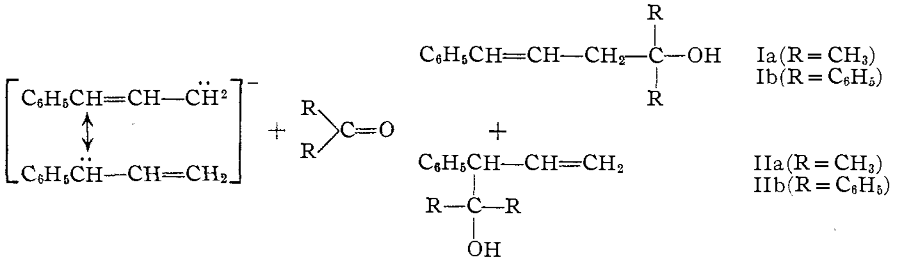
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXIII. The Reaction of the Sodium Derivative of Allylbenzene with Carbonyl Compounds

BY TOD W. CAMPBELL[1] AND WILLIAM G. YOUNG

In a continuation of the study of allylic sodium compounds,[2] the sodium derivative of allylbenzene in liquid ammonia solution has been allowed to react with a number of carbonyl compounds. The reaction mixtures were then examined for products of types I and II

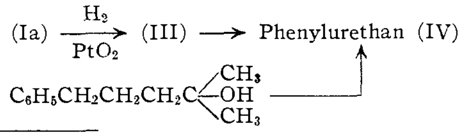

$$\left[C_6H_5CH{=}CH{-}\ddot{C}H^2 \updownarrow C_6H_5\ddot{C}H{-}CH{=}CH_2\right]^- + R_2C{=}O \longrightarrow C_6H_5CH{=}CH{-}CH_2{-}C(R)_2{-}OH + C_6H_5CH(C(R)_2OH){-}CH{=}CH_2$$

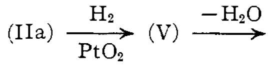
Ia(R = CH_3)
Ib(R = C_6H_5)
IIa(R = CH_3)
IIb(R = C_6H_5)

In similar reactions, allylic Grignard reagents have been shown[3] to give reaction products of type II only. However, the allylic sodium compound gives mixtures of both types I and II the composition depending upon the carbonyl compound.

Carbon dioxide, when allowed to react with sodium allylbenzene in liquid ammonia, gave only a 2% yield of carboxylic acids, since the sodium derivative was decomposed by the ammonium carbamate which formed rapidly. However, a sufficient quantity of the carboxylic acids was obtained for separation and analysis. The mixture was treated with hot alkali to rearrange the liquid phenylvinylacetic acid into the more easily handled solid methyltropic acid, $C_6H_5\underset{CO_2H}{C}{=}CHCH_3$.[3a] The resulting mixture was found to be about 90% methylatropic acid and 10% of β-benzalpropionic acid, by fractional crystallization. This corresponds to 90% of type II and 10% of type I in the above equation.

Acetone, under similar conditions, gave a mixture of tertiary carbinols (Ia and IIa) in fair yield, which could be separated easily by a precise fractional distillation. The characterization of the products is represented by the equations


$$(Ia) \xrightarrow[PtO_2]{H_2} (III) \longrightarrow \text{Phenylurethan (IV)} \qquad (III) = C_6H_5CH_2CH_2CH_2C(CH_3)_2OH$$


$$(IIa) \xrightarrow[PtO_2]{H_2} (V) \xrightarrow{-H_2O} C_6H_5C(=C(CH_3)_2){-}CH_2CH_3 \text{ (VI)}$$

Compound (VI) was ozonized, and propiophenone was characterized as its 2,4-dinitrophenylhydrazone. From the distillation data and the physical constants, the original mixture of carbinols was found to be 35% (Ia) and 65% (IIa).

Substitution of benzophenone for acetone in the reaction with the sodium derivative gave a 75% yield of a single reaction product, diphenylcinnamyl carbinol (1,1,4-triphenylbutene-3-ol-1), which was characterized as (VII)

$$(Ib) \xrightarrow[PtO_2]{H_2} C_6H_5CH_2CH_2CH_2C(C_6H_5)_2OH \text{ (VII)}$$

Compound (VII) was synthesized independently, and the properties were shown to be identical to those of the product obtained by hydrogenating (Ib).

Additional proof of structure of compounds of type (I) was obtained from their absorption spectra which showed characteristic maxima.[4]

Experimental

Carbonation of Sodium Allylbenzene.—The sodium derivative was made in the usual way[2,5] from 0.25 mole of allylbenzene and 0.25 mole of sodamide in liquid ammonia. A large excess of powdered Dry Ice was added all at once to the liquid ammonia solution of the sodium compound. The ammonia was allowed to evaporate, and the acids were taken up in dilute sodium hydroxide solution. The alkaline solution was boiled for an hour to isomerize phenylvinylacetic acid to methylatropic acid,[3a] and then cooled and acidified. The solid acids were taken up in ether, the ethereal solution was dried, and the ether removed. The residual solid was fractionally crystallized from aqueous methanol. In this manner pure methylatropic acid (m. p. and mixed m. p. with authentic sample, 134°) and pure β-benzalpropionic acid (m. p. and mixed m. p. with an authentic sample, made according to the method of Fittig and Jayne,[6] was 84–85°. The composition of intermediate fractions was determined by comparing their melting points with a melting point–composition diagram. Of the total yield of acids, 1.16 g. (89%), was methylatropic acid, and (11%) was β-benzalpropionic acid.

Other similar experiments, in which the sodium derivatives were prepared both from allylbenzene and propenylbenzene, showed about the same composition.

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[1] Abbott Laboratories Research Fellow, 1944–1945.

[2] Campbell and Young, THIS JOURNAL, **69**, 688 (1947).

[3] (a) Gilman and Harris, *ibid.*, **49**, 1825 (1927); **53**, 354 (1931); **54**, 2074 (1932); Ou Kuin Hou, *Ann. chim.*, **13**, 175 (1940); (c) Young and Roberts, THIS JOURNAL, **66**, 543 (1944); **67**, 148; 319 (1945); **68**, 649; 1472 (1946); (d) Lane, Roberts and Young, *ibid.*, **66**, 543 (1944).

[4] Campbell, Linden, Godshalk and Young, *ibid.*, **69**, 880 (1947).

[5] Levy and Cope, *ibid.*, **66**, 1684 (1944).

[6] Fittig and Jayne, *Ann.*, **216**, 98 (1883).

The carbonation of cinnamylmagnesium bromide gave only phenylvinylacetic acid, as has been reported by Gilman and Harris.[3a]

The Reaction of Sodium Allylbenzene with Acetone.—Sodium allylbenzene was prepared from 118 g. (1 mole) of allylbenzene and 23 g. of sodium (as sodamide) in three liters of liquid ammonia. To the resulting solution was added 58 g. (1 mole) of pure dry acetone. As soon as the red color of the sodium derivative was discharged, strongly basic substances were decomposed by the addition of ammonium chloride, to prevent rearrangement of the double bond in any of the products. The ammonia was then allowed to evaporate, and the organic material was taken up in hexane, and the resulting solution was dried over anhydrous magnesium sulfate. The products were distilled through a distilling column packed with a one foot glass spiral. After removal of the hexane, a forerun of allylbenzene-propenylbenzene mixture (60 g.) was obtained. The addition products were then distilled, and separated into eighteen fractions

Fraction	B. p. °C.	Mm.	Wt., g.	$n^{25}\mathrm{D}$
1–8	128–132	27	31.7	1.5220–1.5250
9 and 10	126–139	20	4.9	1.5280–1.5396
11–17	139–144	20	12.0	1.5437–1.5460
18	Residue (polymer)		10.0	....

Representative fractions of these tertiary carbinols gave good yields of benzoic acid when oxidized with alkaline permanganate, and could be dehydrated by heating with a crystal of iodine.

Fractions 1–8 were combined and redistilled through a column packed with platinum gauze, which has been described previously.[2] The pure carbinol (IIa) was isolated at 113.5° (13 mm.); $n^{25}\mathrm{D}$ 1.5220; d^{25}_4 0.97360; MR_D 55.21 (calculated for (IIa) 55.07).

Anal.[7] Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.49; H, 9.20.

A crystalline phenylurethan could not be prepared.

Structure Proof for Carbinol (IIa).—Compound (IIa), (2-methyl-3-phenyl-4-pentenol-2), was hydrogenated in the presence of platinum oxide. A sample of carbinol weighing 5.1534 g. absorbed 724 ml. of hydrogen (corrected for reduction of the oxide) at 24° and 750 mm. This corresponds to a molecular weight 176.7; calcd. for $C_{12}H_{16}O$, 176.2. This saturated carbinol (V) was dehydrated to (VI) by heating with a crystal of iodine. The unsaturated hydrocarbon boiled at 197° (750 mm.). The dehydration product (VI) was ozonized and propiophenone was isolated at its 2,4-dinitrophenylhydrazone (VII), m. p. and mixed m. p. 192° after purification. The dehydration product (2.27 g.) gave 2.20 g. (50%) of crude propiophenone-2,4-dinitrophenylhydrazone.

Isolation and Structure Proof of Dimethylcinnamyl Carbinol (Ia).—Fractions 11–17 (see above) were combined and distilled through the same platinum-packed column. Carbinol (Ia) was obtained at 132° (15 mm.); $n^{25}\mathrm{D}$ 1.5460. The distillate solidified on standing to a white crystalline solid, m. p. 38–39°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.10; H, 9.17.

The carbinol gave a phenylurethan, m. p. 102°.

Anal. Calcd. for $C_{19}H_{21}O_2N$: C, 77.26; H, 7.48. Found: C, 77.08; H, 7.18.

Hydrogenation of carbinol (Ia) gave a substance (III) whose phenylurethan melted at 102° (depression with corresponding unsaturated urethan). Its melting point was not depressed by addition of the phenylurethan of dimethyl-(γ-phenylpropyl)-carbinol, prepared after the method of Bogert, Davidson and Apfelbaum.[8]

Absorption Spectrum of Dimethylcinnamyl Carbinol (IIa).—The higher-boiling carbinol (IIa) had an absorption spectrum characteristic of a compound with a double bond in conjugation with a benzene ring (4). It had the following maxima

Wave length, mmu.	293	284	250
Max.	1910	2165	17,500

Composition of the Original Mixture of Carbinols.—From the distillation data and physical constants, the composition of the original mixture of carbinols was calculated to be 35% (Ia) and 65% (IIa). These values are considered accurate within ±5%.

The Reaction of Sodium Allylbenzene with Benzophenone.—To 0.25 mole of sodium allylbenzene was added a precooled solution of benzophenone (46 g., 0.25 m.) in 200 ml. of dry toluene. The mixture was stirred until the ammonia evaporated; during the time the color changed slowly from bright red to orange. An equal volume of water was then added, and the toluene layer was separated and dried. Upon removal of the solvent, the reaction product was obtained as a yellowish solid. This material was fractionally crystallized from methanol. Only one product could be isolated. It formed white needles, m. p. 94–94.5°; yield, 52 g. (75%).

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.55; H, 6.87.

Hydrogenation of the Carbinol (Ib).—The carbinol (7.50 g.) in 200 ml. of 95% ethyl alcohol was hydrogenated at room temperature and atmospheric pressure in the presence of platinum oxide catalyst. The theoretical amount of hydrogen was absorbed in about two hours. The product (VII) crystallized in white needles from ethanol; m. p. 72–73°.

Independent Synthesis of (VII).—Ten grams (0.025 mole) of ethyl γ-phenylbutyrate b.p. 135–140° (13 mm.) was added to 0.125 *M* of phenylmagnesium bromide. The reaction mixture was decomposed after four hours. Repeated crystallization of the solid reaction product from ligroin, gave a 50% yield of diphenyl (γ-phenylpropyl)-carbinol, which melted at 73°.[9] This substance did not depress the melting point of the hydrogenation product (VII) mentioned above.

Ozonization of the Unsaturated Carbinol (VIII).—The carbinol (1.5 g.) was ozonized in the usual way and the ozonide decomposed under reductive conditions.[10] Benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone (m. p. and mixed m. p. 237°).

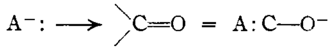
The Absorption Spectrum of Carbinol VIII.—The spectrum has again the characteristic maxima[4] due to conjugation.

Wave length, mmu.	294	284	254
Max.	1097	1908	20,500

Discussion of Results

In a previous communication[2] it has been shown that addition of a proton to the sodium derivative of allylbenzene gives a mixture of hydrocarbons which is radically different from that obtained by hydrolysis of cinnamylmagnesium chloride.

The reactions reported in the present communication involve the nucleophilic attack of the allylbenzene anion of the carbonyl carbon atom.



$$A^-: \longrightarrow \rangle C{=}O \;=\; A{:}C{-}O^-$$

Here again, significant differences are apparent in the products of the reactions studied, when they

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[7] We are indebted to Mr. Bruce F. Day and Mr. Welton Burney for analyses reported in this paper.

[8] Bogert, Davidson, and Apfelbaum, THIS JOURNAL, **56**, 959 (1934).

[9] Kharasch and Winehouse, *J. Org. Chem.*, **1**, 209 (1936), report 74° as the melting point of this substance, made by another method.

[10] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

are compared with the products from the corresponding Grignard reagent. Instead of the products of secondary addition observed with the Grignard reagent,[3] mixtures were obtained, the composition depending on the carbonyl compound employed.

The composition of the reaction mixture is a direct measure of the ratio of the rates of formation of products at the primary and the secondary carbon atoms of the allylic carbanion, K_p/K_s. For carbon dioxide, this ratio is about 0.1, phenylvinylacetic acid being formed about ten times as rapidly as β-benzalpropionic acid. For acetone the ratio is about 0.5, and for benzophenone, the ratio is quite large, since only one addition product could be isolated.

Nothing can be said about the absolute values of K_p and K_s, however, among the factors which could affect these constants and their ratio, steric effects probably play a prominent role.

Summary

1. The reactions of sodium allylbenzene with carbon dioxide, acetone, and benzophenone have been studied.
2. The reaction products are different from those obtained in similar reactions of allylic Grignard reagents, in that mixtures are produced which depend on the nature of the carbonyl group, while the Grignard reagent in all cases gives only one product, that of secondary addition.
3. It is considered that these mixtures arise due to different rates of reaction at the primary and the secondary carbon atom of the allylbenzene carbanion.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 21, 1947

[CONTRIBUTION FROM THE LABORATORY OF RADIOCHEMISTRY, UNIVERSITY OF CINCINNATI]

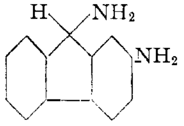
The Resolution of 9,2-Substituted Fluorenes[1]

BY FRANCIS EARL RAY AND ELIZABETH KREISER[2,3]

According to present-day theories there are two structures which may be assigned to fluorene. One is a uniplanar structure,[4] the other is a folded ring structure with the planes of the six-membered rings inclined at an angle of 20° to the plane of the five-membered ring.[5] If this latter be the case, substitution of the 9-carbon atom can produce two possible isomers, depending on whether the substituent group is *cis* or *trans* to the inclined six-membered rings.

The previous attempts to prove that fluorene possessed a non-planar structure by isolation of *cis–trans* isomers were unsuccessful.[6] Resolution of a fluorene substituted only on the 9-carbon would also be conclusive evidence for a non-planar form.

Bader[7] attempted to resolve the classically asymmetric 2,9-diaminofluorene, I, with *d*-tartaric acid and also by the aldehyde condensation with *d*-helicin and failed. He explained his failure by a novel theory that optical isomers do not exist in this case because of a mutual repulsion between the two amino groups that destroys the tetrahedral arrangement of the 9-carbon atom by forcing the substituents on the 9-carbon into the same plane.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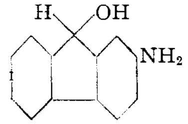
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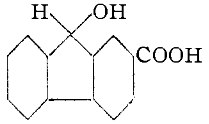
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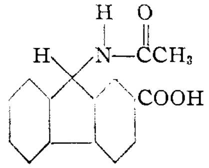
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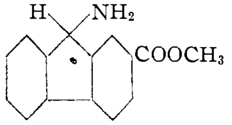
V

Later Bennett and Noyes[8] attempted to resolve 2,9-diaminofluorene using *d*-camphorsulfonic acid, *d*-phenylaminoacetic acid and *d*-hydroxymethylene camphor. These attempts, as well as an attempt to resolve 2-amino-9-hydroxyfluorene, II, with *d*-camphorsulfonic acid, were unsuccessful. Their opinion was that failure to resolve these compounds was caused by lack of the proper experimental conditions rather than any inherent symmetry. They, nevertheless, point out that Billon[9] was unable to resolve analogous compounds of the type $ArCHNH_2Ar'$.

It is of considerable importance that the possibility of resolving compounds with a 9-asymmetric carbon be thoroughly explored because if

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[1] Reported at the Chicago meeting of the American Chemical Society, September, 1946.

[2] Sloan-Kettering Institute for Cancer Research Fellow 1946–1947.

[3] A portion of the thesis submitted to the Graduate School, University of Cincinnati, by Elizabeth Kreiser in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947.

[4] Pinck and Hilbert, THIS JOURNAL, **59**, 8 (1937).

[5] Cook and Iball, *Chem. Ind.*, 467 (1936).

[6] Kliegl, Weng and Wiest, *Ber.*, **63**, 1262, 1631 (1930).

[7] Bader, Thesis, Ludwig Maximilian University of Munich, 1926.

[8] Bennett and Noyes, THIS JOURNAL, **52**, 3437 (1930).

[9] Billon, *Ann. chim. phys.*, [10] **7**, 314, 384 (1927).