were collapsed, their fibrils loosened from one another, indicating that materials between the fibrils had been removed (Fig. 1). The residue is free of hyphae, which suggests that the loss in wood constituents is due to hydrolysis rather than fungous attack. Loss of weight through hydrolysis rather than decay is also suggested by the low alkali-soluble content of the fossil materials.

Acknowledgments.—The authors further acknowledge receiving the woods through the kindness of I. W. Bailey of the Bussey Institute, R. W. Chaney of the University of California, and E. F. Smith of the Eldorado National Forest; identification of the specimens by G. J. Griffin of the Forest Products Laboratory and by I. W. Bailey; examination for indications of decay by C. A. Richards of the Bureau of Plant Industry.

Summary

Samples of pine, cedrus and sequoia woods mined from the Miocene auriferous gravels about 200 feet below the surface of the ground in California have been analyzed. A marked decrease has occurred in the extraneous and the carbohydrate content of the woods. On the other hand, the lignin content of the residues is abnormally high as compared with that of a normal wood of the same genus. On the basis of the original wood, the lignin has decreased less than any other constituent.

Microscopical examinations of the residue and the relation between the alkali solubility and cellulose content of the fossil woods indicate that decomposition was due to agencies other than fungous attack. Hydrolysis appears likely.

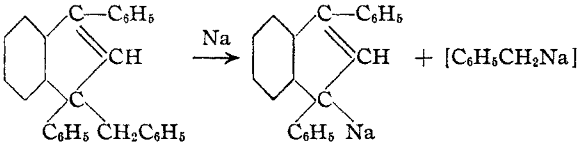
MADISON, WISCONSIN RECEIVED APRIL 20, 1934

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Sodium on 1-Benzyl-1,3-diphenylindene

BY C. FREDERICK KOELSCH

In an attempt to obtain further information about the rearrangement which occurs when sodium reacts with 1,1,3-triphenylindene,[1] the action of sodium on the hydrocarbon 1-benzyl-1,3-diphenylindene has been investigated. It was expected that either the 1-benzyl or the 1-phenyl would migrate, but neither of these expectations was realized. Instead the benzyl group is simply cleaved from the molecule, resulting in the formation of toluene[2] and the sodium derivative of 1,3-diphenylindene.



A similar but very much slower reaction takes place when 9-benzyl-9-phenylfluorene is treated with sodium. The benzyl group is cleaved and 9-phenylfluorylsodium is formed.

Experimental

1-Benzyl-1,3-diphenylindene.—The vigorous reaction between 40% sodium amalgam and 1,3-diphenylindene dissolved in ten times its weight of ether requires external cooling and is complete after less than thirty minutes of shaking. The excess amalgam should be separated as soon as possible after the reaction is over, for if the supersaturated solution is allowed to stand the 1,3-diphenylindylsodium crystallizes and renders it impossible to remove the amalgam.

The deep yellow ether solution of diphenylindylsodium from 10 g. of the hydrocarbon is rapidly decolorized and heat is evolved when an excess of benzyl chloride is added. The ether, etc., is removed with steam and the residue is crystallized from acetic acid, giving 10.5–11.5 g. of benzyldiphenylindene which forms colorless needles that melt at 100–102°.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.9; H, 6.1. Found: C, 94.0; H, 6.1.

Cleavage of Benzyldiphenylindene.—The hydrocarbon (10 g.) dissolved in 100 ml. of ether starts to react within five minutes when it is shaken with an excess of 40% sodium amalgam, and the reaction is complete after one hour. The resulting yellow solution is hydrolyzed, and the ether and toluene are removed with steam. The residue is crystallized from acetic acid, giving 6.5 g. (90%) of 1,3-diphenylindene. The substances volatile with steam are shaken with an excess of concentrated hydrochloric acid, which dissolves the ether and leaves 1.25 g. (50%) of pure toluene, identified by its boiling point and by conversion into 2,4-dinitrotoluene.

Other reactions of the 1,3-diphenylindylsodium obtained (A) by this cleavage and (B) from 1,3-diphenylindene are summarized in Table I. The yields in all cases are nearly

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(1) Ziegler and Crössmann, *Ber.*, **62**, 1768 (1929); *cf.* Koelsch, THIS JOURNAL, **56**, 480, 1337 (1934).

(2) Sodium benzyl reacts with ether to give toluene, Schorigin, *Ber.*, **43**, 1931 (1910).

quantitative; the products are crystallized from acetic acid.

TABLE I

REACTIONS OF DIPHENYLINDYLSODIUM

No.	Source of RNa	Reagent	Product 1-( )-1,3-diphenylindene
1	A	CH_3I	Methyl
2	B	CH_3I	Methyl
3	A	C_6H_5COCl	Benzoyl
4	B	C_6H_5COCl	Benzoyl
5	A	*p*-ClC_6H_4COCl	*p*-Chlorobenzoyl

No.	M. p., °C.	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	59–60	$C_{22}H_{18}$	93.6	6.4	93.1	6.4
2	59–60[a]	$C_{22}H_{18}$	93.6	6.4	93.5	6.4
3	150–152[b]	$C_{28}H_{20}O$[c]	90.2	5.4	89.9	5.5
4	150–152[d]	$C_{28}H_{20}O$	..	...	..	...
5	133–135[e]	$C_{28}H_{19}OCl$	82.7	4.7	82.8	4.8

[a] Mixed m. p. with No. 1. [b] No desoxybenzoin, which would be formed if sodium benzyl remained as such, was present in the products. [c] *Mol. Wt.* Calcd.: 372. Found (Rast): 398. [d] Mixed m. p. with No. 3. [e] Crystallized from ligroin. Crystallized from acetic acid, *p*-chlorobenzoyldiphenylindene forms white plates that melt at 88–90° and contain one molecule of acetic acid. Found: C, 77.0; H, 5.0. $C_{28}H_{19}OCl + C_2H_4O_2$ requires: C, 77.1; H, 4.9. Titration of the acetic acid neutralized by boiling the compound with 0.1 *N* sodium hydroxide gives values of 500–630 for the molecular weight (calcd. 466).

Oxidation of 1-Methyl-1,3-diphenylindene.—Before it was recognized that the reaction between benzyldiphenylindene was simply cleavage, the structures of the products were investigated by oxidation.

Ten grams of methyldiphenylindene from benzyldiphenylindene (Table I, No. 1) is dissolved in 50 ml. of acetic acid and a solution of 10 g. of chromic acid in dilute acetic acid is added slowly, keeping the temperature at 23–27° by external cooling. After remaining at this temperature for twelve hours, the mixture is poured into water and ether. The substance not soluble in sodium carbonate (3 g.) melts at 147–149° alone or mixed with an authentic sample of *o*-dibenzoylbenzene. No benzoic acid is formed. The substance soluble in sodium carbonate separates from acetic acid in colorless prisms that melt at 139–140° and analyze for **_o_-benzoyl-α,α-diphenylpropionic acid,** yield, 2.8 g.

Anal Calcd. for $C_{22}H_{18}O_3$: C, 79.9; H, 5.5. Found: C, 79.7; H, 5.5.

On oxidation with an excess of chromic acid in acetic acid at 80° the keto acid is converted into *o*-dibenzoylbenzene.

Oxidation of _p_-Chlorobenzoyldiphenylindene.—The chloro ketone (Table I, No. 5) (10 g.) is oxidized by chromic acid in acetic acid at 80–85° to dibenzoylbenzene and *p*-chlorobenzoic acid in nearly quantitative yields. Only a few mg. of benzoic acid is formed.

Cleavage of 9-Benzyl-9-phenylfluorene.—One-half gram of the hydrocarbon dissolved in 10 ml. of ether starts to react with an excess of 40% sodium amalgam after shaking for one and one-half hours. The color deepens very slowly, but after five days of shaking the solution deposits orange crystals of 9-phenylfluorylsodium. The hydrocarbon mixture obtained by hydrolysis and crystallization from acetic acid melts unsharply, but it can be separated completely into its constituents by carefully seeding its supersaturated solution in ligroin first with 9-benzyl-9-phenylfluorene and then with 9-phenylfluorene. There is obtained 0.3 g. of the first and 0.15 g. of the second pure hydrocarbon.

Summary

1-Benzyl-1,3-diphenylindene is rapidly cleaved by sodium amalgam in ether to toluene and 1,3-diphenylindylsodium. Similarly but much more slowly 9-benzyl-9-phenylfluorene is cleaved by this reagent to 9-phenylfluorylsodium.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 20, 1934