic ketones with methylmagnesium iodide and phenylmagnesium bromide barenic ketyls besides methyl and phenyl radicals are formed:

$$(I) + RMgX \longrightarrow PhC \underset{\underset{B_{10}H_{10}}{\overset{\diagup}{\underset{O}{\diagdown}}}{\overset{}{}}}{---} C \overset{\cdot}{\underset{\underset{OMgX}{|}}{---}} C --- Ph + R\cdot \qquad R = CH_3; Ph \qquad (II)$$

However, for the more complete understanding of the mechanism of this reduction further investigation is necessary.

EXPERIMENTAL

The action of ethylmagnesium bromide on 1-phenyl-2-benzoylbarene

1-Phenyl-2-benzoylbarene (1.2 g) in ether was added to EtMgBr (from 0.7 g of EtBr) in 20 ml of ether. Ethylene was evolved. The mixture was refluxed for 30 min, cooled and treated with dilute (1:4) hydrochloric acid. The ether layer was dried over magnesium sulfate. The residue remaining after removal of the ether was recrystallized from hexane/benzene to yield 0.9 g of (phenylbarenyl)phenylcarbinol, m.p. 120–121°. In the mother liquor phenylbarene was discovered by the thin-layer chromatography on alumina.

The action of isopropylmagnesium bromide on 1-phenyl-2-benzoylbarene

iso-PrMgBr (0.03 M) in 20 ml of ether was added to a solution of 2.4 g (7.5 mmol) of 1-phenyl-2-benzoylbarene in 15 ml of ether at 20°. The mixture was stirred for 1 h at 34°, cooled to 10° and treated as usual. The residue remaining after the removal of ether was recrystallized from hexane to yield 2.2 g (91 %) of (phenylbarenyl)phenylcarbinol, m.p. 120–121°. In the mother liquor phenylbarene was discovered by thin-layer chromatography on alumina.

The reaction of isopropylmagnesium bromide with 1-methyl-2-p-toluoylbarene

iso-PrMgBr (0.01 M) in 10 ml of ether was added at 20° to a solution of 1-methyl-2-p-toluoylbarene (0.8 g) in 10 ml of ether. The mixture was stirred for 1 h at 34°. Propene was evolved. The product was recrystallized from pentane to give 0.7 g (87 %) of (phenylbarenyl)-p-tolylcarbinol, m.p. 78–79°. (Found: C, 47.70; H, 8.60; B, 38.89. $C_{16}H_{24}B_{10}O$ calcd.: C, 47.47; H, 7.97; B, 38.88 %.)

The reaction of isopropylmagnesium bromide with bis(phenylbarenyl) ketone

iso-PrMgBr (0.015 M) in 10 ml of ether was added at 20° to a solution of bis(phenylbarenyl) ketone (2.33 g) in 15 ml of ether and 10 ml of benzene. The mixture was stirred for 1 h at 34° and treated as usual. The product was purified by recrystal-

lisation from the mixture of heptane and benzene to give 2.1 g (90%) of bis(phenyl-barenyl)carbinol, m.p. 270–271°. (Found: C, 43.24; H, 6.99; B, 45.12. $C_{17}H_{32}B_{20}O$ calcd.: C, 43.54; H, 6.88; B, 46.16%.)

The action of n-butyllithium on 1-phenyl-2-benzoylbarene

(a) To 1.62 g (5 mmol) of ketone in 15 ml of ether was added n-butyllithium (0.015 M) in benzene. The mixture was stirred for 1 h at 35° and treated as usual. From the residue remaining after the removal of solvent 0.87 g (80%) of phenylbarene and 0.1 g of (phenylbarenyl)phenylcarbinol were isolated. In an other experiment the reaction mixture was treated with carbon dioxide. Phenylbarenecarboxylic acid was isolated and converted to methyl phenylbarenylcarboxylate, m.p. 84–85°.

(b) n-Butyllithium (0.015 M) in benzene was added at —50° to a solution of 1.62 g (5 mmol) of 1-phenyl-2-benzoylbarene in 25 ml of ether. The mixture was stirred at —50° for 1 h, treated with aqueous methanol and then with diluted hydrochloric acid. The ether/benzene layer was dried over magnesium sulfate. There was obtained 0.3 g of (phenylbarenyl)phenylcarbinol, m.p. 120°, and 0.8 g phenylbarene.

The reaction of phenylmagnesium bromide with phenylbarenylcarbonyl chloride

To 10 ml of a stirred ether solution of chloride (1.42 g) was added a solution of PhMgBr prepared from 0.79 g of bromobenzene in 15 ml of ether. The mixture was stirred for 1 h at 20° and for 1 h at 34°. After usual treatment 0.5 g of 1-phenyl-2-benzoylbarene, m.p. 76°, and 0.3 g of bis(phenylbarenyl) ketone, m.p. 217°, were isolated.

The reaction of methylbarenyllithium with 1-phenyl-2-(p-chlorobenzoyl)barene

The solution of methylbarenyllithium prepared from 0.14 g of methylbarene in benzene was added to a solution of 0.3 g of 1-phenyl-2-(p-chlorobenzoyl)barene in 5 ml of benzene. The mixture was stirred for 2 h at 25°, treated with diluted hydrochloric acid and washed with water. In the benzene solution phenylbarene, methylbarene, 1-phenyl-2-(p-chlorobenzoyl)barene and 1-methyl-2-(p-chlorobenzoyl)barene were discovered by thin-layer chromatography on silica gel.

*Vinylbarene**

Pure vinylacetylene was passed through a solution of decaborane (60 g) and dimethylaniline (120 g) in 300 ml of toluene for 2 h at 60–70° and for 4–5 h at 80–90°. After the stopping of the evolving of hydrogen the reaction mixture was cooled. The toluene solution was decanted from the resinous products, washed with hydrochloric acid from dimethylaniline and dried over sodium sulfate. The residue after removal of toluene was extracted with hexane or heptane. After the solvent had been removed the product was distilled in vacuum and purified by recrystallisation from aqueous methanol to give 70–75 g of vinylbarene, m.p. 76–77°.

Methyl phenylbarenylcarboxylate

A solution of phenylbarenecarboxylic acid (10 g) in 30 ml of benzene and PCl_5 (8.5 g) were refluxed for 1 h. Benzene and $POCl_3$ were removed in vacuum. To the

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* Vinylbarene was prepared together with E. KUKULINA.

residue methanol (30 ml) was added by cooling. The mixture was refluxed for 10 min. Methanol (15 ml) was removed and the residue was cooled. Methyl phenylbarenyl-carboxylate was filtered. After recrystallisation from methanol was isolated 9.2 g (87 %) of pure product, m.p. 84–85° (Found: C, 44.23; H, 6.73; B, 38.73. $C_{10}H_{18}B_{10}O_2$ calcd.: C, 43.25; H, 6.48; B, 38.85 %.)

Methyl vinylbarenylcarboxylate

Vinylbarenecarboxylic acid (10 g) prepared by carboxylation of vinylbarenyl-lithium in ether/benzene solution and PCl_5 (10 g) in benzene (30 ml) were heated for 30 min. After the treatment as in the above experiment methyl vinylbarenylcarboxylate (8.3 g) was prepared, m.p. 42–43°. (Found: C, 32.11; H, 7.04. $C_6H_{16}B_{10}O_2$ calcd.: C, 31.58; H, 7.03 %.)

The action of n-butyllithium on methyl phenylbarenylcarboxylate

To a solution of methyl phenylbarenylcarboxylate (2 g) in ether (20 ml) was added 30 ml of (1.1 M) butyl lithium in benzene. The mixture was refluxed for 30 min and cooled. Two ml of this solution was treated with water and phenylbarene was discovered in organic layer by the thin-layer chromatography on alumina. Methyl phenylbarenylcarboxylate was absent in the organic layer. The rest of part of the reaction mixture had been carboxylated by the solid carbon dioxide and crude phenyl-barenecarboxylic acid (1.1 g) was isolated, m.p. 141–142° (from heptane). The reaction of methyl vinylbarenylcarboxylate with butyllithium is similar to this above reaction.

The action of methylmagnesium ioide on 1-phenyl-2-benzoylbarene

CH_3MgBr (0.015 M) in ether was added to phenylbenzoylbarene (1.62 g). The mixture was stirred for 1 h at 34° and treated as usual. The ether was removed and the residue was dissolved in hexane. From the hexane solution (phenylbarenyl)phenyl-carbinol (0.65 g, 40 %) was isolated, m.p. 120–121°. In mother liquor phenylbarene was discovered. The gas which was evolved in the course of reaction was analysed by gas–liquid chromatography. The gas contained 60 % of methane and 40 % of ethane.

The action of phenylmagnesium bromide on phenylbenzoylbarene

PhMgBr (0.03 M) in ether was added to a solution of ketone (3.24 g) in ether (25 ml) at 20°. The mixture was stirred for 1 h at 34° and treated as usual. By the recrystallisation from hexane and methanol the following compounds were isolated: triphenylcarbinol, m.p. 156–157°, (phenylbarenyl)phenylcarbinol, m.p. 120–121°, biphenyl, m.p. 68°, and phenylbarene, m.p. 67°. All the compounds were identified by the thin-layer chromatography on alumina.

The action of methylmagnesium iodide on bis(phenylbarenyl) ketone.

CH_3MgI (0.015 M) in ether was added to a solution of bis(phenylbarenyl) ketone (2.33 g). The mixture was stirred for 1 h at 34° and treated as usual. Bis(phenyl-barenyl)carbinol (1.9 g, 81 %), m.p. 270–272°, was prepared. From the mother liquor 0.1 g of phenylbarene was isolated also.

SUMMARY

It has been found that the reaction of Grignard reagents and organolithium compounds with barenic ketones containing the direct bond between carbonyl group and barene carbon atom proceeds abnormal and does not give barenic tertiary alcohols. Instead of this, cleavage of the carbon–carbon bond between the carbonyl group and the carbon atom of the barenic nucleus and the reduction of barenic ketones to barenic secondary alcohols take place. The reduction of barenic ketones under the action of CH_3MgI and $PhMgBr$ proceeds through the formation of free radicals. The action of Grignard reagents and n-butyllithium on esters of barenecarboxylic acids results also in the cleavage of carbon–carbon bond between the carboxyl group and the carbon atom of barenic nucleus.

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