

the yield up to 30% by carrying out the reaction in the presence of a catalytic amount of triethylamine or pyridine under refluxing conditions. In their synthesis, labeled silver carbonate was prepared from sodium carbonate-C¹⁴, which in turn was obtained by liberation of carbon dioxide from barium carbonate-C¹⁴ followed by absorption in sodium hydroxide solution.

We have now found that silver carbonate is obtained in about 90% yield by stirring barium carbonate with aqueous silver nitrate. This simplified the whole procedure very much by eliminating the need of intermediate preparation of labeled sodium carbonate. Silver carbonate and excess of ethyl iodide in dry ether at room temperature in the dark gave diethyl carbonate in about 40% yield based on the barium carbonate used.

EXPERIMENTAL

Silver carbonate-C¹⁴. Since silver carbonate is unstable in the light and darkens when exposed even to diffuse room light for several hours, it had to be prepared and handled in the dark. Silver nitrate (4.3 g.) in 10 cc. of water was added gradually to a stirred suspension of 2.473 g. of barium carbonate-C¹⁴ (0.0538 ± 0.0006 mc./mole) in 10 cc. of water. After stirring for 30 min., the pale yellow precipitate formed was filtered off with a sintered-glass filter, and washed with water until silver ion was no more detected, then with ethanol, and finally with dry ether. The dried material weighed 3.4 g. In a preliminary experiment with ordinary barium carbonate, silver carbonate prepared was analyzed for silver by dissolving it in dilute nitric acid followed by precipitation and weighing of silver chloride (Found: Ag, 70.60. Calcd. for Ag₂CO₃: Ag, 78.23).

Diethyl carbonate-(carbonyl-C¹⁴). Silver carbonate-C¹⁴ (3.4 g.), 5.0 g. of ethyl iodide, and 20 cc. of ether were placed in a 100-cc. Erlenmeyer flask, and the mixture was allowed to stand for 50 hr. in the dark with occasional agitation. It was, after addition of 1.405 g. of non-labeled diethyl carbonate, filtered with a sintered-glass filter, and the residue was washed with two portions of 10 cc. of ether. The filtrate and washings were combined and distilled through a Vigreux column, yielding 1.8 g. of diethyl carbonate-(carbonyl-C¹⁴), b.p. 122-126°.

A half gram of the diluted labeled ester obtained above and 0.7 g. of hydrazine hydrate were heated at 120° for 6 hr. in an oil bath. The solid precipitate, on 3 crystallizations from ethanol, gave carbonylhydrazide-C¹⁴ of a constant activity of 0.0167 = 0.0006 mc./mole, m.p. 152.0-152.5°. The diluted ester, therefore, had an activity of 0.0167 mc./mole, and this value indicated that 0.630 g. of diethyl carbonate-(carbonyl-C¹⁴) had been formed before the dilution corresponding to a yield of 42.8% based on the barium carbonate-C¹⁴ used. The total recovery of radioactivity in the product from the active barium carbonate was 37.9%.

Radioactivity determinations. The carbonylhydrazide-C¹⁴ (40 mg.) was oxidized according to the method of Van Slyke and Folch,³ and the liberated carbon dioxide was converted into barium carbonate and counted on an "infinitely thick" layer with an end-window Geiger-Müller counter. The count was corrected for background and compared with a standard barium carbonate-C¹⁴ of a known activity.

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Further Experiments on the Alkylation of Benzene with C¹⁴-Labeled Ethyl Chloride

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In a previous paper,² we reported alkylation of benzene with C¹⁴-labeled ethyl chloride and aluminum chloride in which no isomerization of the ethyl group occurred. We also found that C¹⁴-labeled ethyl chloride was extensively isomerized by treatment with aluminum chloride in the absence of benzene. The latter result raised the question of why no isomerization of the ethyl group occurred during the alkylation, since the two processes probably involve the same intermediate, whether it is a carbonium ion³ or a complex.⁴

We have now carried out further experiments with C¹⁴-labeled ethyl chloride with the aim of learning more about the relationship of isomerization and alkylation. In the previous work,² ethyl-2-C¹⁴ chloride was mixed with aluminum chloride and kept at room temperature for one hour. In two experiments, the degree of isomerization was found to be 84% and 92%, respectively. In order to obtain a better estimate of the rate of the isomerization, we have now allowed ethyl-1-C¹⁴ chloride to stand over aluminum chloride for *six minutes* and then determined the extent of isomerization as before by recovering the ethyl chloride and adding it to benzene in the presence of fresh aluminum chloride. The ethylbenzene produced was found to contain all the C¹⁴ in the α -position, hence no detectable isomerization of ethyl-1-C¹⁴ chloride occurred in six minutes. One may estimate that the rate of isomerization of ethyl-1-C¹⁴ chloride by aluminum chloride is probably faster but of the same order of magnitude as the rate of isomerization of ethyl-1-C¹⁴ bromide by aluminum bromide;⁵ however, the former system is heterogeneous and the latter is homogeneous, so comparison is difficult.

Assuming that the same intermediate is involved in isomerization and alkylation, the fact that no isomerization was observed when alkylation with labeled ethyl chloride was carried out at 80° may be attributed to the fact that the intermediate reacted with benzene much faster than it underwent

(1) Taken from the M.A. thesis of Stellakis G. Panayides, University of Texas, 1957.

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(3) (a) C. C. Price, *Org. Reactions*, Vol. III, 7 (1946); (b) L. M. Nash, T. I. Taylor, and W. v. E. Doering, *J. Am. Chem. Soc.*, **71**, 1516 (1949).

(4) H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6279 (1953).

(5) F. L. J. Sixma and H. Hendriks, *Rec. trav. chim.*, **75**, 169 (1956), reported that at 25° the isomerization of ethyl-1-C¹⁴ bromide containing 0.045 mole aluminum bromide per mole of organic halide was 63% complete in 48 hr.

rearrangement.² This seems reasonable since the rate of isomerization of ethyl-1-C¹⁴ bromide is much slower than that of *n*-propyl bromide,^{4,5} whereas the rates of alkylation of benzene by ethyl and *n*-propyl halides must not be very different. Support for this viewpoint of competition between alkylation and isomerization has recently been afforded by the very interesting work of Baddeley and Williamson.⁶ We hoped that lowering the temperature at which labeled ethyl chloride was allowed to react with benzene might result in reducing the rate of alkylation more extensively than the rate of isomerization, so that alkylation with rearrangement might be observed. For this reason, alkylation of benzene with ethyl-1-C¹⁴ chloride at room temperature was carried out, using other conditions and amounts exactly as in the previous experiments. The ethylbenzene and diethylbenzene produced were separated by fractional distillation and degraded to benzoic acid and phthalic acid, respectively. Radioassay of these acids showed that 96% of the C¹⁴ was in the α -positions of the side chains. This corresponded to 4% isotopic rearrangement accompanying the alkylation.

A second experiment was carried out which was identical with this one except that ten times as much aluminum chloride was used. The ethylbenzene and diethylbenzene were distilled as before; degradation gave benzoic acid and phthalic acid which contained only 92% of the C¹⁴ in the α -positions of the side chains, corresponding to 8% isotopic rearrangement. Although the extent of rearrangement was small in both alkylations, it was well outside the range of the experimental error (*ca.* 1%) and the close agreement of the molecular activity *per ethyl group* in the benzoic acid and phthalic acid assays attested to the reality of the rearrangement.

EXPERIMENTAL

Synthesis of ethyl-1-C¹⁴ chloride. Acetic-1-C¹⁴ acid was prepared from methylmagnesium iodide and BaC¹⁴O₃ ("diluted" with Na₂CO₃) using essentially the method of Spector,⁷ modified to a scale of 1 millimole of carbonate. The acetic-1-C¹⁴ acid was extracted from aqueous solution into ether in a continuous liquid-liquid extractor and the ether solution was dried first over calcium chloride and then over magnesium sulfate. After some of the ether had been removed by distillation, the remaining solution was added to an ether solution of lithium aluminum hydride. (Ordinary acetic acid was added in known amount before the continuous ether extraction and just before the reduction reaction in order to dilute the radioactive material and thus avoid handling losses.) The reaction mixture was stirred at room temperature for 13 hr. and then decomposed with water and dilute sulfuric acid. The ether was removed by distillation through a 50-cm. glass helix-packed column, and ethyl-1-C¹⁴ alcohol was distilled through the same column. Three

portions of ordinary ethyl alcohol were added to the residual aqueous solution and distilled through the column to scavenge all of the radioactive alcohol.

The ethyl-1-C¹⁴ alcohol was radioassayed in the form of its 3,5-dinitrobenzoate.⁸ This derivative was first recrystallized from ethyl alcohol, but progressive loss of radioactivity with each recrystallization was observed. This was undoubtedly due to replacement of the active alcohol group in the ester by inactive groups from the solvent. Substitution of Skellysolve B for alcohol in the recrystallization avoided this complication. From 46.8 mg. of BaC¹⁴O₃ (6.50 mc./m. mole) there was obtained 31 ml. of ethyl-1-C¹⁴ alcohol (1.74 μ c./m. mole); this corresponded to a radiochemical yield of 59%.

Ethyl-1-C¹⁴ chloride was prepared from ethyl-1-C¹⁴ alcohol by treatment with aluminum chloride.⁹ This was found to be much easier to control than the reaction with phosphorus pentachloride which was used previously.² The product was radioassayed in the form of its mercuric chloride derivative,¹⁰ which was purified by recrystallization from 60% ethyl alcohol.

Radioassays were made by means of wet-oxidation and vibrating-reed electrometry as described previously.¹¹

Treatment of ethyl-1-C¹⁴ chloride with aluminum chloride for 6 min. A 15-ml. (at 0° C.) portion of ethyl-1-C¹⁴ chloride was transferred in a vacuum line onto 2 g. of solid aluminum chloride. The mixture was quickly brought to room temperature and atmospheric pressure and allowed to stand 6 min. At the end of this time the product was passed through an Ascarite trap to remove hydrogen chloride, a bromine water trap to remove ethylene, and two drying tubes containing, respectively, calcium chloride and magnesium sulfate. The ethyl chloride recovered amounted to 11 ml. (at 0° C.). A 1-ml. sample was converted to the mercuric chloride derivative and radioassayed; 0.524 μ c./m. mole.

The remaining 10 ml. of ethyl chloride was dissolved in 31 ml. of cold dry benzene and the solution was added dropwise to a stirred mixture of 1.5 g. of aluminum chloride and 24 ml. of dry benzene heated on a steam cone. Heating and stirring were continued for 1.25 hr. and the reaction mixture was decomposed with ice water and worked up in the usual way. By distillation through a 50-cm. glass helix-packed column there was obtained 4.3 g. of ethylbenzene, b.p. 133–136°. A 1-ml. sample was oxidized by permanganate to benzoic acid. It was found that satisfactory yields could be obtained without resorting to the bromination used previously² if the following procedure was followed. In a 150-ml. flask equipped with a reflux condenser and a magnetic stirrer was placed 1 ml. of ethylbenzene, 2 g. of potassium permanganate, and 30 ml. of water. The mixture was heated to gentle reflux and stirred until the permanganate color disappeared; then another 2 g. of permanganate was added. Five grams of permanganate were decolorized in this way and heating and stirring were continued for a total of 30 hr. The mixture was filtered, the manganese dioxide was washed with hot water, the washings were added to the filtrate, and the combined filtrate was extracted with two 10-ml. portions of ether. The aqueous solution was heated to boiling and acidified with hydrochloric acid. The benzoic acid was filtered from the cooled solution and recrystallized from 50% ethyl alcohol; 542 mg., m. p. 120.5–121°. Radioassay of an 8.3-mg. sample gave 0.522 μ c./m. mole. The benzoic acid was sublimed and re-assayed (6.9 mg.); 0.523 μ c./m. mole. The radioactivity of the benzoic acid was thus the same as

(8) 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. 212.

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(10) Ref. 8, p. 244.

(11) R. M. Roberts and S. G. Brandenberger, *J. Am. Chem. Soc.* **79**, 5484 (1957).

(6) G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647 (1956).

(7) L. B. Spector, Atomic Energy Commission, MDDC 532; cf. M. Calvin *et al.*, *Isotopic Carbon*, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 177.

