stances and volatile acids. Glycerol, for example, would not be present in this fraction, but succinic, lactic and acetic acids, as well as unreacted glucose, would be. The low level of radioactivity in this fraction indicated that the fermentation was essentially complete. Analyses for glucose[19] on several of the residual solutions likewise indicated complete fermentation.

Acknowledgments.—The authors wish to express their appreciation to Drs. W. Manning and G. Hennig of the Argonne National Laboratory for the use of laboratory space for some of this work, and to Drs. W. Libby and A. Turkevich of the Institute for Nuclear Studies for the use of their counting equipment.

Summary

1. Glucose-1-C^{14} has been prepared by a modified Fischer–Kiliani synthesis from *d*(−)-arabinose and $HC^{14}N$. An over-all radiochemical yield of 10% was obtained.

2. A method is described for the degradation of isotopically labeled ethyl alcohol to determine quantitatively the relative amounts of radioactivity in the CH_3 and $-CH_2OH$ groups.

3. Glucose-1-C^{14} has been fermented by yeast and the distribution of radioactivity in the products ascertained. About 95% of the total radioactivity fermented appeared in the methyl group of the alcohol obtained. This result gives quantitative support to the currently accepted mechanism for the alcoholic fermentation.

4. About 3% of the radioactivity of glucose-1-C^{14} appeared in the carbon dioxide produced in the fermentation. Several alternative explanations of this deviation from the fermentation mechanism are discussed.

CHICAGO 37, ILL. RECEIVED NOVEMBER 25, 1949

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[19] P. Shaffer and A. Hartmann, *J. Biol. Chem.*, **45**, 349, 365 (1921).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reactions of 2-Arylcyclohexanones. III. Cyanoethylations and Mannich Reactions[1]

BY W. E. BACHMANN AND L. B. WICK[2]

2-Phenylcyclohexanone reacted readily with acrylonitrile in the presence of Triton B (40% aqueous benzyltrimethylammonium hydroxide) at the 2-position to give a monocyanoethylated product 2-oxo-1-phenylcyclohexanepropionitrile (II).[3] The ketonitrile was hydrolyzed to the corresponding acid (III) in good yield by a mixture of hydrochloric acid and acetic acid. The successful monocyanoethylation of 2-phenylcyclohexanone, in contrast to the difficulty of obtaining other than polycyanoethylated products from cyclohexanone and 2-methylcyclohexanone[4] even with limited amounts of acrylonitrile, is attributed to the reactive hydrogen atom on the carbon atom attached to the carbonyl group and the phenyl group.

6-Benzal-2-phenylcyclohexanone (V) was cyanoethylated to the crystalline 3-benzal-2-oxo-1-phenylcyclohexanepropionitrile (VI) in 83% yield; the product was identical with that produced by reaction of benzaldehyde with II. Hence, in the preparation of VI from 2-phenylcyclohexanone, the order in which the two reactions, benzalation and cyanoethylation, are employed is not important. By carrying out the benzalation first, one deals with solids in both steps. These reactions definitely establish the structure of II.

In order to introduce the cyanoethyl group in the 6-position of 2-phenylcyclohexanone, the hydrogen atom in the 2-position was replaced by a bromine atom. The crystalline 2-bromo-2-phenylcyclohexanone (VII) was obtained in good yield by bromination of 2-phenylcyclohexanone in carbon tetrachloride. Treatment of the bromoketone with Triton B and acrylonitrile yielded a cyanoethylated product which was unsaturated and contained no halogen. This product (XI) must have resulted in virtue of the dehydrobrominating action of the Triton B either prior to or after cyanoethylation. Since it was observed that the solution of 2-bromo-2-phenylcyclohexanone remained neutral during the first additions of Triton B, cyanoethylation must have proceeded *via* the unsaturated ketone 2-phenyl-2-cyclohexenone (X) at least to some extent. The unsaturated ketone can be prepared in good yield by the action of hot 2,6-dimethylpyridine on the bromoketone. The unsaturated ketonitrile (XI) was hydrolyzed to the unsaturated ketoacid. Hydrogenation of the double bond and the carbonyl group followed by oxidation of the alcohol group yielded the crystalline 2-oxo-3-phenylcyclohexanepropionic acid (XII), which was shown to be different from the isomeric acid III. Only one racemic mixture of the two possible diastereoisomeric forms of XII was obtained in crystalline form.

6-Benzal-2-phenylcyclohexanone (V) reacted

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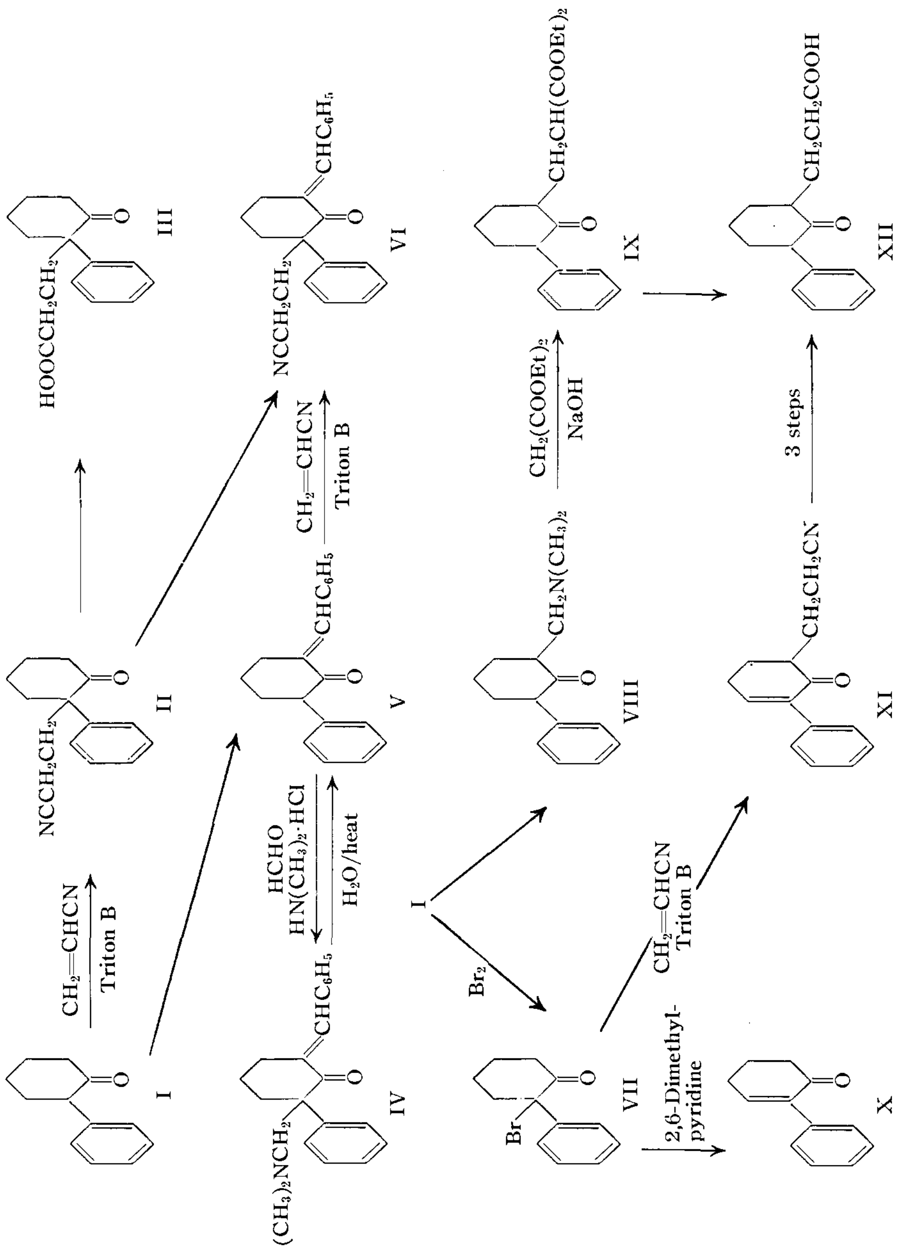
[1] Paper II, Bachmann and Wick, THIS JOURNAL, **72**, 2000 (1950).

[2] From the Ph.D. dissertation of L. B. Wick. Present address: Department of Chemistry, Coe College, Cedar Rapids, Iowa.

[3] After our work had been completed, the preparation of this compound from 2-phenylcyclohexanone and β-chloropropionitrile was reported by Boekelheide, THIS JOURNAL, **69**, 790 (1947).

[4] Bruson, "Organic Reactions," Vol. V, p. 100 (1949).



with formaldehyde and dimethylamine hydrochloride to give a crystalline base (after addition of alkali) in 75% yield. The analysis of the product agreed with that of a Mannich base and differed from that of a compound formed by addition of dimethylamine to the double bond conjugated with the carbonyl group. This indicated that the compound was 6-benzal-2-dimethylaminomethyl-2-phenylcyclohexanone (IV). This structure was proved to be correct by showing that the compound still possessed the conjugated system and lacked the active hydrogen atom at the 2-position. The presence of the conjugated system was shown by the absorption spectrum (Fig. 1), which was similar to that of 6-benzal-2-phenylcyclohexanone (V). Both unsaturated ketones possessed a strong absorption band lacking in 2-phenylcyclohexanone. The absorption maxima of IV at 292 mμ ($\log \epsilon = 4.23$) and of V at 290 mμ ($\log \epsilon = 4.24$) correspond to the maximum of benzalcamphor at 290 mμ ($\log \epsilon = 4.32$).[5] The absence of a hydrogen at the 2-position was shown by the failure of the compound to react with acrylonitrile under the conditions which led to cyanoethylation of V. The Mannich base IV readily undergoes hydrolytic cleavage in aqueous alcohol on a steam-bath and reverts completely to the original ketone V, formaldehyde and dimethylamine in a few minutes. Under the same conditions the base is stable in 5% or concentrated hydrochloric acid. The detection of formaldehyde in the products of the cleavage was further proof that the original compound was the product of a Mannich reaction.

The Mannich reaction of 2-phenylcyclohexanone with formaldehyde and dimethylamine hydrochloride proceeded smoothly to give the hydrochloride of 6-dimethylaminomethyl-2-phenylcyclohexanone (VIII). The free base reacted readily with methyl iodide to form a quaternary salt. In view of the reactivity of the hydrogen atom in the 2-position as manifested in the preceding reactions and in other reactions,[6] it seemed advisable to show whether the basic group had entered the 2- or the 6-position. The 6-position in 2-phenylcyclohexanone had the advantage of possessing two hydrogen atoms on

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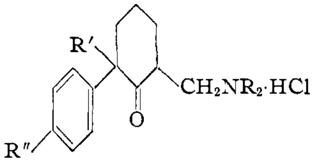
[5] Lowry and French, *J. Chem. Soc.*, 1921 (1924).

[6] Bachmann, Fujimoto and Wick, THIS JOURNAL, **72**, 1995 (1950).

TABLE I

MANNICH SALTS FROM 2-ARYLCYCLOHEXANONES



(R)₂	R'	R''	M. p.,[a] °C.	Calcd. C	Calcd. H	Calcd. Cl	Calcd. N	Found C	Found H	Found Cl	Found N
$(CH_3)_2$	H	H	168–169	67.2	8.3	13.3	5.2	66.9	8.2	13.8	4.8
$-(CH_2)_5$	H	H	225–226[b]	70.3	8.5	11.5	4.5	70.6	8.8	11.2	4.2
$-(CH_2)_2-O-(CH_2)_2-$	H	H	171–172.6[c]	65.9	7.8	11.5	4.5	66.2	7.8	11.6	4.4
$(CH_3)_2$	CH_3	H	160–161[d]	68.2	8.6	12.6	5.0	68.1	8.8	12.6	4.9
$(CH_3)_2$	H	OCH_3	175–176[e]								
$(CH_3)_2$	H	$CH(CH_3)_2$	172–173[f]	69.8	9.1	11.4	4.5	69.7	9.1	11.6	4.5

[a] The m. p.s are for purified samples. [b] Yield of crystalline hydrochloride, 40%; m. p. 220–225°, after one recrystallization from methanol. [c] Yield of base, 48%; hydrochloride crystallized from methanol in colorless needles. [d] Yield of base, 40%; hydrochloride, colorless needles from methanol. [e] Yield, 20%; m. p. reported, 170°. This compound is recorded in a table (p. 295) in the article by Lee, Ziering, Berger and Heineman in Jubilee Volume, Emil Barell, Hofmann–LaRoche, Basle, 1946. [f] Prepared in 36% yield by G. I. Fujimoto in this Laboratory; thin, colorless plates from acetone.

the carbon atom. The Mannich base (VIII) was converted into the substituted malonic ester IX by reaction with diethyl malonate in the presence of a small amount of powdered sodium hydroxide in boiling toluene, a procedure employed so successfully on gramine by Howe, Zambito, Snyder and Tishler.[7] Hydrolysis and decarboxylation of IX gave the previously prepared 2-oxo-3-phenylcyclohexanepropionic acid (XII), which showed that the Mannich reaction had taken place in the 6-position of 2-phenylcyclohexanone. It is of interest that the identical form of XII was produced by the two different methods.

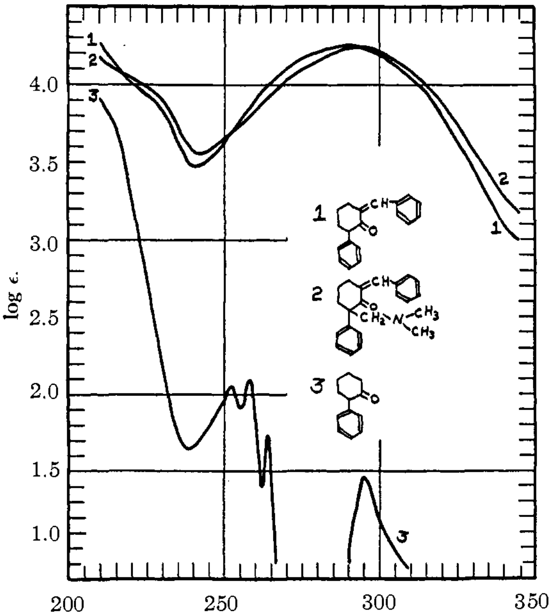


Fig. 1.—Ultraviolet absorption spectra.

Mannich bases were prepared also from formaldehyde and the following 2-arylcyclohexanones and secondary amines in the form of salts: 2-phenylcyclohexanone and piperidine and morpholine; 2-methyl-2-phenylcyclohexanone and dimethylamine; 2-(*p*-anisyl)-cyclohexanone and dimethylamine; and 2-(*p*-isopropylphenyl)-cyclohexanone and dimethylamine. Only one of the two possible stereoisomeric forms of the products (Table I) was isolated in a crystalline form in each instance.

Experimental

Cyanoethylation of 2-Phenylcyclohexanone and 6-Benzal-2-phenylcyclohexanone.—To a stirred mixture of 10 g. of 2-phenylcyclohexanone, 80 ml. of dioxane and 1 ml. of Triton B was added a solution of 3.6 g. of acrylonitrile in 10 ml. of dioxane; the temperature of the solution rose to 45°. After two hours the solvent was removed and the 2-oxo-1-phenylcyclohexanepropionitrile (II) was distilled under reduced pressure; yield 9.2 g. (70%); b. p. 150–160° at 0.4 mm. From 1 g. of the product 1.1 g. of colorless needles of 3-benzal-2-oxo-1-phenylcyclohexanepropionitrile (VI) was obtained; m. p. 83–84° in agreement with that reported.[3]

To the orange-red solution of 0.5 g. of 6-benzal-2-phenylcyclohexanone (V)[3] and 0.1 ml. of Triton B in 5 ml. of dioxane a solution of 0.2 ml. of acrylonitrile in 1 ml. of dioxane was added with swirling in the course of a few minutes; the color of the solution became pale yellow during this time. After twelve hours water and ether were added and the product which was isolated from the ether layer was recrystallized from alcohol; yield of colorless 3-benzal-2-oxo-1-phenylcyclohexanepropionitrile, 0.5 g. (83%); m. p. 82–83.5° alone and 82.5–84° when mixed with the product prepared from benzaldehyde and II.

2-Oxo-1-phenylcyclohexanepropionic Acid (III).—A solution of 1 g. of the nitrile (II) in 20 ml. of acetic acid and 10 ml. of concentrated hydrochloric acid was refluxed under nitrogen for twelve hours. After the removal of the solvents under reduced pressure, the residual acid was purified by solution in 5% sodium carbonate solution; the reprecipitated acid (0.95 g. or 88%; m. p. 110–112°) crystallized from dilute ethanol in fine colorless needles; m. p. 112–113.5°, raised to 114–114.5° by further recrystallization.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4. Found: C, 73.2; H, 7.4.

Bromination of 2-Phenylcyclohexanone.—A solution of 3.85 g. of bromine in 20 ml. of carbon tetrachloride was

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[7] Howe, Zambito, Snyder and Tishler, THIS JOURNAL, **67**, 38 (1945).

added slowly to a stirred solution of 4 g. of pure 2-phenylcyclohexanone which was kept at 0–5°. The bromine reacted rapidly. Removal of the solvents under reduced pressure left 5.5 g. of solid, which when triturated with methanol yielded 4.1 g. of colorless crystals with m. p. 95–97° and 0.5 g. with m. p. 88–92°. The **2-bromo-2-phenylcyclohexanone** (VII) crystallized from methanol in colorless plates; m. p. 103–104°.[8]

Anal. Calcd. for $C_{12}H_{13}OBr$: C, 56.9; H, 5.2; Br, 31.5. Found: C, 56.7; H, 5.4; Br, 31.1.

Dehydrobromination of 2-Bromo-2-phenylcyclohexanone.—A solution of 1 g. of the bromoketone in 15 ml. of 2,6-dimethylpyridine was refluxed for one hour. After most of the solvent had been removed under reduced pressure, ether was added and the solution was washed with hydrochloric acid and with bicarbonate solution; evaporation of the ether left 0.7 g. of solid; m. p. 85–90°. After one recrystallization from petroleum ether (60–75°), the **2-phenyl-2-cyclohexenone** (X) formed colorless needles; yield 0.64 g. (92%); m. p. 92–94°, raised to 95–95.5° by further recrystallization. The unsaturated ketone absorbed bromine in carbon tetrachloride without evolution of hydrogen bromide and decolorized aqueous potassium permanganate.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.8; H, 7.0. Found: C, 84.0; H, 7.2.

6-Benzal-2-dimethylaminomethyl-2-phenylcyclohexanone (IV).—A mixture of 1 g. of 6-benzal-2-phenylcyclohexanone, 0.6 g. of dimethylamine hydrochloride and 0.5 g. of paraformaldehyde in 10 ml. of ethanol was refluxed for eighteen hours. The base, which was liberated from an aqueous solution of the hydrochloride with alkali and extracted with ether, gradually crystallized; yield 0.9 g. (75%); m. p. 104–106°. After several recrystallizations from ethanol the Mannich base was obtained in clusters of small colorless needles; m. p. 105–106°. The ultraviolet spectra of the base and of the other two compounds in Fig. 1 were measured in alcohol.

Anal. Calcd. for $C_{22}H_{25}NO$: C, 82.7; H, 7.9; N, 4.4. Found: C, 83.0; H, 7.8; N, 4.1.

Hydrolytic Cleavage of the Mannich Base IV.—A mixture of 0.1 g. of 6-benzal-2-dimethylaminomethyl-2-phenylcyclohexanone, 5 ml. of 95% ethanol and 3 drops of water was heated on a steam-bath; the solid went into solution and an amine odor developed. After thirty minutes of heating, the solvents were removed in a current of air and dilute hydrochloric acid was added. The colorless solid after one recrystallization from ethanol yielded 60 mg. (73%) of 6-benzal-2-phenylcyclohexanone; m. p. 87.5–88.5° alone and when mixed with an authentic specimen. A similar result was obtained when the Mannich base was heated in 2 cc. of ethanol and 2 cc. of water for only three minutes. In another experiment 0.1 g. of the Mannich base was heated with a solution of 0.1 g. of dimedone in 3.5 cc. of 50% ethanol; in less than a minute an oily precipitate of 6-benzal-2-phenylcyclohexanone appeared. After one-half hour, the mixture was evaporated in a current of air, the residue was treated with 5% sodium hydroxide, and the insoluble ketone was removed by filtration. Acidification of the filtrate gave the dimedone derivative of formaldehyde in 50% yield which was identified by its m. p. (188–189°) and mixed m. p. with an authentic specimen.

The Mannich base was recovered practically quantitatively when a solution of 0.2 g. of the base in 10 ml. of 5% hydrochloric acid or in 10 ml. of concentrated hydrochloric acid was heated on a steam-bath for one to two hours.

Mannich Reactions on 2-Arylcyclohexanones.—A mixture of 2.5 g. of 2-phenylcyclohexanone, 1.4 g. of dimethylamine hydrochloride and 1.4 g. of paraformaldehyde in 20 ml. of ethanol was refluxed for sixteen hours. A few drops of a saturated alcoholic solution of hydrogen chloride and 50 ml. of anhydrous ether were added to the cooled solution. The hydrochloride of 6-dimethylaminomethyl-2-phenylcyclohexanone (VIII) (1.65 g., m. p. 155–160°) was removed by filtration; from the filtrate an additional 0.8 g. of the hydrochloride of the same purity (total yield, 62%) was obtained by means of water, liberation of the free base with alkali, and treatment of the base (1 g.) with 4 ml. of 2 *N* alcoholic hydrogen chloride. An analytical sample was obtained as colorless needles by recrystallization from methanol.

The products from 2-methyl-2-phenylcyclohexanone and from 2-(*p*-anisyl)-cyclohexanone[6] were made by the above procedure; those from 2-phenylcyclohexanone and piperidine hydrobromide and morpholine hydrobromide were prepared by refluxing in isoamyl alcohol for fifteen to twenty minutes; and the product from 2-(*p*-isopropylphenyl)-cyclohexanone[6] was made by heating on a steam-bath with 37% formalin and filtering the product which crystallized on cooling. The results are shown in Table I.

6-Dimethylaminomethyl-2-phenylcyclohexanone Methiodide.—A solution of 1 g. of the Mannich base and 0.5 ml. of methyl iodide in 10 ml. of absolute ethanol soon deposited crystals of the methiodide. After three hours at room temperature, 1.05 g. (66%) of the product was collected; m. p. 200–205°. After several recrystallizations from ethanol the methiodide formed small colorless needles; m. p. 214–216°.

Anal. Calcd. for $C_{16}H_{24}INO$: I, 34.0. Found: I, 34.1.

2-Oxo-3-phenylcyclohexanepropionic Acid (XII). (a) **From the Mannich Base VIII.**—By the procedure described for a similar case,[7] a mixture of 1 g. of 6-dimethylaminomethyl-2-phenylcyclohexanone, 0.7 g. of diethyl malonate and 0.07 g. of powdered sodium hydroxide in 8 ml. of toluene was refluxed under nitrogen for five hours. Hydrolysis of the resulting substituted malonic ester IX by refluxing with 20 ml. of acetic acid and 10 ml. of concentrated hydrochloric acid under nitrogen for fourteen hours gave 0.52 g. (50%) of acid; m. p. 120–124°. One recrystallization of the product from dilute ethanol yielded colorless prisms of XII; m. p. 128–129°; further recrystallization raised the m. p. to 129–130°. A mixture of the acid and its isomer III melted at 95–110°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4; neut. equiv., 249. Found: C, 73.0; H, 7.4; neut. equiv., 246.

(b) **From 2-Bromo-2-phenylcyclohexanone.**—Fifteen ml. of Triton B was added slowly to a solution of 5 g. of the bromoketone in 100 ml. of *t*-butyl alcohol at room temperature; the solution remained neutral and the temperature increased 5° during the first additions. After the addition of a solution of 1.1 g. of acrylonitrile in 10 ml. of *t*-butyl alcohol, the mixture was allowed to stand for five hours. The isolated product (presumably XI), which contained no halogen and showed unsaturation to potassium permanganate solution and to bromine in carbon tetrachloride, was refluxed with 40 ml. of acetic acid and 20 ml. of concentrated hydrochloric acid for twelve hours; the resulting acid (2.3 g.) was a liquid.

A solution of 0.5 g. of the unsaturated ketoacid in 20 ml. of methanol absorbed two mole equivalents of hydrogen in one hour in the presence of 50 ml. of Adams catalyst. To a solution of the isolated product in 10 ml. of acetic acid a solution of 0.4 g. of chromic acid anhydride in 5 ml. of 80% acetic acid was added slowly. After twelve hours the acidic product was isolated and purified through its sodium salt and then recrystallized from dilute ethanol; yield 0.2 g. (40%); m. p. 126–128°. A mixture of the product with the acid in (a) melted at 127–129°.

Summary

Cyanoethylation of 2-phenylcyclohexanone by acrylonitrile took place in the 2-position. The resulting nitrile was hydrolyzed to 2-oxo-1-phenylcyclohexanepropionic acid. A method is described for introducing the cyanoethyl group into the 6-position.

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[8] Another modification with m. p. 68.5–69° was obtained recently in this Laboratory by E. J. Fornefeld. He has also obtained further proof for the structure of the compound.

6-Benzal-2-phenylcyclohexanone was cyanoethylated and also converted into a Mannich base.

The preparation of 2-phenyl-2-cyclohexenone is described.

Six Mannich salts were prepared from four 2-arylcyclohexanones. The Mannich base from 2-phenylcyclohexanone was converted into 2-oxo-3-phenylcyclohexanepropionic acid, which was synthesized also by another method.

ANN ARBOR, MICH. RECEIVED JANUARY 23, 1950

[CONTRIBUTION NO. 272 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthesis of 2,2-Dimethylalkanoic Acids from Ethylene

BY DONALD D. COFFMAN AND J. R. ROLAND

The free radical-initiated polymerization of styrene in the presence of carbon tetrachloride has been found to yield products presumed to be terminated by $-Cl$ and $-CCl_3$ end-groups.[1] Also, the polymerization of ethylene in the presence of halogenated methanes has been described. Carbon tetrachloride as a chain transfer agent gave a series of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, $Cl(CH_2CH_2)_nCCl_3$, among which members having n values of 1 to 4, inclusive, have been identified.[2] Chloroform gave the α,α,α-trichloroalkanes, $H(CH_2CH_2)_nCCl_3$, ranging in n values from 1 to 6.[3]

This type of free radical-initiated reaction has now been extended to the synthesis of 2,2-dimethylalkanoic acids from ethylene and isobutyric acid. The reaction proceeds smoothly without perceptible formation of products other than the mixed carboxylic acids. This is the first known example of a chain reaction in which an alkanoic acid as transfer agent has been utilized with ethylene to obtain a family of carboxylic acids the identities of which indicate the course of reaction.

The reaction of ethylene with isobutyric acid has been brought about under a variety of conditions. It proceeds readily at 250° with benzalazine catalyst, employing high pressures of ethylene containing up to 100 parts per million of oxygen. At lower concentrations (*e. g.*, 2–5 ppm.), oxygen alone also induced the reaction. The structure of the products was demonstrated to be that of 2,2-dimethylalkanoic acids, $H(CH_2CH_2)_nC(CH_3)_2COOH$, by the identification of 2,2-dimethylbutanoic acid (6–13%), 2,2-dimethylhexanoic acid (4–8%), 2,2-dimethyloctanoic acid (3–5%) and 2,2-dimethyldecanoic acid (2%) isolated in the proportions indicated from the reaction of 200 g. of isobutyric acid with ethylene at 700 atm. pressure. The proportions of the individual dimethylalkanoic acids that comprise the whole product depend on the concentration of ethylene relative to that of isobutyric acid, and are subject to some control by adjustment in the ethylene pressure or the amount of isobutyric acid employed. Mixtures of acids having neutral equivalents from 132 to 728 have been prepared in this way. The low iodine numbers (less than 4) indicate the nearly complete absence of higher olefinic products.

It appears likely that the 2,2-dimethylalkanoic acids originate by the following mechanism in which R· is the initiating free radical.

$$(1)\quad R\cdot + HC(CH_3)_2COOH \longrightarrow RH + \cdot C(CH_3)_2COOH$$

$$(2)\quad \cdot C(CH_3)_2COOH + C_2H_4 \longrightarrow HOOCC(CH_3)_2(CH_2CH_2)\cdot$$

$$(3)\quad HOOCC(CH_3)_2(CH_2CH_2)\cdot + nC_2H_4 \longrightarrow HOOCC(CH_3)_2(CH_2CH_2)^{\cdot}_{n+1}$$

$$(4)\quad HOOCC(CH_3)_2(CH_2CH_2)^{\cdot}_{n+1} + HC(CH_3)_2COOH \longrightarrow HOOCC(CH_3)_2(CH_2CH_2)_{n+1}H + \cdot C(CH_3)_2COOH$$

This is analogous to the mechanism proposed by Joyce[2] and Kharasch[4] for the synthesis of α,α,α-trichloroalkanes.

Experimental

Reaction of Ethylene with Isobutyric Acid.[5]—A silver-lined pressure vessel of 400-ml. capacity was purged with nitrogen and charged with 200 g. of isobutyric acid. The vessel was closed, evacuated, and connected to a reservoir of ethylene containing 2–5 parts per million of oxygen. Ethylene at 300 atm. pressure was introduced, and the tube and its contents were heated and agitated. During a reaction time of fourteen hours, the temperature was maintained at 247–251° and the pressure at 850–980 atm. by periodic addition of ethylene. The cumulative absorption of ethylene amounted to 735 atm. After cooling the vessel to room temperature, the pressure was released, the vessel was opened, and the contents discharged. Distillation of this reaction mixture gave 155 g. of isobutyric acid and 64 g. of alkali-soluble higher boiling acids. The mixed monobasic acids had a neutral equivalent of 328. The iodine number was 2.9, and the molecular weight determined ebullioscopically was 364.

By operation in the foregoing manner employing benzalazine catalyst (0.2 g.) and ethylene containing about 10 parts per million of oxygen, a series of reactions were carried out under different conditions of pressure and temperature with various ratios of reactants in order to determine the effects of these variables. As shown in Table I,

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[1] (a) Price, *Ann. N. Y., Acad. Sci.*, **44**, 351 (1943); (b) Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937); **A181**, 81 (1937); (c) Breitenbach, Springer and Abrahamczik, *Oesterr. Chem. Ztg.*, **41**, 182 (1938); (d) Springer, *Kautschuk*, **14**, 212 (1938); (e) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

[2] Joyce, Hanford and Harman, THIS JOURNAL, **70**, 2529 (1948).

[3] Harmon, Ford, Hanford and Joyce, *ibid.*, **72**, 2213 (1950).

[4] Kharasch, Jensen and Urry, *ibid.*, **69**, 1100 (1947).

[5] Roland and Harmon, U. S. Patent 2,433,015 (December 23, 1947); Coffman, U. S. Patent 2,433,016 (December 23, 1947).