96. *Synthetical Experiments with Benzhydrylsodium.*

By Ernst Bergmann.

The alkali-organic compounds have been used for many syntheses by Schlenk and his co-workers, but a systematic study of their applicability for preparative purposes has never been made. The present paper gives a list of experiments made with benzhydrylsodium, which is easily accessible from benzhydryl methyl ether and sodium (Ziegler and Thielmann, *Ber.*, 1923, **56**, 1740; Schlenk and Bergmann, *Annalen*, 1928, **464**, 18). The work parallels in some respects the extensive synthetical studies of Schlenk and Ochs (*Ber.*, 1916, **49**, 608) with triphenylmethylsodium and of Bergmann and Ukai (*Ber.*, 1933, **66**, 54) with phenylstyrylmethylsodium. Benzhydrylsodium was chosen for the present experiments, not only because of its easy availability, but also since it does not incline so much to enolising reactions with carbonyl compounds as triphenylmethylsodium (see, *e.g.*, Schlenk, Hillemann, and Rodloff, *Annalen*, 1931, **487**, 135, for the reaction with ethyl diphenylacetate, and Schlenk and Bergmann, *Annalen*, 1930, **479**, 74, for the interaction with benzylacetone).

The reaction between benzhydrylsodium and aromatic ketones and thio-ketones has been studied systematically by Bergmann and Wagenberg (*Ber.*, 1930, **63**, 2585). They also reported some experiments with Δ^{α}-unsaturated ketones which led to addition at the carbon double bond. These results seemed worthy of extension; the following list includes the reactions with many compounds of the type mentioned; the table, which is self-explanatory, shows that *usually* benzhydrylsodium undergoes 1 : 4-addition to Δ^{α}-unsaturated carbonyl compounds. In view of this fact it is remarkable that ethyl phenylpropiolate reacts like a saturated ester; it gives a carbinol as with phenylmagnesium bromide (Hess and Weltzien, *Ber.*, 1921, **54**, 2511); the structure of the product follows from the fact that it is attacked by acetyl chloride. If it had the alternative formula

$$CHPh_2 \cdot CPh{:}CH \cdot CO \cdot CHPh_2,$$

one molecule of benzhydrylsodium having reacted with the ester group, and another added to the triple bond, the product should be stable towards acetyl chloride. The behaviour of the Δ^{α}-unsaturated carbonyl compounds is all the more remarkable since phenyl-lithium reacts with benzylideneacetophenone as with any saturated ketone (Lüttringhaus, *Ber.*, 1934, **67**, 1602).

The table shows that benzhydrylsodium reacts with enolisable esters to a certain extent in the normal way; some of it, however, is converted into diphenylmethane by the enolic form. Acyl chlorides of the corresponding type do not give condensation products, but react exclusively in their enolic form. Even with ethyl α-bromopropionate, normal condensation occurs, although it should incline largely to enolisation (compare the enolisation of bromoacetones: Hughes, Watson, and Yates, J., 1931, 3318; Watson and Yates, J., 1932, 1207). Only with ethyl fluorene-9-carboxylate did the enolic reaction prevail.

The reactions with benzhydrylsodium lead to rather highly phenylated substances. It seemed interesting to know whether very high phenylation of this type gives stable products or not. Here the experiment with β-benzpinacolin is instructive. The condensation product decomposes spontaneously according to the scheme :

$$CPh_3 \cdot COPh + CHPh_2Na \longrightarrow CPh_3 \cdot CPh(OH) \cdot CHPh_2 \longrightarrow CHPh_3 + Ph \cdot CO \cdot CHPh_2$$

This reaction recalls similar observations of Kohler, Richtmyer, and Hester (*J. Amer. Chem. Soc.*, 1931, **53**, 205) and Bergmann and Wolff (*ibid.*, 1932, **54**, 1644).

Some of the experiments described herein were carried out at the Berlin University in collaboration with Dr. Alfred von Christiani.

Experimental.

For each experiment, 5 g. of benzhydryl methyl ether were split with sodium in about 200 c.c. of ether (2 days' shaking); the solution was decanted from the excess of sodium in a nitrogen atmosphere (Schlenk tube). Where any other quantity of the ether was used, it is noted in parentheses after the figure giving the amount of the reagent.

Reagent.	Wt., g.	Product.	Wt., g.	M. p.	B. p./mm.	Found, %. C.	Found, %. H.	Calc., %. C.	Calc., %. H.	Remarks.
β-Phenylethyl chloride	2·8	$CH_2Ph\cdot CH_2\cdot CHPh_2$	3·5	47°	225°/21	92·8	7·5	92·6	7·4	Needles, from MeOH [1]
α-Phenylethyl chloride	2·8	$CHPhMe\cdot CHPh_2$	2·3	76	220/16	—	—	—	—	From MeOH [2]
Chlorodimethyl ether	2	$OMe\cdot CH_2\cdot CHPh_2$	4·5	—	198/19	85·0	7·6	84·9	7·5	
Formaldehyde	1	$OH\cdot CH_2\cdot CHPh_2$	2·7	59—60	—	84·6	7·3	84·8	7·1	From light petroleum
Benzaldehyde	4·8 (9)	$OH\cdot CHPh\cdot CHPh_2$	9	88—89	234/16	—	—	—	—	Needles, from EtOH or C_6H_6 [3]
Acetone	2·6 (9)	CH_2Ph_2	7·5	—	—	—	—	—	—	
Dibenzyl ketone	4·2	CH_2Ph_2	3·2	—	—	—	—	—	—	
Benzil	4·8 (9)	Tetraphenylethane	—	—	209	—	—	—	—	Transfer of the metal from the alkali-organic compound to benzil
		Benzoin	—	—	135	—	—	—	—	
β-Benzpinacolin	6·2	$Ph\cdot CO\cdot CHPh_2$	—	—	135	—	—	—	—	
		$CHPh_2$	—	—	92	—	—	—	—	
Benzoin ethyl ether	4	$CHPh(OEt)\cdot CPh(OH)\cdot CHPh_2$	4	140	—	85·3	7·0	85·3	6·8	Rhombic crystals, from EtOH
Benzylideneacetophenone oxide	4·5	$Ph\cdot CH(O)CH\cdot CPh(OH)\cdot CHPh_2$	4·5	179—180	—	85·9	6·2	85·7	6·1	Needles, from $Pr^{\beta}OH$
p-Chlorobenzophenone	6·7 (7)	$C_6H_4Cl\cdot CPh(OH)\cdot CHPh_2$	6·3	176—178	—	81·1	5·7	81·3	5·5	From $Pr^{\beta}OH$. Dehydration with boiling AcCl gives *p*-chlorotetraphenylethylene, needles, m. p. 166—167°, from $Pr^{\beta}OH$ [4]
pp'-Dichlorobenzophenone	5	$(C_6H_4Cl)_2C(OH)\cdot CHPh_2$	7·3	183—184	—	74·7	5·1	74·5	4·8	Needles, from light petroleum [5]
pp'-Dibromobenzophenone	6	$(C_6H_4Br)_2C(OH)\cdot CHPh_2$	5·8	197	—	—	—	—	—	Needles, from $Pr^{\beta}OH$. Dehydration as above gives *pp'*-dibromotetraphenylethylene, needles, m. p. 205°, from light petroleum [6]
p-Methoxybenzophenone	4·5	$OMe\cdot C_6H_4\cdot CPh(OH)\cdot CHPh_2$	2	—	—	85·5	6·5	85·2	6·4	From $Pr^{\beta}OH$. *p*-Methoxytetraphenylethylene forms needles, m. p. 131—132° [7]
Benzylideneacetone	2	(CH_2Ph_2 and) $CHPh(CH_2\cdot COMe)\cdot CHPh_2$	1	137	—	88·2	6·9	87·9	7·0	Needles, from $Pr^{\beta}OH$
Benzylideneacetophenone	4·5	$CHPh(CH_2\cdot COPh)\cdot CHPh_2$	7·3	182—184	—	—	—	—	—	Needles from AcOH. No reaction with Br
p-Methoxybenzylidene acetophenone	4·8	$OMe\cdot C_6H_4\cdot CH(CH_2\cdot COPh)\cdot CHPh_2$	6·8	146—148	—	85·5	6·6	85·7	6·4	From $Pr^{\beta}OH$; stable towards Br
Cinnamylideneacetophenone	8 (10)	$CHPh{:}CH\cdot CH(CH_2\cdot COPh)\cdot CHPh_2$	6·7	151—152	—	89·6	6·5	89·6	6·5	Needles, from AcOH or $Pr^{\beta}OH$; adds Br; stable against boiling AcCl
Benzophenonephenylmethylhydrazone	5·8	$Ph_2C{:}N\cdot NPhMe$ [and some $(CHPh_2)_2$]	4·5	149—151	—	87·7 N 6·2	6·5	87·2 N 6·2	6·6	Stout yellowish prisms, from C_6H_6 [8]
Benzyl benzoate	4·3	$Ph\cdot CO\cdot CHPh_2$	2·1	135	—	—	—	—	—	
Benzonitrile	2·3		4·1	135	—	—	—	—	—	
Ethyl *o*-methoxybenzoate	3·3	$OMe\cdot C_6H_4\cdot CO\cdot CHPh_2$	2·3	86—87	—	83·6	5·9	83·4	6·0	Needles, from MeOH
Methyl *o*-fluorobenzoate	2·5	$C_6H_4F\cdot CO\cdot CHPh_2$	—	84—85	—	82·7	5·2	82·7	5·2	Diamond-shaped prisms, from light petroleum
Ethyl phenylpropiolate	3·5	$CPh{:}C\cdot C(CHPh_2)_2\cdot OH$	1·8	178—179	—	90·4	6·1	90·5	6·0	Lancet-shaped crystals, from amyl alcohol; adds 1 mol. Br
Ethyl fluorene-9-carboxylate	5·4	CH_2Ph_2	—	—	—	—	—	—	—	
Acetyl chloride	3·5 (9)	,,	—	—	—	—	—	—	—	
Phenylacetyl chloride	7 (9)	,,	—	—	—	—	—	—	—	
Ethyl α-bromopropionate	4·1	$CHPh_2\cdot CHMe(CO\cdot CHPh_2$ and	—	130—131	—	89·2	6·7	89·2	6·7	Needles, from $Pr^{\beta}OH$ or petroleum
		(after hydrolysis) $CHPh_2\cdot CHMe\cdot CO_2H$	—	160—161	—	80·0	6·7	80·0	6·7	Leaflets, from 25% AcOH
Ethyl *iso*butyrate	2·4	(CH_2Ph_2 and) $CHMe_2\cdot CO\cdot CHPh_2$	1·5	75—76	—	85·7	7·6	85·4	7·6	Needles, from light petroleum
Ethyl α-benzylpropionate	3·8	(CH_2Ph_2 and) $CH_2Ph\cdot CHMe(CO\cdot CHPh_2$	1·8	—	250—252/16	88·0	7·1	87·9	7·1	
Ethyl dibenzylacetate	5·4	(CH_2Ph_2 and) $(CH_2Ph)_2CH(CO\cdot CHPh_2$	2·2	107—108	—	89·2	6·7	89·2	6·7	Prismatic plates, from MeOH
Methyl cinnamate	4	$CHPh_2\cdot CHPh(CH_2\cdot CO_2Me$	—	126—127	—	83·7	7·0	83·6	6·7	Prisms, from MeOH or petroleum

[1] Ziegler, Grabbe, and Ullrich, *Ber.*, 1924, **57**, 1983.
[2] Schlenk and Bergmann, *Annalen*, 1928, **465**, 45.
[3] Gardeur, *Chem. Zentr.*, 1897, II, 661.
[4] Found: C, 85·1; H, 5·4. Calc. for $C_{26}H_{19}Cl$: C, 85·2; H, 5·2%. Compare Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2954; Norris and Tibbett, *J. Amer. Chem. Soc.*, 1921, **42**, 2091.
[5] Boiling acetyl chloride gives an anomalous product, m. p. 185—186° (from propyl alcohol), which has the composition $C_{26}H_{20}O_3Cl_2$ of a peroxide of the above carbinol.
[6] Found: C, 64·0; H, 3·7. Calc. for $C_{26}H_{18}Br_2$: C, 64·1; H, 4·1%.
[7] Found: C, 89·4; H, 6·2. Calc. for $C_{27}H_{22}O$: C, 89·4; H, 6·1%.
[8] For similar reactions, see Bergmann and Rosenthal, *J. pr. Chem.*, 1932, **135**, 267.

For other reactions of benzhydryl sodium, see Schlenk and Bergmann, *Annalen*, 1928, **464**, 1; 1930, **479**, 72; Bergmann and Weiss, *Ber.*, 1931, **64**, 1488.