

hydroxide solution, separated, washed, and dried with anhydrous calcium chloride. The crude material (810 g.) was placed in a flask and about half of it distilled through a 22-plate column. Melting points and boiling ranges of the fractions are shown in Table I. The distillation was stopped when the change in boiling point indicated that 4,5-dichloro-*o*-xylene was beginning to distil; this compound was isolated by chilling the residue and then recrystallizing the solid portion from methanol.

A 1.3-g. sample from fraction 7 was twice recrystallized from chilled methanol yielding fine white crystals of m.p. 29.1–29.3°. The infrared spectrum of the crystals which had been melted by crushing between salt plates was obtained using the Naval Powder Factory's Perkin-Elmer 12-C spectrometer. Using the method of Hinkel and co-workers, a mononitro derivative was prepared from a 16-g. mixture of equal portions of fractions 6, 7 and 8. The product, after recrystallization once from ethanol and twice from petroleum ether (b.p. 35–65°), melted at 84.0–84.1°. The dinitro derivative prepared from 1 g. of fraction 7 by the method of Hinkel and co-workers and recrystallized twice from ethanol melted at 175.1–175.1°.

TABLE I

DISTILLATE FRACTIONS FROM CRUDE DICHLORO-*o*-XYLENE

Fraction	B. range, °C.	P, mm.	Wt., g.	Wt. %	M.p., °C.
1	55.0–90.2	27.5	41.8	5.16	Below –15
2	90.0–90.2	27.5	45.4	5.60	–7.2 to –6.5
3	90.0–90.2	27.5			
	73.5–74.0	9	32.1	3.96	–6.2 to –5.2
4	74.0–94.5	9	20.1	2.48	Below –15
5	94.5–96.0	9	19.8	2.44	9.7 to 12.0
6	95.8–96.5	9	46.9	5.79	16.0 to 17.0
7	96.3–96.3	9	52.2	6.44	16.8 to 17.8
8	96.3–96.8	9	40.5	5.00	16.2 to 17.3
9	96.6–96.9	9	45.4	5.60	13.5 to 14.2
10	96.7–97.6	9	28.5	3.52	9.0 to 10.8
11	97.7–99.0	9	35.1	4.33	1.5 to 3.2

Acknowledgment.—Discussions of synthetic methods with Dr. S. N. Wrenn are gratefully acknowledged.

(8) All melting points were determined using a calibrated, partial immersion thermometer.

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The Reaction of Silver Cyclobutanecarboxylate with Bromine¹

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The production of cyclobutyl bromide by the action of bromine on silver cyclobutanecarboxylate has been demonstrated by Cason and Way.^{2,3} There are also formed in this reaction a C₉H₁₄O₂ ester mixture³ and a tribromide C₄H₇Br₃.

The nature of this tribromide has now been elucidated. It is 1,2,4-tribromobutane⁴ formed by a theoretically interesting cleavage of the cyclobutane ring under the conditions of the Hunsdiecker degradation.

(1) Research supported by the Research Corporation and by the Office of Naval Research.

(2) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

(3) Cf. J. D. Roberts and H. E. Simmons, Jr., *THIS JOURNAL*, **73**, 5487 (1951).

(4) We are indebted to Dr. Saul Winstein who originally suggested this structure for the tribromide.

Experimental⁵

Reaction of Silver Cyclobutanecarboxylate with Bromine.

—The techniques employed have been described previously^{2,6}; ca. 0.2 mole of silver cyclobutanecarboxylate was used in each experiment.

When silver salt was added during 2.5 hours to excess of bromine in carbon tetrachloride at 10–12°, cyclobutyl bromide, b.p. 106–108°, b.p. 46–48° at 100 mm., *n*_D²⁵ 1.4768, *d*₄²⁵ 1.43, was obtained in 44% yield; also produced in this reaction were ester (ca. 6%) and tribromide (ca. 10%).

Bromine was added dropwise (until color persisted) to silver salt in carbon tetrachloride at 25°. No monobromide was noted; the yield of ester⁷ was 60%, that of tribromide 5%. A high-boiling fraction, b.p. ca. 125° at 2 mm., *n*_D²⁵ ca. 1.516, *d*₄²⁵ ca. 1.60, was obtained, probably formed (in 8% yield) by addition of bromine to allylcarbinyl cyclobutanecarboxylate.³

Silver salt was added (1.5 hours) to a refluxing solution of excess bromine in carbon tetrachloride. The only identified product was tribromide, yield 60%, b.p. 72–74° at 3 mm., *n*_D²⁵ 1.5661–1.5679, *d*₄²⁵ 2.21, m.p. –20 to –15°. A portion was recrystallized from ether at –80° and redistilled, *n*_D²⁵ 1.5683, m.p. unaltered.

Anal. Calcd. for C₄H₇Br₃: C, 16.3; H, 2.4. Found: C, 16.1; H, 2.5.

Identification of Tribromide.—A portion of the above tribromide was treated with magnesium in ether and the product carbonated.⁸ The resulting allylacetic acid was converted to the *p*-bromophenacyl ester, m.p. 58.5–59.5°, not depressed when mixed with authentic material, m.p. 59.5–60°.⁹

3,4-Dibromobutanol-1,¹⁰ was treated with a saturated solution of hydrogen bromide in glacial acetic acid at 0°; the temperature was raised slowly (20 hours) to 100° and was maintained there for two hours. The yield of 1,2,4-tribromobutane, b.p. 56–59° at 1 mm., *n*_D²⁵ 1.5588, was 82%. Another sample of tribromide was available,⁶ obtained by Hunsdiecker degradation of 1,2,4-butanetricarboxylic acid. A comparison of the infrared spectra¹¹ of the three tribromide specimens establishes that the tribromide from silver cyclobutanecarboxylate (all the evidence indicates a high degree of purity for this material) has the same structure as the other two.

(5) Microanalyses by Dr. A. Elek, Los Angeles.

(6) J. C. Conly, *THIS JOURNAL*, **75**, 1148 (1953).

(7) The *n*_D²⁵ 1.4528 of a portion indicates³ slight contamination. Equivalents of cyclobutyl bromide and silver cyclobutanecarboxylate in carbon tetrachloride, after standing at room temperature for twelve days, gave a 75% yield of ester mixture, *n*_D²⁵ 1.4496.

(8) J. von Braun and H. Deutsch, *Ber.*, **44**, 3699 (1911).

(9) L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950).

(10) Formed in 60% yield from allyl carbinol, H. Pariselle, *Ann. chim.*, [8] **24**, 317 (1911).

(11) Spectra reproduced in the Ph.D. thesis of J. C. Conly, California Institute of Technology, 1950.

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The Addition of Water to Diphenylacetylene-1,2-C₁₄¹¹

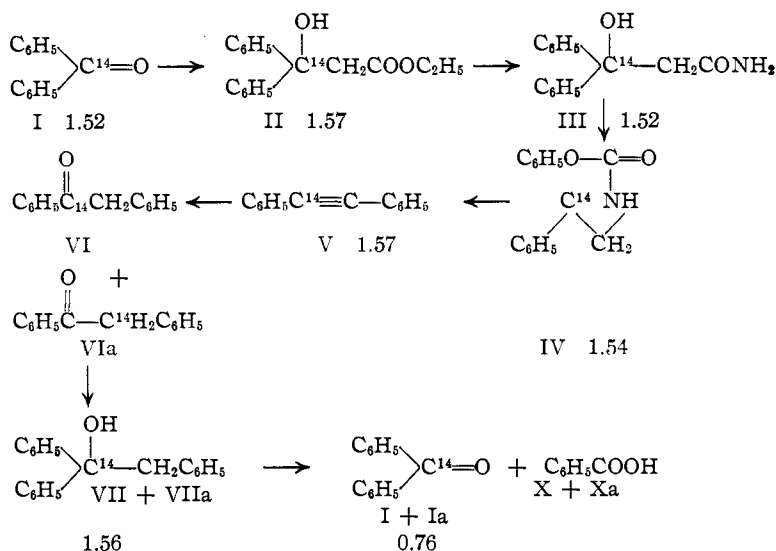
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During the course of another investigation, a sample of diphenylacetylene-1,2-C₁₄ was prepared by the series of reactions recently described by Newman and Kutner.² It appeared of interest to explore the possibly unsymmetrical addition of the

(1) This document is based upon work performed under Contract Number W-7405-eng. 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) M. S. Newman and A. Kutner, *THIS JOURNAL*, **73**, 4199 (1951). The writer is indebted to Professor Newman for suggesting the investigation of this hydration, for providing in advance of publication a copy of his and Dr. Kutner's manuscript, and for friendly advice.



elements of water across the C¹²-C¹⁴ triple bond (*i.e.*, the isotope effect),³ of this substance.

This has now been done. The series of reactions employed is shown in the scheme above. The arabic numerals represent the radioactivities in microcuries per millimole. The average of ten determinations upon the compounds I through VII was $1.55 \pm 0.02 \mu\text{c. of C}^{14}/\text{mmole}$ (average derivation). When this is compared with the value of $1.52 \pm 0.01 \mu\text{c. of C}^{14}/\text{mmole}$ which is twice the observed activity of the degradation product, I + Ia, it is apparent that any isotope effect in the hydration of diphenylacetylene must be less than 1-2%. The results of the assays upon the other degradation product, benzoic acid (X), could not be applied to this study, since the low value obtained, $0.66 \mu\text{c. of C}^{14}/\text{mmole}$, indicates that the benzoic acid obtained must have been diluted during the oxidation of VII + VIIa with benzoic acid from some inactive source.

Experimental⁴

Diphenyl Ketone-C¹⁴.—Thirty-five grams of aluminum chloride was added portionwise to a mixture of 56 g. of benzene, 60 ml. of carbon disulfide, 28.1 g. of benzoyl chloride and 50.1 mg. of benzoic acid containing about 1 mc. of carbon-14. After stirring overnight, the mixture was hydrolyzed, the product processed and then distilled. The distillate was 26.34 g. (72%); the still was chased with 21.33 g. of inactive benzophenone, of which 19.70 g. was recovered in the distillate, making a total of 46.04 g. (253 mmoles) of crystalline benzophenone. A portion of this was converted to the oxime, m.p. 141°, which was recrystallized for assay. The assay showed 1.50, 1.53 $\mu\text{c. of C}^{14}/\text{mmole}$.

Ethyl 3-Hydroxy-3,3-diphenylpropionate-3-C¹⁴.—This was prepared by the procedure of Rupe and Busolt,⁵ in essentially quantitative yield as a solid, which, after crystallization, melted at 85-86°. It contained 1.56, 1.58 $\mu\text{c. of C}^{14}/\text{mmole}$.

3-Hydroxy-3,3-diphenylpropionic Acid-3-C¹⁴ Hydrazide.—This was prepared by refluxing the above ester, 13.5 g., with a mixture of 10 ml. of 95% hydrazine hydrate and 25 ml. of ethanol for three hours. The yield was 16 g. of colorless solid which after crystallization from benzene melted at 130° and contained 1.52 $\mu\text{c. of C}^{14}/\text{mmole}$.

(3) Cf. G. A. Ropp and O. K. Neville, *Nucleonics*, **9**, 22 (1951), for a general review of the isotope effect.

(4) C-14 assays were accomplished by wet combustion of the compounds and ionization chamber counting of the evolved carbon dioxide on a vibrating reed electrometer. Melting points were taken upon a Kofler hot-stage.

(5) H. Rupe and E. Busolt, *Zer.*, **40**, 4587.

5,5-Diphenyl-2-oxazolidone-4-C¹⁴.—A solution of the hydrazide (7.2 g.) in 60 ml. of acetic acid and 6 ml. of 6 *N* hydrochloric acid was treated, with stirring, with a solution of 2.1 g. of sodium nitrite in 15 ml. of water. The suspension of white solid which formed was heated on the steam-bath until cessation of gas evolution and the resulting clear yellow solution cooled and diluted with water. The pale yellow crystalline solid which formed was filtered (4.1 g.), m.p. 196-198°, and crystallized from ethanol to give colorless crystals melting at 200°, and containing 1.56, 1.52 $\mu\text{c. of C}^{14}/\text{mmole}$.

Diphenyl-(acetylene-1-C¹⁴).—The above oxazolidone was converted through the nitroso compound to the acetylene by the procedure described by Newman and Kutner.³ The acetylene was obtained in 60% yield as a pale cream solid, m.p. 52-55°. Recrystallization from alcohol-water gave colorless needles melting at 56-57° and containing 1.59, 1.56 $\mu\text{c. of C}^{14}/\text{mmole}$.

Benzyl Phenyl Ketone-C¹⁴.—A portion of the above acetylene (0.50 g.) was warmed with a mixture of 5 ml. of concentrated sulfuric acid and 15 ml. of acetic acid until a clear solution resulted (about one hour), then a few crystals of mercuric chloride was added and warming continued for a few minutes. The solution was poured into water, and the pale yellow precipitate filtered and air-dried. It weighed 500 mg. and melted at 51-52°. The mixture melting point of this with authentic desoxybenzoïn (m.p. 51-52°) showed no depression but the mixture melting point with diphenylacetylene (m.p. 56-57°) was 35-45°.

Benzyl diphenyl-(carbinol-C¹⁴).—The above product was added to the Grignard solution prepared from 3 g. of bromobenzene and 0.5 g. of magnesium, and the resulting turbid suspension stirred overnight. Hydrolysis and crystallization of the product from hexane gave 480 mg. of nearly colorless needles which melted at 88° and contained 1.56 $\mu\text{c. of C}^{14}/\text{mmole}$.

Oxidation of Benzyl diphenylcarbinol-C¹⁴.—After about 100 mg. of the above material had been reserved for analysis, the residual product was heated for one hour on the steam-bath with a solution of 0.5 g. of chromic oxide in 10 ml. of acetic acid. The dark green solution was poured into water, and the water solution was ether extracted. This ether extract was shaken with 1 *N* sodium hydroxide and water, then dried and evaporated. The residual darkish oil was heated with hydroxylamine hydrochloride, pyridine and ethanol to give after crystallization from dilute ethanol, 150 mg. of benzophenone oxime, whose melting point and mixture melting point with authentic oxime (m.p. 141°) was 141°. It contained 0.756, 0.758 and 0.763 $\mu\text{c. of C}^{14}/\text{mmole}$. The alkaline extract obtained above was acidified and ether extracted. The darkish oil obtained from the ether was treated with a large excess of thionyl chloride and the solution heated under vacuum to remove excess thionyl chloride and any acetyl chloride. The residue from this was dissolved in benzene and treated with excess aniline. The benzene solution after washing with water and drying was evaporated, and the residual solid crystallized from benzene. The benzanilide was so obtained as colorless plates which melted at 161° and contained 0.690, 0.656, 0.660 and 0.676 $\mu\text{c. of C}^{14}/\text{mmole}$.

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Dielectric Constant for the Dioxane-Water System from 20 to 35°

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This paper is a report of the dielectric constants of dioxane-water mixtures over the range of tem-

(1) Address communications to James L. Hall.