perature there was obtained 262 mg. (88%) of a yellow insoluble complex (C) whose appearance, solubility properties and infrared spectrum were quite different from those of complex A. In particular, the infrared spectrum of C showed a very strong absorption band at 9.4 μ which is absent in that of A.

Anal. Calcd. for $(C_{30}H_{25}OPdCl)_x$: C, 66.3; H, 4.5; Pd, 19.6; EtO, 8.3. Found: C, 65.6; H, 4.7; Pd, 19.8; EtO, 8.3.

Treatment of complex C with hydrogen chloride in chloroform regenerated the cyclobutadiene complex B in virtually quantitative yield. When complex A was stirred with ethanol for 18 hr. it was recovered unchanged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

A Mechanism for the Cleavage of Unsaturated Acids with Molten Alkali

BY WILLIAM A. BONNER AND ROBERT T. REWICK[1]

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A radiochemical and stoichiometric study of the scission of α,β-unsaturated acids with molten potassium hydroxide has been undertaken, using the cleavage of 2-phenylacrylic acid into formic and phenylacetic acids as a prototype. 2-Phenylacrylic-1-C^{14} acid yielded essentially non-radioactive formic acid, along with phenylacetic acid labeled exclusively at the carboxyl function. These results indicate that the formic acid product arose exclusively from the methylene carbon of 2-phenylacrylic acid and that no molecular rearrangements accompanied the fission, conclusions confirmed by similar experiments with 2-phenylacrylic-2-C^{14} acid. The alkali fusion of 2-phenylacrylic acid was accompanied by the liberation of over one mole of hydrogen and the production of no methanol, while the fusion of formaldehyde polymer with alkali yielded hydrogen, methanol and formic acid. A consistent mechanism for the alkali cleavage of α,β-unsaturated acids is proposed, involving β-hydroxylation followed by a retrograde aldol reaction.

Although the scission of an α,β-unsaturated acid into two acid fragments by action of molten alkali is a general reaction[2] recognized for over one-hundred years, no mechanistic study of this interesting process seems so far to have been undertaken. In the mid-nineteenth century Chiozza[3] and Kraut[4] noted the formation of benzoic and acetic acids along with hydrogen when cinnamic acid was added to molten potassium hydroxide. Later investigators made similar findings: acrylic acid yielded formic and acetic acids,[5] crotonic acid gave acetic acid,[6] and 2-phenylacrylic acid produced formic and phenylacetic acids[7] when fused with potassium hydroxide. Longer chain, non-conjugated fatty acids were observed to undergo a similar fission with molten alkali, with the interesting additional feature that the double bond usually migrated into the α,β-position prior to cleavage. Thus oleic acid yielded palmitic and acetic acids[8,9] and undecylenic acid gave nonanoic and acetic acids[10] under these conditions. That cleavage could occur prior to complete migration of the double bond into the conjugated position, however, was shown by Noorduyn[11] who isolated formic, acetic, propionic, butyric and valeric as well as C_{14}–C_{17} - acids when oleic acid was treated with potassium hydroxide at 260–280°. In view of the lack of fundamental information on such reactions, we have now undertaken their study from a mechanistic viewpoint. 2-Phenylacrylic acid was selected as the prototype for investigation in view of the ease of isolation of its reaction products and the smoothness (*e.g.*, lack of charring) with which its fusion with potassium hydroxide was found to proceed.

The first question to be considered was the origin of the formic and phenylacetic acids produced when 2-phenylacrylic acid is cleaved with molten alkali. While the results described in the literature might argue that eq. 1 should summarize the cleavage path we felt in view of the very stringent reaction conditions that neither 2, a combination of 1 and 2, nor the possibility of accompanying molecular rearrangement could be excluded *a priori*. A distinction between 1 and 2

$$CH_2|{=}C(Ph){-}C^{14}OOH \longrightarrow HCOOH + PhCH_2C^{14}OOH \quad (1)$$

$$CH_2{=}C(Ph)|{-}C^{14}OOH \longrightarrow HC^{14}OOH + PhCH_2COOH \quad (2)$$

should be possible using carboxyl-labeled 2-phenylacrylic acid, 1 affording carboxyl-labeled phenylacetic acid and 2 labeled formic acid.

The radiochemical consequences of the alkali fusion of 2-phenylacrylic-1-C^{14} acid are summarized in the first line of Table I, where it is seen that only 6.3% of the original radioactivity was associated with the formic acid product. The bulk of the label was located in the carboxyl group of the phenylacetic acid product, as demonstrated by oxidation of the latter to benzoic acid bearing less than 0.3% of the base radioactivity. These results argue for the essentially total intervention of 1 as the cleavage pattern of 2-phenylacrylic acid, with significant contributions of 2, C2–C1 phenyl migration or C2–C3 phenyl migration being specifically excluded.

TABLE I

RELATIVE RADIOACTIVITIES ON FUSION OF LABELED 2-PHENYLACRYLIC ACIDS WITH POTASSIUM HYDROXIDE

2-Phenylacrylic acid labeled at	Formic acid	Phenylacetic acid	Benzoic acid
C1: 1.000	0.063	1.013	0.0027
C2: 1.000	0.015	1.021	1.012

To confirm these conclusions we have also undertaken the alkaline cleavage of 2-phenylacrylic-

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[1] The authors are grateful to the National Science Foundation (NSF-G9479) for its generous support of this investigation.

[2] F. C. Whitmore, "Organic Chemistry," 2nd. Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 258 ff.

[3] L. Chiozza, *Ann.*, **86**, 264 (1853).

[4] K. Kraut, *ibid.*, **147**, 113 (1868).

[5] E. Erlenmeyer, *ibid.*, **191**, 376 (1878).

[6] A. Kekule, *ibid.*, **162**, 318 (1872).

[7] K. Kraut, *ibid.*, **148**, 242 (1868).

[8] F. Varrentrapp, *ibid.*, **35**, 196 (1840).

[9] F. G. Edmed, *J. Chem. Soc.*, **73**, 632 (1898).

[10] F. Becker, *Ber.*, **11**, 1413 (1878).

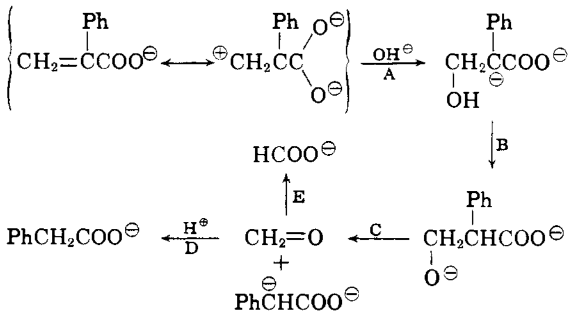
[11] A. C. Noorduyn, *Rec. trav. chim.*, **38**, 340 (1919).

2-C^{14} acid. In this case (Table I) the essential non-radioactivity of the formic acid and complete location of the label on the methylene carbon of the phenylacetic acid product were also in accord with the intervention of 1 and the exclusion of molecular rearrangements during the cleavage of 2-phenylacrylic acid.

The phenylacetic acid products from each of the above reactions showed higher radioactivity assays than their 2-phenylacrylic acid precursors. The fusion of carboxylic acids with alkali is known to produce decarboxylation,[12] and decarboxylations have been shown to be subject to normal isotope effects.[13] If decarboxylation competes with the above cleavages, a normal isotope effect in the decarboxylation process would require that the cleavage products be slightly more radioactive than the starting material. This explanation agreed with our additional observation that small amounts of polymeric material (styrene polymer?) accompanied the above 2-phenylacrylic acid fusions.

A mechanism consistent with the radiochemical data in Table I is presented in Chart I. The addition of $OH^{\ominus}$ at C-3 (step A) results from a reasonable postulate for the polarization of the 2-phenylacrylate ion and accords with the known isolation of β-hydroxyvaleric (along with 2-pentenoic) acid by action of concentrated alkali on 3-pentenoic acid[14] (presumably after preliminary migration of the double bond from β,γ to α,β[15]). Whether the proton shift in step B occurs by addition and abstraction or by direct migration is inconsequential. The final stages, C and D, constitute a reversal of the aldol reaction whose mechanism[16] and reversibility[16,17] are well known.

CHART I



Step E of Chart I, the conversion of the intermediate formaldehyde into the formic acid product, is one for which little precedent appeared available. We have investigated this step by studying the over-all stoichiometry of the alkali cleavage of 2-phenylacrylic acid. In principle, step E might be achieved in one or more of three ways, 3–5,

$$CH_2{=}O + KOH + 1/2O_2 \longrightarrow HCOOK + H_2O \quad (3)$$

$$2CH_2{=}O + KOH \longrightarrow CH_3OH + HCOOK \quad (4)$$

$$CH_2{=}O + KOH \longrightarrow HCOOK + H_2 \quad (5)$$

each requiring a different stoichiometry, 6, 7 and 8,

$$CH_2{=}C(Ph)COOH + 2KOH + 1/2O_2 \longrightarrow PhCH_2COOK + HCOOK + H_2O \quad (6)$$

$$2CH_2{=}C(Ph)COOH + 3KOH \longrightarrow 2PhCH_2COOK + HCOOK + CH_3OH \quad (7)$$

$$CH_2{=}C(Ph)COOH + 2KOH \longrightarrow PhCH_2COOK + HCOOK + H_2 \quad (8)$$

respectively, for the over-all cleavage process. Several investigators have noted the production of hydrogen during the alkali fusion of cinnamic acid,[3,4] suggesting the partial intervention, at least, of eq. 8. However, since hot potassium hydroxide and benzaldehyde afford not only benzoic acid and hydrogen[18] but also benzyl alcohol,[19] a Cannizzaro process such as 4, requiring 7 as the stoichiometry, could not be excluded.

When 1.73 millimoles of 2-phenylacrylic acid was fused with potassium hydroxide on a vacuum line, 2.54 millimoles (147%) of gas was liberated. Mass spectrometric analysis of the gas showed it to be at least 98% hydrogen and to contain no methanol. Similarly, when cinnamic acid was fused with potassium hydroxide the evolved gases were 94% hydrogen and no benzyl alcohol could be isolated, only benzoic and acetic acids being obtained. To us these observations exclude 6 and 7 as the stoichiometry of the cleavage reaction and eliminate 3 and 4 as operative processes for the conversion of the formaldehyde intermediate of Chart I into formic acid. The excess volume of hydrogen (47% above that required by 8) noted on the above reaction of 2-phenylacrylic acid was apparently engendered by further alkali degradation of the sodium formate product. Boswell earlier noted the formation of hydrogen and sodium carbonate on fusion of sodium formate with alkali,[20] and we have found that fusion of sodium formate with potassium hydroxide under the conditions of our reaction yielded 87% of the gas volume required by 9.

$$HCOONa + KOH \longrightarrow NaKCO_3 + H_2 \quad (9)$$

The intervention of 5 in the accomplishment of step E of Chart I finds precedent in the previously noted production of hydrogen during the alkali fusion of benzaldehyde.[18,19] We have confirmed the validity of 5 by the fusion of paraformaldehyde with potassium hydroxide, noting the production of formic acid and the liberation of gaseous products. Mass spectrometric analysis of the latter indicated a composition including 75% hydrogen and 20% methanol. The presence of methanol in this gas sample, in contrast to its absence in the gases liberated during alkali fusion of 2-phenylacrylic acid, indicates that the Cannizzaro process 4 must have competed with 5 in the paraformalde-

[12] C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, N. Y. (Reinhold Publ. Corp.), 1929, p. 330 ff.

[13] P. E. Yankwich and M. Calvin, *J. Chem. Phys.*, **17**, 109 (1949); J. Bigeleisen, *ibid.*, **17**, 425 (1949); P. E. Yankwich, E. C. Stivers and R. F. Nysham, *ibid.*, **20**, 344 (1952); G. A. Ropp and V. F. Raaen, *J. Am. Chem. Soc.*, **74**, 4992 (1952).

[14] R. Fittig and J. G. Spenzer, *Ann.*, **283**, 69, 74 (1894).

[15] R. P. Linstead and co-workers, *J. Chem. Soc.*, 363, 616, 2579 (1927); 2343 (1928); G. A. R. Kon and C. J. May, *ibid.*, 1549 (1927).

[16] Y. Pocker, *Chemistry & Industry*, 599 (1959); A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 283 ff.

[17] S. M. Gupta and S. S. Deshapande, *J. Indian Chem. Soc.*, **30**, 228 (1953); E. H. Usherwood, *J. Chem. Soc.*, **123**, 1717 (1923); **125**, 435 (1924).

[18] F. Wöhler and J. Liebig, *Ann.*, **3**, 253 (1932).

[19] J. U. Nef, *ibid.*, **298**, 302 (1897).

[20] M. C. Boswell, *Can. Chem. and Metallurgy*, **10**, 139 (1926).

hyde fusion. The absence of methanol in the 2-phenylacrylic acid case is presumably due to the low steady state concentration of the formaldehyde intermediate in Chart I, leading to a preference of the "unimolecular" process 5 over the "bimolecular" Cannizzaro path 4. The same argument may be advanced to rationalize the absence of benzyl alcohol in the alkali fusion of cinnamic acid and its presence[19] in the alkali fusion of benzaldehyde. The generality of 5 in competition with 4 under conditions of alkali fusion was further shown with hydratropaldehyde, where the gas evolved contained 90% hydrogen.

Finally, we may speculate briefly on the migration of the α,β-position of the double bonds in higher unsaturated acids prior to scission under conditions of alkali fusion.[8-10] Under the drastic environment involved it appears to us that allylic proton abstraction 10 is a reasonable mechanism for

$$\begin{array}{ll} \mathrm{RCH{=}CHCH_2(CH_3)_{\mathit{n}}\,COOK} \xrightarrow[-\mathrm{H_2O}]{\mathrm{OH^-}} & \\ \qquad\qquad \mathrm{RCH{=}CH^+CH(CH_3)_{\mathit{n}}COOK} & \\ \qquad\qquad\qquad\qquad \updownarrow & (10) \\ \mathrm{RCH_2CH{=}CH(CH_3)_{\mathit{n}}\,COOK} \xleftarrow[-\mathrm{OH^-}]{\mathrm{H_2O}} & \\ \qquad\qquad \mathrm{RCH^+CH{=}CH(CH_3)_{\mathit{n}}COOK} & \end{array}$$

double bond migration. Apparently 10 or its equivalent is able to compete at least partially[11] with the cleavage process (Chart I) until α,β-unsaturation is achieved, whereupon cleavage becomes predominant.

Experimental

Atrolactic-1-C^{14} Acid.—Radioactive potassium cyanide (0.63 millicurie) was diluted with potassium cyanide (54 g., 0.83 mole) and allowed to react with acetophenone (50 ml., 0.42 mole) and concd. hydrochloric acid (105 ml.) according to the procedure of Eliel and Freeman,[21] using proportional quantities of other reagents. A 7.60-g. (11.4%) yield of atrolactic-1-C^{14} acid hemihydrate was obtained, and approximately 70% of the initial acetophenone was recovered. Essentially similar results were obtained in earlier pilot runs. The atrolactic-1-C^{14} acid hemihydrate had a specific radioactivity of 1.352 mc./mole.

Acetophenone-α-C^{14}.—A mixture of benzoic-α-C^{14} acid (approximately 0.15 mc.) and thionyl chloride (5 ml.) was refluxed on the steam-bath for 30 minutes, cooled and transferred to a small distillation apparatus, adding non-radioactive benzoyl chloride (20 ml.). The solution was distilled approximately to dryness at 75° (15 mm.) and the residue was "chased" by distilling two 7.5-ml. portions of non-radioactive benzoyl chloride at the same temperature and pressure, affording 43 g. of radioactive benzoyl chloride. A 0.31 *M* solution of methylmagnesium bromide (100 ml.) was then added inversely with magnetic stirring to the above benzoyl chloride in ether (50 ml.) containing cuprous chloride (1 g.). The Grignard solution was added dropwise at such a rate as to cause mild reflux, and the mixture was stirred for an hour following the addition. Decomposition by addition of cracked ice, followed by customary processing, afforded crude acetophenone-α-C^{14}. This was distilled at 65–70° (9 mm.), "chasing" with non-radioactive acetophenone (25 ml.). A portion of the distilled product (22 g.) was converted to its semicarbazone for radioactivity assay, 0.579 mc./mole.

Atrolactic-2-C^{14} Acid.—The above acetophenone-α-C^{14} was diluted with acetophenone (8 g.) and the resulting 30 g. (0.498 mc./mole) was allowed to react with potassium cyanide (50 g., 0.77 mole) and concd. hydrochloric acid (70 ml.) as above. An unaccountably low yield (2.6 g.) of atrolactic-2-C^{14} acid hemihydrate was obtained and approximately 70% of the initial ketone was recovered unchanged. The acid product was not assayed at this point.

Labeled 2-Phenylacrylic Acids.—After considerable experimentation the following rather critical procedure was found to give the best results in the dehydration of atrolactic acid into 2-phenylacrylic acid.[22] Atrolactic acid hemihydrate (0.50 g.) was placed in a 100-ml. round-bottom flask and covered with concd. hydrochloric acid (25 ml.). The flask was placed in a steam-bath to a depth of 2 cm., then was heated vigorously for 10 minutes. The mixture was cooled in ice and the crude 2-phenylacrylic acid was collected and washed with a minimum of cold water; 0.2 g. (45%), m.p. 105–107°. The hydrochloric acid mother liquors were extracted with ether, yielding a product having m.p. 80–88°, presumably unreacted starting material. A second batch of product, m.p. 104–106°, could be obtained by dehydrating this recovered material in a similar fashion. The combined crude products were recrystallized from dilute ethanol, affording 0.2 g. of pure 2-phenylacrylic acid, m.p. 107–107.2°.

One 0.63-g. portion and three 1.0-g. portions of the above atrolactic-1-C^{14} acid hemihydrate were each dehydrated separately with concd. hydrochloric acid (25 ml.) as described above, producing a total of 1.40 g. (45.5%) of pure 2-phenylacrylic-1-C^{14} acid, m.p. 106.5–107°, specific radioactivity 1.353 mc./mole.

One 0.59-g. and two 1.0-g. portions of the above atrolactic-2-C^{14} acid hemihydrate were dehydrated separately as before, yielding a total of 1.0 g. (47%) of pure 2-phenylacrylic-2-C^{14} acid, m.p. 106.5–107°, specific radioactivity 0.472 cm./mole.

The Alkali Fusion of Labeled 2-Phenylacrylic Acids.—The following procedure was similar to that used in preliminary control experiments involving the alkali fusion of known mixtures of formic and acetic acids. It resulted in approximately quantitative recoveries of each acid from the mixtures. 2-Phenylacrylic acid (0.80 g., 5.4 mmoles) was mixed with powdered potassium hydroxide (3.0 g., 54 mmoles) in a 50-ml. nickel crucible. The covered crucible was heated gently with a bunsen burner, causing the solid to fuse smoothly to a clear, amber melt. After 2–3 minutes the melt was allowed to cool and solidify, then was dissolved in water (10 ml.). The chilled solution was cautiously acidified with concd. sulfuric acid (*ca.* 60 drops), producing a fluffy, white precipitate which was collected and rinsed with a small quantity of cold 3 *N* sulfuric acid. The solid was heated on the steam-bath with water (15 ml,) and the hot solution was filtered from a small quantity of insoluble, low-melting, yellow solid (not obtained during alkali fusion of known mixtures of formic and phenylacetic acids). The latter filtrate was acidified with concd. hydrochloric acid (10 ml.) and chilled, yielding 0.16 g. of pure phenylacetic acid, m.p. 77–77.5°. A single ether extraction of the mother liquors yielded an additional 0.20 g. of crude phenylacetic acid, m.p. 75–77°, which was purified by one recrystallization from water.

The aqueous layer from the latter ether extraction was continuously extracted with ether for 24 hours and the extract was reduced to a volume of 3 ml. by careful distillation through a 450-mm. Vigreux column. The residue was transferred to a micro-distillation apparatus and was carefully fractionated. The formic acid fraction was converted to its S-1-naphthylmethylthiuronium salt, m.p. 183.5° dec., in the manner previously described.[23]

The phenylacetic acid (0.50 g.) from the above cleavage reaction was oxidized quantitatively to benzoic acid by heating its solution in water (15 ml.) containing potassium permanganate (1.28 g.) and 10% sodium hydroxide (5 drops) for an hour on the steam-bath. The crude product was purified by recrystallization from water; m.p. 121.5–122°.

2-Phenylacrylic-1-C^{14} acid (0.90 g., 1.353 mc./mole) was fused with potassium hydroxide (3.4 g.), separating and purifying the reaction products as described above. The purified phenylacetic acid product had m.p. 76.5–77° and a specific radioactivity of 1.371 mc./mole. The purified S-1-naphthylmethylthiuronium formate derivative had a radioactivity assay of 0.0849 mc./mole. The benzoic acid ob-

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[21] E. L. Eliel and J. P. Freeman, *Org. Syntheses*, **33**, 7 (1953).

[22] *Cf.* R. Fittig and C. Wurster, *Ber.*, **13**, 376 (1880); J. J. Bougault, *Bull. soc. chim.*, [4] **3**, 1032 (1908); M. A. Haller, *Compt. rend.*, **146**, 766 (1908).

[23] W. A. Bonner, *J. Am. Chem. Soc.*, **70**, 3508 (1948).

tained by oxidation of the phenylacetic acid product had a specific radioactivity of 0.0036 mc./mole.

The above 2-phenylacrylic-2-C^{14} acid (0.82 g., 0.472 mc./mole) was fused with potassium hydroxide (3.1 g.) in the same fashion. The purified phenylacetic acid product, m.p. 76.5–77°, had a specific radioactivity of 0.482 mc./mole. The benzoic acid obtained on its oxidation had a specific radioactivity of 0.478 mc./mole. The S-1-naphthylmethylthiuronium formate derivative obtained in this experiment had a specific radioactivity of 0.069 mc./mole.

Gaseous Products from the Alkali Fusion of 2-Phenylacrylic Acid.—2-Phenylacrylic acid (254.7 mg., 1.73 mmoles) and powdered potassium hydroxide (1.100 g., 19.6 mmoles) were mixed thoroughly in a small flask and attached into a volume-calibrated vacuum line. Fusion of the mixture was accomplished by gentle flaming as described above, resulting in the evolution of 2.54 mmoles of gas. Mass spectrometric analysis of a sample of this gas indicated the composition: hydrogen, 98%; carbon dioxide < 1%; water < 1%; ethanol < 0.5%. The volume of hydrogen liberated during the above fusion was 147% of the quantity required by eq. 8.

The Alkali Fusion of Paraformaldehyde.—Paraformaldehyde (63.6 mg., 2.13 mmoles) and powdered potassium hydroxide (1.00 g., 17.9 mmoles) were mixed in a small flask, attached into the vacuum line and subjected to fusion as described above; 1.47 mmoles of gas was liberated. Mass spectrometric analysis of the gas sample showed the composition: hydrogen, 75%; methanol, 20%; acetone, 3%; water, trace; unidentified peaks at mass 72, 73, < 1%; formaldehyde, nil. The volume of hydrogen liberated in this experiment corresponded to approximately 52% of that required by eq. 5. A blank fusion of potassium hydroxide (1 g.) alone led to only a negligible evolution (7×10^{-3} mmole) of gas.

In another experiment paraformaldehyde (0.25 g.) and powdered potassium hydroxide (3.80 g.) were fused as before. The cooled melt was dissolved in water and the solution was acidified and extracted continuously with ether for 24 hours. The ether extract was extracted repeatedly with water, titrating each water layer with standard alkali to the phenolphthalein end-point. After 6 extractions, removal of formic acid (0.148 g. by titration) appeared approximately complete and the neutral aqueous extracts were evaporated *in vacuo* to dryness. The residue was treated with S-1-naphthylmethylthiuronium chloride as before, affording 0.62 g. (74% based on formic acid titer, 28% based on paraformaldehyde) of S-1-naphthylmethylthiuronium formate, m.p. 183.2° dec., mixed m.p. with an authentic sample undepressed.

The Alkali Fusion of Sodium Formate.—To demonstrate that the anomalously high hydrogen evolution during the alkali fusion of 2-phenylacrylic acid arose from the formic acid produced in its cleavage, the following experiment was undertaken. Sodium formate (142.6 mg., 2.10 mmoles) and potassium hydroxide (1.5 g.) were mixed in a small flask and attached into the vacuum line as usual. During the fusion there was liberated 1.82 mmoles of hydrogen (87% of the theoretical volume required by eq. 9). When phenylacetic acid (1 g.) and potassium hydroxide (3.5 g.) were fused in the vacuum line, the final pressure of the system was 26 mm., the vapor pressure of the water of neutralization at the temperature of the experiment. No discernible hydrogen evolution was noted.

The Alkali Fusion of Cinnamic Acid.—When cinnamic acid (1.85 mmoles) and potassium hydroxide (18 mmoles) were fused as before, considerable charring was noted and no clean melt was obtained as with 2-phenylacrylic acid. The volume of gas liberated corresponded to 2.29 mmoles. It had the following mass spectrometrically determined composition: hydrogen, 94%; methane, 1.6%; carbon dioxide, 2%; benzene, < 1%; toluene, 0.5%; water, 0.5%.

In a larger scale fusion of cinnamic acid (1.25 g.) with potassium hydroxide (5 g.) an attempt was made to isolate any benzyl alcohol formed by the Cannizzaro reaction. The cooled fusion mixture was dissolved in water and the alkaline solution was extracted thoroughly with ether. Evaporation of the extract yielded only a negligible amount (0.04 g.) of yellow solid and no benzyl alcohol. The alkaline layer was acidified and extracted twice with ether. The extract was dried, decolorized and freed of solvent to yield 1.0 g. (97%) of crude benzoic acid, m.p. 90–95°. This was purified by vacuum sublimation, m.p. 119–120°, mixed m.p. with an authentic sample 120–121.5°. Continuous extraction of the acidified aqueous layer for 24 hours with ether gave an extract, evaporation of which afforded a small liquid residue. This was titrated with alcoholic potassium hydroxide and found to contain approximately 0.31 g. (60%) of acetic acid. The latter was converted to its S-1-naphthylmethylthiuronium salt as usual, m.p. 159.6°, mixed m.p. with an authentic sample 160.5°.

The Alkali Fusion of Hydratropaldehyde.—Hydratropaldehyde (1.5 mmoles) and powdered potassium hydroxide (3 g.) were mixed by stirring and fused as usual in the vacuum line. Comparatively strong flaming for a longer period of time was required before gas evolution (1.02 mmoles, 68%) was noted. Mass spectrometric analysis of the liberated gas indicated the composition: hydrogen, 90%; ethylbenzene, 2%; air, 3%; water, 2%; benzene < 0.5%; methane, < 1%.

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The Synthesis and Chemistry of Fluoroazoalkanes

BY W. J. CHAMBERS, C. W. TULLOCK AND D. D. COFFMAN

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Fluoroazoalkanes ($R_fN{=}NR_f$) have been synthesized by reactions of lower valent metal fluorides and chlorine or bromine with cyanogen chloride and with carbonitriles of fluorocarbons and chlorocarbons. The fluoroazoalkanes have been found to serve as a source of fluoroalkyl radicals and to participate in various syntheses. Thus, with carbon monoxide they yield fluoroalkyl isocyanates; in Diels–Alder additions with 1,3-dienes they form substituted 1,2,3,6-tetrahydropyridazines; and defluorination by a metal carbonyl gives bis-(fluoroalkylidene)-azines ($R_fCF{=}N{-}N{=}CFR_f$). Bis-(perfluoropropylidene)-azine with sodium methoxide yields the symmetrical dimethoxy and tetramethoxy derivatives.

The fluoroazoalkanes as a class have been almost neglected except for the synthesis of the first members. Hexafluoroazomethane has been obtained from silver cyanide and fluorine,[1] from cyanogen iodide and iodine pentafluoride,[2–4] from cyanogen chloride with silver(II) fluoride,[5] by reaction of ethylenediamine or ethyleneimine with fluorine,[6a,b] and by fluorination of hydrogen cyanide with cobalt(III) fluoride.[7,8] Perfluoroazoethane was prepared in good conversions by the reaction of silver(II) fluoride with trifluoroacetonitrile or pentafluoroethyl isocyanate, and perfluoroazobutane was

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