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Abstract

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Cleavage of the C–C Bond in Ketones and Alcohols of the Barene Series under the Action of Bases

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We have previously shown ([1,2]) that in derivatives of barenecarboxylic acids, owing to the strong inductive electron-acceptor effect of the barene nucleus, cleavage of the carbon-carbon bond readily occurs, for example:

$$\underset{B_{10}H_{10}}{HC-C-COOC_2H_5} \xrightarrow[C_2H_5OH]{C_2H_5ONa} \underset{B_{10}H_{10}}{HC-CH} + CO(OC_2H_5)_2$$

We also proposed ([3]) that barene compounds capable of forming anion I as an intermediate should be capable of such facile cleavage of the carbon-carbon bond:

$$\underset{B_{10}H_{10}}{RC-C-C(O^-)} < \longrightarrow \underset{B_{10}H_{10}}{RC-C^-} + O{=}C < \xrightarrow{AH} \underset{B_{10}H_{10}}{RC-CH} + A^- \qquad (I)$$

In the present work, in confirmation of this supposition, we have found that in barene ketones and alcohols, under the action of bases, rupture of the carbon-carbon bond readily takes place. Thus, 1-phenyl-2-benzoylbarene in absolute alcohol solution in the presence of a catalytic amount of sodium ethoxide at 20° is cleaved to phenylbarene and ethyl benzoate:

$$\underset{B_{10}H_{10}}{C_6H_5C-C-COC_6H_5} \xrightarrow[C_2H_5OH]{C_2H_5ONa} \underset{B_{10}H_{10}}{C_6H_5C-CH} + C_6H_5COOC_2H_5$$

Under analogous conditions, bis-(phenylbarenyl)-ketone also readily undergoes alcoholysis of the carbon-carbon bond:

$$\underset{B_{10}H_{10}}{C_6H_5C-C-CO-C-CC_6H_5} \xrightarrow[C_2H_5OH]{C_2H_5ONa} \underset{B_{10}H_{10}}{C_6H_5C-CH} + CO(OC_2H_5)_2$$

With the accumulation of negative groupings, the ease of rupture of the C–C bond increases. Thus, 1-phenyl-2-benzoylbarene is normally reduced by lithium aluminum hydride in ether solution, giving the corresponding secondary alcohol in high yield; under the action of ethylmagnesium bromide in ether on this ketone, reduction of the carbonyl group also occurs:

$$\underset{B_{10}H_{10}}{C_6H_5C{-}C{-}COC_6H_5} \xrightarrow[\text{or } C_2H_5MgBr]{LiAlH_4} \underset{B_{10}H_{10}}{C_6H_5C{-}C{-}CH(OH){-}C_6H_5}$$

However, on treatment of bis(phenylbarenyl) ketone with lithium aluminum hydride, reduction of the carbonyl group does not occur; instead, cleavage of the carbon-carbon bond is observed, with formation of phenylbarene:

$$C_6H_5C{-}C{-}CO{-}C{-}CC_6H_5 \xrightarrow{LiAlH_4} C_6H_5C{-}CH$$

Cleavage of the C–C bond in 1-phenyl-2-benzoylbarene under the action of sodium ethylate may be represented as follows:

$$C_6H_5C{-}C{-}COC_6H_5 \xrightarrow{C_2H_5O^-} [C_6H_5C{-}C{-}C(O^-)(OC_2H_5)C_6H_5] \longrightarrow$$

$$\longrightarrow [C_6H_5C{-}C^- + C_6H_5COOC_2H_5] \xrightarrow{C_2H_5OH} C_6H_5C{-}CH + C_2H_5O^-$$

Cleavage of the C–C bond in alcohols of the barene series was shown using phenylbarenylphenylcarbinol (II) as an example.

When a small amount of sodium amide in liquid ammonia at −40° was allowed to act on this alcohol, benzaldehyde and phenylbarene were isolated along with the starting alcohol. Evidently, this reaction in liquid ammonia solution is an equilibrium one:

$$C_6H_5C{-}C(OH)HC_6H_5 \xrightarrow[NH_3(l.)]{NaNH_2} C_6H_5C{-}C(O^-Na^+)HC_6H_5 \rightleftarrows$$

$$\rightleftarrows C_6H_5C{-}CNa + C_6H_5CHO \xrightarrow{II} C_6H_5C{-}CH + (III)$$

Apparently, in tertiary alcohols of the barene series the carbon-carbon bond should undergo cleavage even more readily than in secondary alcohols. This probably explains our so far unsuccessful attempts to obtain tertiary alcohols by the action of lithium derivatives of barene compounds on ketones, as well as the good yields of barene ketones in the reaction of phenylbarenyllithium with acid chlorides of carboxylic acids:

$$C_6H_5C{-}CLi + R'COCl \longrightarrow C_6H_5C{-}CCOR$$

$$R = CH_3,\ \text{iso-}C_3H_7,\ C_6H_5,\ C_6H_5CB_{10}H_{10}C$$

The ketones obtained by this method are summarized in Table 1.

Table 1

$C_6H_5C{-}CCOR$

No.	R	m.p., °C	Found, % C	Found, % H	Found, % B	Calculated, % C	Calculated, % H	Calculated, % B
1	C_6H_5	76–77	55.68	6.55	33.32	55.45	6.17	33.21
2	iso-C_3H_7	46–47	49.54	7.44	37.10	49.45	7.56	37.16
3	CH_3	67–68	45.51	6.97	41.22	45.62	6.84	41.18
4	$C_6H_5CB_{10}H_{10}C$	217–218	43.99	6.60		43.80	6.42	

* b.p. 169–170°/2 mm.

Experimental Part

Synthesis of ketones by the action of phenyllithium barene on acid chlorides. A benzene solution of phenyllithium barene, prepared by adding a benzene solution of butyllithium to phenylbarene in benzene at 70–75° in an atmosphere of pure nitrogen, was gradually added with stirring to a solution of the acid chloride (taken in slight excess) in benzene at 5–15°. The temperature was maintained within this range by external cooling. After completion of the addition of the lithium derivative, the reaction mixture was briefly heated to 30–40° and cooled. Water was added; the benzene layer was washed with potassium hydroxide solution and with water, and dried over calcium chloride. After removal of the solvent, the ketone was crystallized from methanol. The yield was 70–85% of theory.

Cleavage of the C-C bond in 1-phenyl-2-benzoylbarene. To a solution of 1 g of 1-phenyl-2-benzoylbarene in 10 ml of abs. alcohol was added sodium ethoxide (from 0.01 g of sodium) in 2 ml of abs. alcohol at 20°. After 12 h the alcohol was distilled off in vacuo, water was added to the residue, and the mixture was extracted with ether. The ether was dried over potassium hydroxide. After removal of the ether, the crystalline residue, impregnated with oil, was pressed on a filter. Benzyl benzoate was identified chromatographically in the filtrate. The residue on the filter (0.47 g) was recrystallized from methyl

alcohol; phenylbarene was obtained, mp 65-60°, which gave no depression of the melting point with a known sample of phenylbarene.

The cleavage of bis-(phenylbarene)-ketone was carried out analogously.

Reduction of 1-phenyl-2-benzoylbarene with lithium aluminum hydride. To a solution of 0.06 g of lithium aluminum hydride in 10 ml of ether was added a solution of 1 g of 1-phenyl-2-benzoylbarene in 5 ml of ether. Noticeable heating of the mixture was observed. After 10 min of heating, the solution was cooled, methyl alcohol was added to decompose the excess lithium aluminum hydride, and the mixture was then poured into acidified water. The ether extract was dried over magnesium sulfate. 0.95 g of phenylbarenylphenylcarbinol was obtained, mp 121-122° (from hexane-benzene).

Found, %: C 55.29; H 6.93; B 33.00
$C_{15}H_{22}B_{10}O$. Calculated, %: C 55.25; H 6.75; B 33.10

On reduction of bis-(phenylbarenyl)-ketone with lithium aluminum hydride under analogous conditions, phenylbarene, mp 65-66°, was isolated as the sole product.

Action of ethylmagnesium bromide on 1-phenyl-2-benzoylbarene. A solution of 1 g of 1-phenyl-2-benzoylbarene in ether was added to ethylmagnesium bromide (from 0.2 g of magnesium) in 10 ml of ether. Evolution of ethylene was observed. The mixture was heated for 30 min. After the usual work-up, 0.71 g of phenylbarenylphenylcarbinol was obtained, mp 120-122°, which gave no depression of the melting point with the sample from the preceding experiment.

Cleavage of the C-C bond in phenylbarenylcarbinol. To sodium amide (from 0.02 g of sodium) in 30 ml of liquid ammonia at −40°, with stirring, was added a solution of 1 g of phenylbarenylcarbinol in 6 ml of dry ether. The mixture was stirred at this temperature for 80 min, then solid ammonium chloride and water were added. The reaction products were extracted with ether. The ether extract was washed with water, dilute hydrochloric acid, and again with water. To separate benzaldehyde

The ether solution was shaken with a solution of sodium bisulfite. On decomposition of the bisulfite solution with potash, benzaldehyde was obtained, from which 2,4-dinitrophenylhydrazone with m.p. 234-235° was prepared; it gave no depression of the melting point with an authentic sample. From the ether solution, phenylbarene with m.p. 65-66° and the starting carbinol with m.p. 120-122° were isolated.

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[3] L. I. Zakharkin, V. I. Stanko et al., *DAN*, **157**, 1149 (1964).

Note: Figure translations are in progress. See original paper for figures.