(**D**) **Thermal Stability.**—The thermal stability of sodium β-sodiomethacrylate was determined by placing a small sample of the material in a 20-ml. test-tube through which a slow stream of nitrogen was passed. The tube was placed in an oil-bath and the temperature gradually raised. Gas flow rates to and from the tube were observed, as well as the appearance of the material in the tube.

The material appeared stable until a temperature of 280–290° was reached. Decomposition occurred on prolonged heating at temperatures above 250°.

Preparation of Sodium Methacrylate–Sodium Amide Addition Compound.—Sodium methacrylate and sodium amide (0.1 mole each) were carefully ground together with a mortar and pestle and then placed in a nitrogen-swept test-tube in an oil-bath. The temperature was gradually raised, and at 165° the material turned a bright yellow but no ammonia was evolved. This appearance remained as the temperature was raised to 170°. A sample was removed and treated at room temperature with carbon dioxide. No reaction occurred. The mixture was then heated to 180° where ammonia evolution began and the material began to turn orange-tan in color. The temperature was gradually raised to 200°. The mixture was then cooled to room temperature and treated with carbon dioxide. A vigorous exothermic reaction occurred with a decolorization of the product and a large absorption of gas.

Acknowledgment.—The author is indebted to Dr. R. P. Curry for the interpretation of the infrared spectrum of the compound.

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Carboxylations Effected by Ionizing Radiation

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Irradiation of a mixture of a hydrocarbon and carbon dioxide with high-energy electrons gives carboxylic acids. For instance, toluene is converted to phenylacetic acid. The radiation energy is used inefficiently (G = 0.01–0.1). Formic acid can be used in place of carbon dioxide to obtain carboxylic acids. Irradiation of a mixture of a hydrocarbon and hydrogen cyanide leads to nitriles.

Direct carboxylation of hydrocarbons by carbon dioxide is considered a thermodynamically unfavorable reaction, particularly under non-alkaline conditions. Thus Rabinowitch[1] estimates that ΔF for such carboxylation of methane is 11.8 kcal./mole, of benzene 4.6 kcal./mole.[2] Until recent work by Turton,[3] attempts to accomplish the reaction were unsuccessful, even by the method of generating alkyl radicals in the presence of carbon dioxide. Turton[3] exposed a gaseous mixture of benzene and $C^{14}O_2$ to β-particles from K^{85} and showed that $C_6H_5C^{14}O_2H$ was formed.

$$RH + CO_2 \longrightarrow RCO_2H$$

Ionizing radiation has been used recently to effect carboxylation of compounds other than hydrocarbons. Turton[3] obtained a mixture of the three pyridinecarboxylic acids by applying his method to pyridine. Dose and Ettre[4] showed that amino acids are formed when aqueous amine solutions saturated with carbon dioxide are irradiated with X-rays. In this way they converted ethylamine to a 7:3 mixture of β- and α-alanine. They also obtained pyruvic acid by irradiating an aqueous solution of sodium bicarbonate and acetaldehyde with X-rays.

We have succeeded in carboxylating several hydrocarbons by mixing them with solid carbon dioxide and irradiating the mixture with 2-Mev. electrons. Thus, cyclohexane was converted to cyclohexanecarboxylic acid, cyclohexene to a mixture of cyclohexenecarboxylic acids, and toluene to phenylacetic acid. Under the same conditions, we obtained lactic acid from ethanol and, like Dose and Ettre,[4] α-alanine from ethylamine. Irradiation of a gaseous mixture of methane and carbon dioxide gave acetic acid.

Aliphatic C–H bonds are more readily carboxylated under these conditions than are aromatic C–H bonds. No methylbenzoic acids were detected in the toluene experiment and no benzoic acid was detected in an experiment with benzene under the conditions of our cyclohexane experiment. In view of Turton's elegant work,[3] some benzoic acid must have been formed in our experiment, but in too small amount to be easily found by our less sensitive methods.

Yields and efficiencies were low. Thus, exposure of a mixture of 750 g. of solid carbon dioxide and 500 ml. of cyclohexane to 2.6 × 10^5 joules of electronic energy (equivalent to all the energy in our 500-watt beam of 2-Mev. electrons during nine minutes) gave only 229 mg. (0.04% yield) of cyclohexanecarboxylic acid. The efficiency of energy utilization in terms of G, the molecules of product formed per 100 electron-volts of energy absorbed, was only 0.07.

Carboxylation can also be effected with formic acid in place of carbon dioxide. Irradiation of formic acid solutions of cyclohexane or benzene with 2-Mev. electrons gave cyclohexanecarboxylic acid and benzoic acid, respectively. Again efficiency was low (G = 0.01–0.02). Since formic acid carboxylates benzene under the influence of ionizing radiation much more readily than does carbon

$$RH + HCO_2H \rightsquigarrow RCO_2H$$

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[1] E. L. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 184.

[2] This does not mean, of course, that the formation of a new C–C bond by carboxylation is invariably an unfavorable reaction. Formation of acids by carboxylation of Grignard reagents or sodium phenolates are familiar reactions. T. T. Tchen, F. A. Loewus and B. Vennesland, *J. Biol. Chem.*, **213**, 547 (1955), find that ΔF for the enzyme-catalyzed carboxylation of phosphoenol pyruvate is −7.2 kcal./mole.

[3] C. N. Turton, A/Conf. 15/P/284, Second United Nations Internatl. Conf. on the Peaceful Uses of Atomic Energy (March 4, 1958).

[4] K. Dose and K. Ettre, *Z. Naturforsch.*, **13B**, 784 (1958).

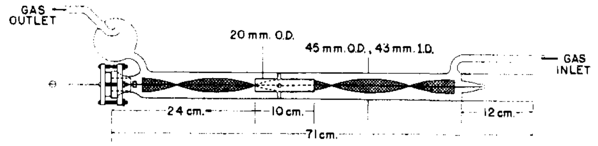

Fig. 1.—Apparatus for irradiation of liquid-gas mixtures.

dioxide, there must be important differences in the mechanisms by which the two reagents accomplish carboxylation.

In a related reaction, electron-irradiation of solutions of hydrogen cyanide in cyclohexane, in benzene and in toluene led, respectively, to cyclohexanecarbonitrile, benzonitrile and a mixture of tolunitriles (G = 0.05–0.2). Traces of isocyanides were formed simultaneously. Aromatic hydrogens

$$RH + HCN \rightsquigarrow RCN + RNC$$

were more easily substituted by a nitrile group than were aliphatic hydrogens.

Although dinitriles were probably formed in very small amount in the hydrogen cyanide experiments, none were isolated. A better way to make dinitriles is to expose aliphatic nitriles to ionizing radiation. Propionitrile gave a mixture of α-methylglutaronitrile and adiponitrile (G = 0.18). De-

$$2CH_3CH_2CN \rightsquigarrow NCCH(CH_3)CH_2CH_2CN + NC(CH_2)_4CN$$

hydrogenative couplings of this sort are well known for hydrocarbons,[5] alcohols[6] and aliphatic acids,[7] although coupling of acids occurs only in aqueous solutions. Propionitrile coupled either when pure or in aqueous solution, behaving like an alcohol rather than an acid in this respect.

Acknowledgments.—We are indebted to Drs. F. W. Hoover, C. S. Cleaver and T. L. Cairns for valuable suggestions during the course of this work.

Experimental

Equipment.—Irradiations were performed with 2-Mev. electrons from a vertical 2-Mv. Van de Graaff accelerator manufactured by High Voltage Engineering Corp. The beam current was ordinarily 250 microamperes, corresponding to a power output of 500 watts. The energy absorbed in a given system was estimated from a knowledge of the power output, the cross-section and average intensity of the electron beam, and the geometry of the system. Suitable corrections were made for energy lost when the beam entered the reaction mixture through a wall of the reaction vessel. The estimates are only accurate enough to give G within ±50%, but this suffices to show the order of magnitude of G in each case.

Carboxylation by Carbon Dioxide.—About 750 g. of pulverized solid carbon dioxide was placed in a Pyrex baking dish with inside dimensions 16 cm. × 25 cm. × 4.5 cm. Ethanol (310 ml.) was intimately mixed with the solid carbon dioxide, and the dish was covered loosely with aluminum foil. The mixture was passed through a beam of 2-Mev. electrons 75 times, absorbing 11 joules/cm.^{2} at each pass. The total energy received was 3.3×10^5 joules.

The carbon dioxide was allowed to evaporate. The ethanolic reaction mixture was filtered and heated to 40° (15 mm.) to remove ethanol and other volatile material. The residue, a tan oil weighing 1.69 g., was chromatographed on silicic acid according to the procedure of Marvel and Rands.[8] The chromatography indicated that the residue contained 0.31 mmole of acetic acid, 0.70 mmole of formic acid, 1.90 mmoles (171 mg., 0.04% yield, G = 0.06) of lactic acid and 0.42 mmole of β-hydroxypropionic acid.

In order to establish the formation of lactic acid unequivocally, the neutralized aqueous layers from the titrated chromatographic fractions thought to contain lactic acid were combined and evaporated to dryness on a steam-bath. The solid residue of sodium lactate was dissolved in 12 ml. of 80% ethanol, the solution was made barely acid to phenol red with a few drops of 0.2 N hydrochloric acid, 0.48 g. (1.73 mmoles) of p-bromophenacyl bromide was added, and the mixture was refluxed one hour. Cooling followed by addition of 10 ml. of water caused the precipitation of 0.35 g. of p-bromophenacyl lactate, m.p. 110–112° after one recrystallization from cyclohexane. It was identified by direct comparison of its melting point, infrared spectrum and X-ray diffraction pattern with those of an authentic sample.

Under similar conditions, cyclohexane was converted to cyclohexanecarboxylic acid (G = 0.07 at 0.04% yield), cyclohexene to a mixture of cyclohexenecarboxylic acids (G = 0.11 at 0.011% yield), toluene to phenylacetic acid (G = 0.010 at 0.006% yield), and ethylamine to α-alanine (G = 0.17 at 0.025% yield).

Methane was converted to acetic acid (G = 0.013 at 0.004% yield) along with smaller amounts of propionic and formic acids in a gas-phase reaction. An equimolar gaseous mixture of carbon dioxide and methane in a 125-l. aluminum vessel 96 cm. in height was irradiated for 60 minutes with a 500-watt beam of 2-Mev. electrons that entered the vessel through a thin aluminum window in the top. The gaseous mixture was subsequently bubbled through water to separate water-soluble acids, which were removed from the water by extraction with ether.

Cyclohexanecarboxylic acid, phenylacetic acid, acetic acid and the mixture of cyclohexenecarboxylic acids were isolated by chromatography.[8] The first three were identified by comparison of their p-bromophenacyl esters with authentic specimens.

Part of the mixture of cyclohexenecarboxylic acids was hydrogenated to cyclohexanecarboxylic acid, identified by its p-bromophenacyl ester. The rest of the mixture was converted to a mixture of crystalline and non-crystalline p-bromophenacyl esters. The solid portion was recrystallized five times from cyclohexane and twice from ethanol to give a crystalline solid, m.p. 78–83°. It was probably a mixture of two of the three possible p-bromophenacyl cyclohexenecarboxylates.

Anal. Calcd. for $C_{15}H_{15}O_3Br$: C, 55.7; H, 4.7. Found: C, 55.6; H, 5.0.

In the experiment with ethylamine, part of the residue remaining after evaporation of unchanged amine and carbon dioxide was chromatographed on an ion-exchange column according to the procedure of Wall.[9] A positive ninhydrin test for an amino acid was obtained only in fractions where one would expect α-alanine. The presence of α-alanine in these fractions was confirmed by paper chromatography using phenol–water, butanol–water–acetic acid and lutidine–ethanol–water–diethylamine mixtures.

Carboxylations were effected with G-values similar to those above by irradiating well-agitated mixtures of cyclohexane or ethanol and gaseous carbon dioxide at 5–25° with 2-Mev. electrons or X-rays.

Undoubtedly many products besides carboxylic acids were obtained in our experiments, but we made no effort to isolate them.

Carboxylation by Formic Acid.—A mixture of 230 g. of benzene and 230 g. of formic acid was placed in the apparatus of Fig. 1, which is constructed on much the same principles as a Nester spinning-band still.[10] The apparatus was half-immersed in a horizontal position in an ice-bath having semi-circles cut in opposite sides of it to hold the apparatus. While the mixture was stirred vigorously by a stirrer of stainless-steel gauze and a slow stream of nitrogen passed through it, a 500-watt beam of 2-Mev. electrons about 20 cm. × 2.5 cm. in cross-section was impinged on the upper surface of the vessel for 60 minutes. It is estimated that about 9×10^5 joules of electronic energy was absorbed by the mixture. Material volatile at 45° (10 mm.)

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[5] H. A. Dewhurst, *J. Chem. Phys.*, **24**, 1254 (1956); E. Collinson and A. J. Swallow, *Chem. Revs.*, **56**, 471 (1956).

[6] W. R. McDonell and A. S. Newton, This Journal, **76**, 4651 (1954); W. R. McDonell, *J. Chem. Phys.*, **23**, 208 (1955).

[7] W. M. Garrison, W. Bennett, S. Cole, H. R. Hammond and B. M. Weeks, This Journal, **77**, 2720 (1955).

[8] C. S. Marvel and R. D. Rands, *ibid.*, **72**, 2642 (1950).

[9] J. S. Wall, *Anal. Chem.*, **25**, 950 (1953).

[10] R. G. Nester, *ibid.*, **28**, 278 (1956).

was removed from the reaction mixture, leaving 13.3 g. of a thick brown oil. Benzoic acid (104 mg., 0.03% yield, G = 0.009) was isolated by chromatography[8] and identified by direct comparison of the melting point and infrared spectrum of its *p*-bromophenacyl ester with those of authentic *p*-bromophenacyl benzoate.

Cyclohexane was similarly converted to cyclohexanecarboxylic acid (0.07% yield, G = 0.02).

Cyanation of Hydrocarbons by Hydrogen Cyanide. A. Benzene.—A solution of 50 ml. of hydrogen cyanide (freshly distilled from phosphorus pentoxide) in 435 ml. of benzene was irradiated with a 500-watt beam of 2-Mev. electrons for 60 minutes under the conditions used in the formic acid experiments. Distillation of the reaction mixture through a six-inch Claisen still-head gave the following fractions boiling above benzene: I, 2.2 g., b.p. 24–75° (23 mm.), $n^{25}\text{D}$ 1.5203; II, 0.4 g., b.p. about 88° (3 mm.), $n^{25}\text{D}$ 1.5662; III, 9.7 g. of resin not volatile at 225° (3 mm.). Fraction II partly crystallized in ice. The solid portion of this fraction, weight 110 mg., was recrystallized from methanol and was identified as biphenyl by its melting point (68–69° alone or mixed with an authentic sample).

The infrared spectrum of fraction I indicated that it was benzonitrile of 90–95% purity. This corresponds to a 1.5% yield based on hydrogen cyanide (G = 0.21). A weak band at 4.7 μ may have been caused by phenyl isocyanide.

In order to characterize fraction I further, 2.0 g. of it was refluxed for an hour with 75% sulfuric acid.[11] Under these conditions, benzonitrile and phenyl isocyanide should be converted to benzoic acid and aniline, respectively. Benzoic acid sublimed into the condenser during the reaction. After recrystallization from water it weighed 0.60 g. It melted at 121–123° alone or mixed with authentic benzoic acid and had the characteristic infrared spectrum of benzoic acid. The hydrolysate was diluted with water and extracted with chloroform. Titration of the extract indicated that it contained an additional 0.7 g. of benzoic acid.

The odor of fraction I suggested that it contained phenyl isocyanide. The presence of aniline in the hydrolysate was demonstrated as follows. The chloroform-extracted hydrolysate was made basic with 10% sodium hydroxide and distilled. The first 40 ml. of distillate was adjusted to *p*H 2 with hydrochloric acid, cooled in ice, and treated successively with 1.0 ml. of 0.5 N sodium nitrite, 1.0 ml. of 0.5 N sulfamic acid and 1.2 ml. of 0.5 M ethanolic 2-naphthol, with 5-minute intervals between additions. The mixture was made basic with 10% sodium hydroxide, causing 0.052 g. of 1-phenylazo-2-naphthol to precipitate. After recrystallization from ethanol it melted at 132–133° alone or mixed with an authentic sample and had the same visible absorption spectrum as an authentic sample. Based on the amount of azo compound isolated, it appears that about 25 mg. of phenyl isocyanide was formed (0.03% yield based on hydrogen cyanide; G = 0.004). No aniline could be detected in distillate subsequent to the first 40 ml.

B. **Toluene.**—The experiment was repeated with toluene in place of benzene. Distillation gave a series of fractions shown by ultraviolet and infrared spectroscopy to consist principally of bitolyls and the four tolunitrile isomers in the following amounts: *para*, 1.1 g.; *ortho*, 1.0 g.; *alpha*, 0.5 g.; *meta*, 0.3 g. The presence of the *p*- and *o*-isomers was further demonstrated by acid hydrolysis[11] of suitable fractions; *p*-toluic and *o*-toluic acid were isolated by fractional crystallization and identified by their melting points and infrared spectra. A small quantity of toluidines was detected in the hydrolysate by means of diazotization and coupling with 2-naphthol. The yield of tolunitriles, based on hydrogen cyanide, was 1.9% (G = 0.27).

C. **Cyclohexane.**—Similar irradiation of a mixture of 425 ml. of cyclohexane and 50 ml. of hydrogen cyanide for 45 minutes gave 3.9 g. (1.2% yield, G = 0.7) of bicyclohexyl (identified by infrared analysis) and 0.4 g. (0.3% yield, G = 0.05) of cyclohexanecarbonitrile. The identity of the nitrile was established by its hydrolysis[11] to cyclohexanecarboxylic acid, isolated as the *p*-bromophenacyl ester.

Dehydrogenative Coupling of Propionitrile.—Propionitrile (550 g.) was placed in a stainless-steel pan 25.3 cm. long and 7.7 cm. wide covered with aluminum foil 0.03 mm. thick. A slow stream of nitrogen passed over the nitrile by means of openings at each end of the pan. The pan was placed in an ice-bath to maintain the temperature of the nitrile at 10–20° and was passed through a beam of 2-Mev. electrons 25 times, receiving 11 joules/cm.^{2} at each pass. Unchanged propionitrile was removed at 100° (50 mm.), and the residue, 2.9 g. of thick dark oil, was stirred and refluxed with 18 ml. of 12 N hydrochloric acid for five hours. The mixture was cooled to 25° and the aqueous portion was decanted from a little resin and evaporated nearly to dryness on a steam-bath. The residue was taken up in water and extracted with five 10-ml. portions of 2-butanone. The combined extracts were dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed on silicic acid[8] to give 114 mg. of a mixture of acids having the peak elution volume characteristic of α-methylglutaric acid and its isomers. Infrared analysis indicated that the mixture was principally α-methylglutaric acid and adipic acid in a 4:1 ratio, with possibly a few per cent. of α,α-dimethylsuccinic acid also present. Based on the amount of acids isolated, propionitrile was converted to a mixture of α-methylglutaronitrile and isomers in about 0.03% yield (G = 0.18).

Similar irradiation of 10% aqueous propionitrile gave the same products in similar proportions; G = 0.15. The mechanism in this experiment, as in the conversion of propionitrile to α-methylglutaronitrile and isomers by Fenton reagent,[12] may involve the attack of hydroxyl radicals on propionitrile.

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[11] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," fourth edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 258.

[12] D. D. Coffman, E. L. Jenner and R. D. Lipscomb, THIS JOURNAL, **80**, 2864 (1958).

WILMINGTON, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. XIII. Salts in which the Cations Bear Carboxyl, Hydroxyl, Alkoxyl or Amino Groups[1,2]

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This paper describes the synthesis and some reactions of carboxy-, hydroxy-, alkoxy- and aminodiphenyliodonium salts and the products of attempted condensations of iodosobenzene with benzenes bearing functional groups.

As part of a program to investigate the electronic effects of the iodonium group in aromatic compounds, this paper reports the synthesis of carboxy-, hydroxy-, alkoxy- and amino-substituted diphenyliodonium salts. A later report will discuss the absorption spectra and acid–base properties of these salts.

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[1] This paper is taken from the dissertation of Irving Lillien, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] References to the recent literature of iodonium salts are given in article XII of this series: F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, in press.

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