

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 indicates 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.