ridine hydrochloride and products varying from dark resins to brown, infusible materials, depending on length of heating. One such resin analyzed correctly (17.48%) for nitrogen (theory for trinitrostyrene, 17.58%) but was not otherwise characterized.

Dehydrohalogenation could be accomplished by heating the chloride at 85–90° until the evolution of HCl was completed as evidenced by testing with moist litmus paper. The products were brittle, resinous substances with a softening temperature of 50–60° which did not change on further heating.

2-(2,4,6-Trinitrophenyl)-ethylpyridinium Chloride.—2-(2,4,6-Trinitrophenyl)-ethyl chloride, 27.6 g. (0.1 mole), was added to 23.7 g. (0.3 mole) of pyridine. After the entire mass had solidified (about 20 minutes) the excess pyridine was extracted with low-boiling petroleum ether. Recrystallization of the residue from a methanol–methyl ethyl ketone mixture gave 17.7 g. (50%) of light yellow to colorless 2-(2,4,6-trinitrophenyl)-ethylpyridinium chloride, m.p. 132.0–134.2°.

Anal. Calcd. for $C_{13}H_{11}O_6N_4Cl$: N, 15.80; Cl, 10.00. Found: N, 15.90; Cl, 9.94.

On dilution of the pyridine extract with water, colorless platelets were deposited which on recrystallization from carbon tetrachloride melted at 63–64°. These were shown, by mixed melting point with an authentic sample, to be 2,4,6-trinitrostyrene.

Preparation of 2,4,6-Trinitrostyrene from 2-(2,4,6-Trinitrophenyl)-ethylpyridinium Chloride.—To a mixture of 5 g. (0.014 mole) of 2-(2,4,6-trinitrophenyl)-ethylpyridinium chloride and 100 ml. of water, 0.75 g. (0.007 mole) of sodium carbonate was added with shaking, forming a cherry-red solution, which gradually turned darker. Pyridine was evolved and a brown precipitate settled. After 20 minutes, the solution was neutralized with dilute hydrochloric acid. Extractions of the precipitate with carbon tetrachloride yielded a solution from which was isolated 1.0 g. (29%) of trinitrostyrene, m.p. 63–64°, which failed to add bromine but did decolorize alkaline permanganate.

Anal. Calcd. for $C_8H_5N_3O_6$: C, 40.18; H, 2.11; N, 17.57. Found: C, 40.44; H, 2.22; N, 17.54.

2-(2,4,6-Trinitrophenyl)-ethyltrimethylammonium Iodide.—To a warm solution of 12.8 g. (0.04 mole) of 2-(2,4,6-trinitrophenyl)-ethyldimethylamine hydrochloride[1] in 80 g. (2.5 moles) of methanol, 9.9 g. (0.07 mole) of methyl iodide and 2.7 g. (0.048) mole of potassium hydroxide pellets were added with vigorous shaking. The brick-red precipitate which began to form in about 20 minutes was promptly separated by decanting and was recrystallized from methanol to give 12.7 g. (75%) of 2-(2,4,6-trinitrophenyl)-ethyltrimethylammonium iodide, m.p. 139–141°.

Addition of Ammonia to 2,4,6-Trinitrostyrene.—To a solution of 0.69 g. of the olefin in 25 ml. of anhydrous ether, 0.5 ml. of anhydrous ammonia was added. On partial evaporation of the solvent, 0.5 g. (70%) of yellow bis-(2,4,6-trinitrophenylethyl)-amine, m.p. 129.5–130.5° after repeated washing with dry ether, separated.

Anal. Calcd. for $C_{16}H_{13}O_{12}N_7$: N, 19.80. Found: N, 19.61.

ORGANIC CHEMISTRY BRANCH
U. S. NAVAL ORDNANCE TEST STATION
INYOKERN, CHINA LAKE, CALIF.

The Dichlorination of *o*-Xylene[1]

BY CARL BOVARS[2]

RECEIVED NOVEMBER 3, 1952

Hinkel and co-workers[3,4] reported that the low temperature, iron-catalyzed dichlorination of *o*-xylene with chlorine gas yielded only the 4,5- and 3,4-dichloro-isomers. The absence of substantial quantities of 3,5-dichloro-*o*-xylene would, of course, be expected because of the ortho–para directive power of the chlorine atom, but the failure of these workers to obtain 3,6-dichloro-*o*-xylene is puzzling in view of the tendency of catalyzed chlorination to occur predominantly in the position para to chlorine already present.[5] In addition, White, Biggs and Morgan[6] reported that 5-nitro-3,4-dichloro-*o*-xylene which was prepared according to the method of Hinkel and co-workers had a melting point higher than the one given by the original authors. White and co-workers attributed the higher melting point to contamination of their product with 3-nitro-4,5-dichloro-*o*-xylene in solid solution.

In the present work a low temperature, iron-catalyzed dichlorination of *o*-xylene was carried out and the products fractionated. 4,5-Dichloro-*o*-xylene was identified by its melting point and the melting point of the mononitro derivative. The distillation fractions in which 3,4-dichloro-*o*-xylene would be expected on the basis of the previous work were found to have melting points substantially higher than that of the pure compound (8–9°[3,4]). Recrystallization of these fractions yielded a compound which melted at the same temperature as that recorded for 3,6-dichloro-*o*-xylene (29°[4]). The infrared spectrum of the compound shows a strong absorption band at 8.03 cm.$^{-1}$, a frequency which is characteristic of 1,2,3,4-tetrasubstituted benzenes.[7] The mononitro derivative prepared from these fractions was found, after purification, to have the melting point recorded for 4-nitro-3,6-dichloro-*o*-xylene (84°[4]) rather than that for 5-nitro-3,4-dichloro-*o*-xylene (78°[3]). To confirm the conclusion that 3,6-dichloro-*o*-xylene was formed in the chlorination, a dinitro-derivative was prepared from one of these fractions. This compound had a melting point closer to the recorded value for 4,5-dinitro-3,6-dichloro-*o*-xylene (174°[4]) than that for 5,6-dinitro-3,4-dichloro-*o*-xylene (172°[3,4]).

No attempt was made to isolate 3,4-dichloro-*o*-xylene which was probably present as a minor constituent in the fractions containing 3,6-dichloro-*o*-xylene. These two isomers have the same boiling point (234°[3,4]). The melting points of the distillation fractions (Table I, below) indicate that the major constituent of fractions 6, 7 and 8 is the 3,6-dichloro-isomer. The decreasing melting points of the later fractions are probably due to the presence of increasing amounts of 4,5-dichloro-*o*-xylene as a contaminant.

Experimental

Five moles of *o*-xylene (City Chemical Corporation, b.p. 143.5–144.5°, $n^{20}D$ 1.5047) with 5.5 g. of iron filings was chlorinated at −10 to 0° using chlorine dried with concentrated sulfuric acid. A total of 32 hours was required for the reaction mixture to gain the weight corresponding to dichlorination. This weight increase was determined after aspirating the reaction product. The chlorinated product was washed with water, refluxed one hour with 10% sodium

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[1] Abstracted mainly from a portion of a thesis on "The Dielectric Properties of Solid Nitrodichloro-*o*-xylenes" directed by Dr. Reuben E. Wood and submitted in partial fulfillment of the requirements for the M.S. degree at The George Washington University, May, 1952.

[2] Research and Development Department, Naval Powder Factory, Indian Head, Md.

[3] L. E. Hinkel, E. E. Ayling and L. C. Bevan, *J. Chem. Soc.*, 1874 (1928).

[4] L. E. Hinkel, E. E. Ayling and T. M. Walters, *ibid.*, 1946 (1934).

[5] H. J. Lucas, "Organic Chemistry," American Book Company, New York, N. Y., 1935, p. 360.

[6] A. H. White, B. S. Biggs and S. O. Morgan, THIS JOURNAL, 62, 16 (1940). 3,4-Dichloro-*o*-xylene is erroneously referred to as 4,5-dichloro-*o*-xylene on p. 17 of this article.

[7] P. J. Launer and D. A. McCaulay, *Anal. Chem.*, 23, 1875 (1951).

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°.[8] 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 coworkers, 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.

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[8] All melting points were determined using a calibrated, partial immersion thermometer.

DEPARTMENT OF CHEMISTRY
THE GEORGE WASHINGTON UNIVERSITY
WASHINGTON, D. C.

The Reaction of Silver Cyclobutanecarboxylate with Bromine[1]

BY E. R. BUCHMAN AND J. C. CONLY

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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 $C_9H_{14}O_2$ ester mixture[3] and a tribromide $C_4H_7Br_3$.

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

Experimental[5]

Reaction of Silver Cyclobutanecarboxylate wth 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., $n^{25}D$ 1.4768, d^{24}_4 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 ester[7] was 60%, that of tribromide 5%. A high-boiling fraction, b.p. *ca.* 125° at 2 mm., $n^{25}D$ *ca.* 1.516, d^{25}_4 *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., $n^{25}D$ 1.5661–1.5679, d^{25}_4 2.21, m.p. −20 to −15°. A portion was recrystallized from ether at −80° and redistilled, $n^{25}D$ 1.5683, m.p. unaltered.

Anal. Calcd. for $C_4H_7Br_3$: 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., $n^{25}D$ 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 spectra[11] 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.

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[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.

[5] Microanalyses by Dr. A. Elek, Los Angeles.

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

[7] The $n^{25}D$ 1.4528 of a portion indicates[3] slight contamination. Equivalents of cyclobutyl bromide and silver cyclobutanecarboxylate in carbon tetrachloride, after standing at room temperature for twelve days, gave[3] a 75% yield of ester mixture, $n^{25}D$ 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.

GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 4, CALIFORNIA

The Addition of Water to Diphenylacetylene-1,2-C_1^{14}[1]

BY JOHN G. BURR, JR.

RECEIVED NOVEMBER 3, 1952

During the course of another investigation, a sample of diphenylacetylene-1,2-C^{14} 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

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[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.