acid, m. p. 255–257° (after sublimation *in vacuo*) (reported m. p. 255–256°, subl.);[19] the yield was 10.7 g. (71%). The acetyl derivative melted at 197.5–198.5° (reported 198.5).[20] The ether filtrate was evaporated yielding 12 g. (66%) of benzophenone. The semicarbazone melted at 163–164° (reported m. p. 164°).[21]

## Summary

1. Benzohydrylamine and certain of its derivatives react with potassium amide in liquid ammonia to form red colored solutions indicating the formation of the corresponding carbanions.

2. Carbonation of the potassium salt of benzohydrylamine has given the corresponding α-amino acid.

3. Carbonation of the carbanion of benzalbenzohydrylamine gives the N-benzohydrylidene α phenylglycine instead of N-benzal α,α-diphenylglycine.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 2, 1948

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[19] Zelinsky and Stadnikoff, *Ber.*, **39**, 1726 (1906).

[20] Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1943, p. 112.

[21] See ref. 5, p. 264.

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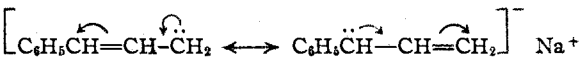
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

# Allylic Rearrangements. XXV. Reaction of the Sodium Derivative of Allylbenzene with α-Haloacetic Acids

BY TOD W. CAMPBELL AND WILLIAM G. YOUNG

The sodium derivative of allylbenzene, which has been the subject of recent investigations[1] undergoes reactions which can best be expressed[1c] as nucleophilic attacks by the resonating anion

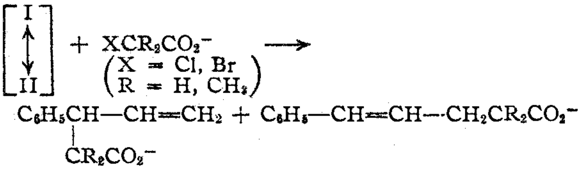


$$\left[C_6H_5\ddot{C}H{=}CH{-}\ddot{C}H_2 \longleftrightarrow C_6H_5\ddot{C}H{-}CH{=}CH_2\right]^- Na^+$$

I II

Since most reactions studied in which steric effects are not serious lead to mixtures of products derived from both of the principal resonance forms of the allylbenzene anion, it seemed odd that the reaction with simple halides[1a] gave, at least principally, products derived from form II above.

In an attempt to clarify the issue, the reaction of sodium allylbenzene with a series of α-haloacetate ions was examined. This particular series was chosen since it should be possible to determine the effect of (a) steric hindrance, (b) polarization and (c) the nature of the ion being displaced, on the manner in which the resonating allylbenzene carbanion reacts in displacement reactions. When the chosen reactants were mixed, a rapid reaction ensued. From the reacaction product was isolated a mixture of carboxylic acids, whose formation can be represented by the equation



$$\begin{bmatrix} I \\ \updownarrow \\ II \end{bmatrix} + \underset{\left(\begin{smallmatrix} X = Cl,\ Br \\ R = H,\ CH_3 \end{smallmatrix}\right)}{XCR_2CO_2^-} \longrightarrow$$

$$\underset{\displaystyle CR_2CO_2^-}{C_6H_5CH}{-}CH{=}CH_2 + C_6H_5{-}CH{=}CH{-}CH_2CR_2CO_2^-$$

All possible combinations of X and R were examined. The individual acids produced were separated and carefully characterized, principally as benzylamine salts.[2] The composition of the original mixtures was estimated to about ± 2% from the characteristic absorption spectrum[3] for the conjugated system.

From the results listed in Table IV, it will be seen that the polarizing effect of the carboxylate ion adjacent to the carbon atom being attacked is probably more important than simple steric hindrance, since the unsubstituted α-haloacetate ions are certainly less hindered than a compound such as α-methallyl chloride.[1a] It will be noted that the addition of methyl groups on the α-haloacetate ions leads to an increasing amount of the product arising from the primary form of the carbanion, as might be predicted from steric effects.[1c] It is also interesting to note that in this series the nature of the halogen being displaced definitely affects the composition of the mixture obtained from the resonating carbanion, the effect becoming more apparent as the number of methyl groups is increased. This effect of the halogen being displaced on the products has not been noted before in any of the reactions of sodium allylbenzene.

## Experimental Part

All melting points are uncorrected.

**Reaction of the Sodium Derivatives of Allylbenzene with α-Haloacetic Acids—General Method.**—The sodium derivative was prepared in 300 ml. of liquid ammonia in the usual manner[1] from 0.1 *M* of allylbenzene. The solution was forced over as rapidly as possible (by the vapor pressure of the liquid ammonia solvent) into a two-liter three-necked flask containing 0.05 mole of the appropriate α-haloacetic acid dissolved in 20 ml. of ether (anhydrous). The flask was equipped with a stirring device and a wide outlet tube to provide for escape of the ammonia vapors. The characteristic red color of the sodium derivative was discharged rapidly. After evaporation of the solvent, water was added, and the carboxylic acids were separated from the non-acidic material. Table I is a résumé of results obtained by this method. Data are averages of several experiments.

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[1] (a) Levy and Cope, THIS JOURNAL, **66**, 1684 (1944); (b) Campbell and Young, *ibid.*, **69**, 688 (1947); (c) *ibid.*, **69**, 3066 (1947).

[2] Buehler, Carson and Edds, *ibid.*, **57**, 2181 (1935).

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

TABLE I

PRODUCTION OF ACIDS BY COUPLING OF AN α-HALOACETIC ACID WITH SODIUM ALLYLBENZENE

| α-Haloacetic acid | Equivalent weight of mixture Theory | Observed | Yield,[a] % of mixed acids | Abs. spectrum of mixture[b] $\epsilon^{\text{Max.}}_{284}$ | $\epsilon^{\text{Max.}}_{294}$ |
|---|---|---|---|---|---|
| $ClCH_2CO_2H$ | 176 | 177 | 43 | 647 | 440 |
| $ClCH(CH_3)CO_2H$ | 190 | 189 | 54 | 784 | 545 |
| $ClC(CH_3)_2CO_2H$ | 204 | 203 | 40 | 1100 | 742 |
| $BrCH_2CO_2H$ | 176 | 176 | 74 | 650 | 450 |
| $BrCH(CH_3)CO_2H$ | 190 | 188 | 67 | 927 | 663 |
| $BrC(CH_3)_2CO_2H$ | 204 | 204 | 72 | 1270 | 919 |

[a] Yield based on α-haloacetic acid. [b] Maximum deviation in values of maximum averaged was 5%, mean deviation about 2%.

**Identification of Acidic Components of the Reaction Mixture from Bromoacetic Acid and Sodium Allylbenzene.**—The mixture of acids, obtained in 74% yield, was partially separated by filtration of the chilled product. The solid separated in this manner from the residual oil was recrystallized several times from ligroin. It formed shining white scales, m. p. 90°, which was identified as 4-phenyl-3-pentenoic acid by its melting point and the melting point (162°) of its dibromide.[4] Its equivalent weight was 176 (calculated for $C_{11}H_{12}O_2$, 176), and it yielded benzoic and succinic acids on ozonization. The benzylamine salt[2] of 4-phenyl-3-pentenoic acid melted at 108°.

*Anal.* Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found: C, 76.40; H, 7.61.

The oily mixture of acids remaining after filtration was dissolved in four times its volume of benzene, and an equivalent amount of potassium hydroxide was added as a 25% solution in methanol. The solid which precipitated was filtered off and found to be nearly pure potassium 4-phenyl-3-butenoate. This separation was purely fortuitous and was not expected. The residual solution was treated with dilute sulfuric acid, dried, and the solvent removed. The oily acid remaining gave a benzylamine salt melting at 97–98°.

*Anal.* Calcd. for $C_{18}H_{21}NO_2$; C, 76.29; H, 7.47. Found: C, 76.26; H, 7.55.

The oily acid was converted by hydrogenation to a solid acid, m. p. 58°. The benzylamine salt of the latter melted at 96–97°.

*Anal.* Calcd. for $C_{18}H_{23}NO_2$: C, 75.75; H, 8.12. Found: C, 75.94; H, 8.21. The hydrogenated acid was shown to be β-phenylvaleric acid (see below), thus the liquid acid was β-vinylhydrocinnamic acid. It could not be 2-phenyl-2-pentenoic acid, since the absorption spectrum of the liquid acid indicated that the double bond was out of conjugation with the benzene ring.[3]

**Synthesis of β-Phenylvaleric Acid.**—β-Ethylcinnamic acid, m. p. 94°, was synthesized through the Reformatsky reaction from propiophenone and ethyl bromoacetate.[5] Its benzylamine salt melted at 139–140°. *Anal.* Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found: C, 76.34; H, 7.43. This acid (19.70 g.) absorbed 2740 ml. of hydrogen at 750 mm. and 23° (theory 2750) over platinum oxide in ethyl acetate. The acid melted at 58° after recrystallization from warm (35°) methanol, to which water had been added to the cloud point. Its benzylamine salt melted at 96.5°. Neither the melting point of the acid, nor the melting point of the benzylamine salt, was depressed by addition of the corresponding product obtained by hydrogenation of β-vinylhydrocinnamic acid described above.

**Separation of the Reaction Products from α-Bromopropionic Acid and Sodium Allylbenzene.**—The methods described above could not be used to separate this mixture of acids. Benzylamine was added to the mixture, and the mixture of solid benzylamine salts was fractionally crystallized. It was possible to isolate the spectroscopically pure benzylamine salt of the *secondary* acid, α-methyl-β-vinylhydrocinnamic acid, m. p. 145.5°, by fractional crystallization from ethyl acetate. *Anal.* Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80. Found: C, 76.35; H, 7.87. The benzylamine salt of the primary acid could not be obtained optically pure, by direct recrystallization.

The residual impure benzylamine salt, which was rich in the primary acid, was dissolved in glacial acetic acid. An equivalent amount of bromine in acetic acid was added, followed by dilution with water, to give an oily dibromo-acid and a solid dibromo-acid. The solid was isolated and purified by recrystallization from aqueous ethanol; long, lustrous needles, m. p. 133°. This solid dibromo-acid was refluxed with zinc dust in isopropyl alcohol. The resulting oily acid was isolated and converted to a benzylamine salt, which was recrystallized from Skellysolve C, giving long needles, m. p. 119°. *Anal.* Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80. Found: C, 76.58; H, 7.92. The absorption spectrum[3] of the salt indicated that it was derived from the primary acid.

**Separation of Acids Derived from the Sodium Derivative of Allylbenzene and α-Bromoisobutyric Acid.**—The primary acid was obtained by filtration of the partially solidified mixture. It was obtained optically pure on recrystallizing from methanol–water. It formed massive prisms, m. p. 104°. Its benzylamine salt melted at 145.5°. *Anal.* Calcd. for $C_{20}H_{25}NO_2$: C, 77.13; H, 8.09. Found: C, 77.23; H. 8.28. The secondary form of the acid could not be obtained spectroscopically pure.

**Absorption Spectra of the Pure Acids Derived from the Primary Form of the Allylbenzene Carbanion.**—The absorption spectra of these acids and their benzylamine salts were taken on the Beckmann ultraviolet spectrophotometer and are tabulated in Table II.

TABLE II

| Acid | Absorption spectra of acid 293 Max. | 284 Max. | 250 Max. | Absorption spectra of benzylamine salt 293 Max. | 284 Max. | 250 Max. |
|---|---|---|---|---|---|---|
| $C_6H_5CH{=}CHCH_2CH_2CO_2H$ | 791 | 1120 | 18,470 | 820 | 1260 | 17,020 |
| $C_6H_5CH{=}CH{-}CH_2CH(CH_3)CO_2H$ | (850)[a] | (1250)[a] | (18,800)[a] | 850 | 1385 | 18,500 |
| $C_6H_5CH{=}CHCH_2C(CH_3)_2CO_2H$ | 978 | 1380 | 19,030 | 971 | 1498 | 19,980 |

[a] Estimated values from benzylamine salt.

**Composition of Original Reaction Mixture by Spectral Analysis.**—From the extinction coefficients quoted above, the percentage composition was calculated from the formula

$$(\%\text{ of Compound I}) = \frac{\epsilon^{\text{mixture}}_{\text{molar}}}{\epsilon^{\text{Pure I}}_{\text{molar}}} \times 100$$

TABLE III

| α-Haloacetic acid | Composition of mixture x = Cl, per cent from anion primary | secondary | Composition of mixture x = Br, per cent from anion primary | secondary |
|---|---|---|---|---|
| $XCH_2CO_2H$ | 57.2 | 42.8 | 57.6 | 42.4 |
| $XCH(CH_3)CO_2H$ | 63.4 | 36.6 | 76.0 | 24.0 |
| $XC(CH_3)_2CO_2H$ | 77.2 | 22.8 | 93.3 | 6.7 |

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[4] Fichter and Bauer, *Ber.*, **31**, 2002 (1898).

[5] Shriner, "The Reformatsky Reaction" in "Organic Reactions," Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1942, p. 1.

where (I) is derived from the primary form of the allylbenzene carbanion. It was assumed that the acid derived from the secondary form of the allylbenzene carbanion would have extinction coefficients of approximately zero at 294 mμ, 20 at 283 mμ and $\epsilon_{\text{molar}}^{\text{mixture}}$ was accordingly corrected. The results are tabulated in Table III.

## Summary

1. Sodium allylbenzene has been prepared and allowed to react with a series of α-haloacetic acids to give mixtures of substituted γ-benzalbutyric and hydrocinnamic acids.

2. The observed results have been discussed with regard to the possible influences which may alter the course of the reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

# Perfluoro-2-butyne and its Hydrogenation Products

BY ALBERT L. HENNE AND WILLIAM G. FINNEGAN

Preceding articles have reported fluorinated compounds with a $CF_3$ group adjacent to another function, double bond, acid, alcohol or halide. A compound, $CF_3C{\equiv}CCF_3$, with a triple bond flanked by two $CF_3$ groups has now been prepared[1] and examined. In line with our expectations, the triple bond is so sluggish that it does not appreciably accept halogens at room temperature; it is however very sensitive to alkaline oxidation, and breaks quantitatively to give two moles of trifluoroacetic acid. In addition, it easily accepts one mole of hydrogen on Raney nickel to yield $CF_3CH{=}CHCF_3$, presumed to be the *cis*-isomer; it takes up two molecules of hydrogen with equal facility to form $CF_3CH_2CH_2CF_3$.

**Preparation of $CF_3C{\equiv}CCF_3$.**—A three-liter flask heated on an electric nest is equipped with a sealed stirrer and a reflux condenser of the "down draft and overflow return" type the outlet of which leads to a Dry Ice-cooled receiver. This type of condenser permits high rates of reflux without flooding; it receives vapors at its top and syphons the condensate from its bottom back to the boiler. The flask is loaded with six moles (420 g.) of zinc dust, six moles (1380 g.) of dried and distilled $CF_3CCl{=}CClCF_3$[2] and 900 ml. of absolute alcohol. Constant stirring and refluxing is maintained for ten days, with a liquid temperature of about 40°. At the end of this period, distillation is performed until the liquid in the flask reaches 78°; the distillate is combined with the reaction product which had been collected in the chilled receiver during the ten-day period. Rectification of this combined material yields 477 g. (49.1% conversion, 54.4% net yield) of $CF_3C{\equiv}CCF_3$, b. p. $-24.7°$ to $-24.5°$; 5 g. of an intermediate fraction, b. p. $-20°$ to $+24°$; 14 g. of impure $CF_3CH_2CH_2CF_3$, b. p. 25° to 27°; 322 g. of impure $CF_3CCl{=}CHCF_3$ (mixed *cis* and *trans*), b. p. 31 to 37°; 31.5 g. of an intermediate cut; and 140 g. of recovered $CF_3CCl{=}CClCF_3$, b. p. 65 to 67°. The material balance is thus 90%. Refractionation of the ($-20$ to $+24°$) intermediate yielded 4 g. of a compound boiling within one degree of 6°; this will be referred to as "the 6° cut." Wojcik[1] mentions a (0 to $+5°$) cut, and states that it is "a $C_4F_6$ isomer."

The main reaction product was quantitatively oxidized in a sealed vessel by the procedure previously reported[3] to give 1.74 moles of trifluoroacetic acid per mole of $CF_3C{\equiv}CCF_3$, identified as its amide. The next most important product, $CF_3CCl{=}CHCF_3$, was found identical with a by-product obtained in the preparation of $CF_3CCl{=}CClCF_3$ and previously reported[2] as "presumably $CF_3CCl{=}CFCF_3$" on account of its ability to yield two moles of trifluoroacetic acid when oxidized. Recalculation of the atomic refraction *AR*F for fluorine on this new basis gave the excellent value of 1.07.

**Hydrogenation of $CF_3C{\equiv}CCF_3$.**—In a one-liter pressure vessel, 3.43 moles (556 g.) of $CF_3C{\equiv}CCF_3$ was hydrogenated by means of 3.5 moles of hydrogen at an initial pressure of 100 atm. and with 5 g. of Raney nickel and 10 ml. of absolute alcohol as catalyst. Reduction started at room temperature and proceeded rapidly with a large evolution of heat. A leak caused some material loss. The reduced material was distilled from the pressure vessel (heated to 50°) directly into a receiver cooled with Dry Ice. Rectification of this distillate gave 100 g. of recovered $CF_3C{\equiv}CCF_3$, and 368 g. of material boiling from 0 to $+33°$. The latter material was refractionated to give 119 g. of $CF_3CH_2CH_2CF_3$ and 191 g. of $CF_3CH{=}CHCF_3$. The material balance in the reduction step was only 83% on account of the leakage; the distillation steps had a material balance of 90%.

**Identification.**—The saturated derivative $CF_3CH_2CH_2CF_3$ was analyzed for fluorine: 68.6% calcd., 68.2% found. The identity of the olefin and that of the alkyne are derived from the facts that both yielded two molecules of $CF_3CO_2H$ on oxidation, and were transformed into the analyzed

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[1] Others have also obtained this derivative recently: W. T. Miller, Cornell, and E. T. McBee, Purdue, private communications; Wojcik, American Chemical Society fall meeting, New York, N. Y., 1947.

[2] Henne and Trott, THIS JOURNAL, 69, 1820 (1947).

[3] Henne and Zimmerschied, *ibid.*, 69, 281 (1947).