

was found to boil at 167.0° at 767 mm. and the refractive index at 20° was 1.4780 and at 25° was 1.4718.

Infrared spectrograms of *n*-propyl- and isopropylgermanium trichlorides, and of the product from the direct reaction of *n*-propyl chloride on germanium, were obtained by means of a Baird recording spectrophotometer, using solutions of the substances in chloroform. Comparison of the spectrograms showed marked similarity between those for *n*-propylgermanium trichloride and the product of direct reaction, especially in the region of wave numbers 1350 to 1230 cm^{-1} and 1000 to 1100 cm^{-1} . The band at wave numbers 880 to 910 cm^{-1} which is characteristic⁵ of isopropyl groups was lacking in the pattern for the product of direct reaction. The spectrogram of *n*-propyl bromide resembled that of the product of direct reaction as well as that of *n*-propylgermanium trichloride.

Discussion

Comparison of the physical constants and the infrared absorptions indicates that the substance from the vapor-solid reaction of *n*-propyl chloride and germanium is principally *n*-propylgermanium trichloride, and that rearrangement of the propyl groups occurred only to a minor degree during their transfer to germanium. Rearrangement of *n*-propyl to isopropyl groups has been observed as a result of the pyrolysis of *n*-propyl bromide at 280°,⁶ but the time required for the rearrangement may have been longer than the time involved in transfer of the *n*-propyl groups to germanium. The results obtained here indicate that most of those *n*-propyl groups which ultimately become bonded to germanium are protected from rearrangement during transfer, probably because they are in the form of *n*-propyl copper³ most of the time instead of in the form of free radicals. Those propyl groups which are completely lost (and which outnumber those which become attached to germanium) may, of course, suffer rearrangement during the course of their decomposition.

(5) N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

(6) Michael and Lempold, *Ann.*, **379**, 263 (1911); Aronstein, *Ber.*, **14**, 607 (1881); *Rec. trav. chim.*, **1**, 134 (1882).

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Small-Ring Compounds. IX. The Reaction of Silver Cyclobutanecarboxylate with Iodine

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Cyclobutanol was first reported by Perkin¹ in 1894 as the product of the reaction between cyclobutylamine and nitrous acid. However, it was later shown^{2,3} that Perkin's material was actually a mixture of roughly equal amounts of cyclobutanol and cyclopropylcarbinol along with a small amount of allylcarbinol. In 1907, Demjanow and Dojarenko⁴ reported the synthesis of presumably authentic cyclobutanol by hydrolysis of cyclobutyl cyclobutanecarboxylate obtained from the reaction of silver cyclobutanecarboxylate with iodine or the electrolysis of potassium cyclobutanecarboxylate. The product was characterized as

(1) W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 950 (1894).

(2) (a) N. J. Demjanow, *Ber.*, **40**, 4393, 4961 (1907); (b) R. Skrabal, *Monatsh.*, **70**, 420 (1937).

(3) J. D. Roberts and R. H. Mazur, *THIS JOURNAL*, **73**, 2509 (1951).

(4) N. J. Demjanow and M. Dojarenko, *Ber.*, **40**, 2594 (1907); cf. also N. J. Demjanow, *J. Russ. Phys. Chem. Soc.*, **61**, 1861 (1929).

the *N*-phenylcarbamate, m.p. 110–111°. In 1949, cyclobutanol prepared by the lithium aluminum hydride reduction of cyclobutanone⁵ was found to yield a *N*-phenylcarbamate of m.p. 130.6–131.2°. This discrepancy in melting points has prompted us to repeat one of the earlier cyclobutanol preparations.

The reaction of silver cyclobutanecarboxylate with iodine was carried out following the procedure of Demjanow and Dojarenko⁴ as closely as possible. The infrared spectrum for the ester product is given in Fig. 1 along with those of pure samples of the cyclobutylcarboxylate esters of cyclobutanol, cyclopropylcarbinol and allylcarbinol which were prepared by the reaction of the alcohols with cyclobutanecarboxylic acid chloride in pyridine. The infrared spectra indicate that the reaction product is a mixture of ~32% cyclobutyl, ~65% cyclo-

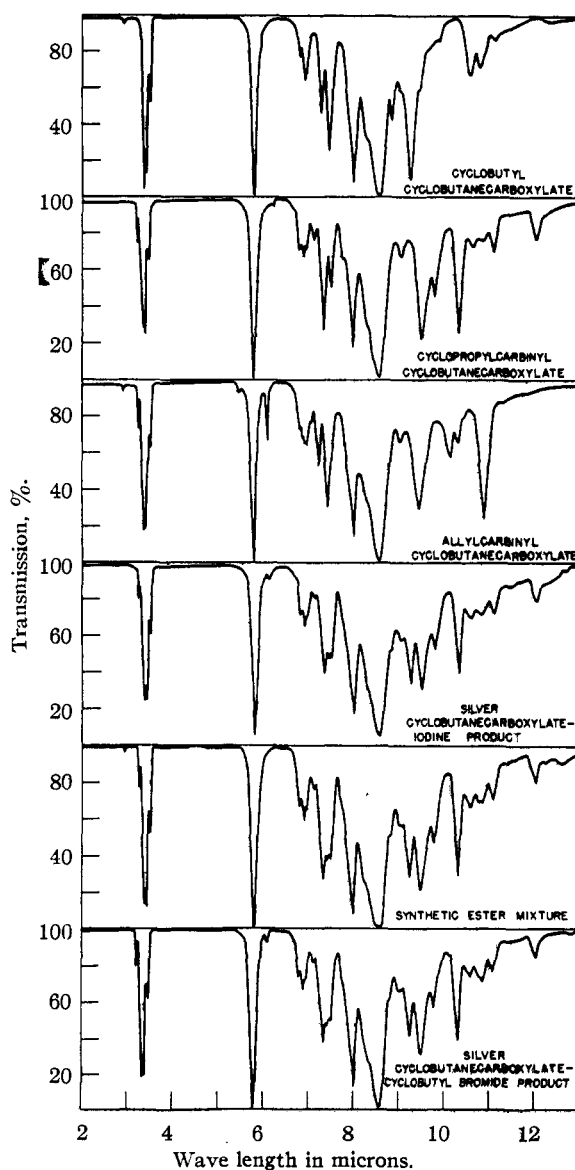
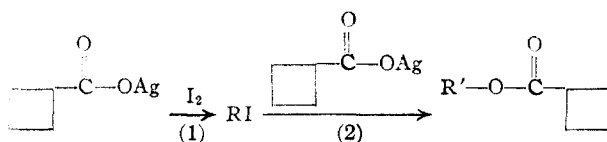


Fig. 1.—Infrared spectra: Baird Spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in the regions 4.2–5.0 μ and 6.2–7.2 μ where carbon tetrachloride was used as solvent.

(5) J. D. Roberts and C. W. Sauer, *THIS JOURNAL*, **71**, 3925 (1949).

propylcarbonyl and ~3% allylcarbonyl cyclobutanecarboxylates. A mixture of the pure esters, corresponding to this composition, had a spectrum (cf. Fig. 1) which was essentially identical to that of the reaction product. A melting point-composition diagram of cyclobutyl and cyclopropylcarbonyl³ N-phenylcarbamates revealed that these substances form solid solutions (no melting point depression) and that the melting point (110–111°) previously reported⁴ corresponds to a composition of ~45% cyclobutyl and ~55% cyclopropylcarbonyl N-phenylcarbamates. This composition compares favorably with that of the ester mixture considering the possibility for changes during the hydrolysis of the esters and the crystallization of the N-phenylcarbamates.

The silver salt-iodine reaction is probably best represented as occurring in two steps



where R- may or may not be the same as R'. It seems unlikely that the rearrangement occurs in step (1) since Cason and Way⁶ have found that the reaction of silver cyclobutanecarboxylate with bromine in carbon tetrachloride at low temperatures yields pure cyclobutyl bromide.⁷ Reactions of organic halides with silver salts often proceed by means of carbonium ion intermediates.⁸ Although the conditions for carbonium ion formation might be considered to be relatively unfavorable in the silver cyclobutanecarboxylate-iodine reaction, a mechanism, involving formation and rearrangement of the cyclobutyl carbonium ion is indicated by the findings^{3,9} that other carbonium-ion type reactions of cyclobutyl derivatives give mixtures of products similar to that obtained in the present instance. Evidence confirming the possibility of rearrangement in reaction (2) was provided by investigation of the reaction of cyclobutyl bromide with silver cyclobutanecarboxylate in the absence of a solvent. A mixture of esters was formed which had an infrared spectrum (Fig. 1) very similar to that of the product of the iodine-silver cyclobutanecarboxylate reaction.¹⁰ The com-

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

(7) The lack of rearrangement in this reaction is in harmony with the free-radical character of halogen-silver salt reactions and the observation that no rearrangement occurs in the vapor-phase chlorination of cyclobutane.⁸

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 138-140.

(9) J. D. Roberts and V. C. Chambers, *THIS JOURNAL*, **73**, 5034 (1951).

(10) Cason and Way⁶ report the formation of cyclobutyl cyclobutanecarboxylate b.p. 89.0–89.1° (16 mm.), n_D^{20} 1.4542, as a by-product of the reaction of silver cyclobutanecarboxylate with bromine. However, no proof of structure was undertaken, because of the similarity of the product to that of Demjanow and Dojarenko⁴ heretofore accepted as cyclobutyl cyclobutanecarboxylate. A sample of the ester previously obtained⁶ was kindly supplied by Professor Cason and was found to have an infrared spectrum identical with that of our ester mixture. The reaction of silver cyclobutanecarboxylate with cyclobutyl bromide has also been investigated by Dr. E. R. Buchman and his co-workers (J. C. Conly, Ph.D. Thesis, California Institute of Technology, 1950) with similar results.

position of the ester mixture as computed from infrared spectrum was ~30% cyclobutyl, ~60% cyclopropylcarbonyl and ~10% allylcarbonyl cyclobutanecarboxylate.

Experimental

Reaction of Silver Cyclobutanecarboxylate with Iodine.—Iodine (22 g., 0.09 mole) and silver cyclobutanecarboxylate⁶ (36 g., 0.18 mole) were thoroughly ground with 1 g. of powdered, soft glass in a mortar. This mixture was rapidly transferred to a dry 2-l. long neck flask and warmed on the steam-bath. At approximately 90°, a vigorous reaction occurred with the evolution of carbon dioxide and condensation of liquid on the walls of the flask. The reaction mixture was heated an additional 30 min. at 100°. The liquid products were then lyophilized into a Dry Ice trap and taken up in ether. The ethereal solution was washed with 0.5 M sodium bisulfite solution, 1% sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. The ether was removed through a glass helix-packed column. The residue was fractionated through a micro column¹¹ and yielded 1.1 g. (8%) of ester mixture; b.p. 92.5–93.5° (20 mm.), n_D^{25} 1.4518. The infrared spectrum is given in Fig. 1.

Anal. Calcd. for $C_6H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.40; H, 8.99.

Cyclopropylcarbonyl Cyclobutanecarboxylate.—Cyclobutanecarboxylic acid chloride (3.6 g., 0.031 mole), prepared from cyclobutanecarboxylic acid and phosphorus trichloride in 92% yield, b.p. 60° (50 mm.), n_D^{25} 1.4528, was added dropwise over 15 min. to a stirred ice-cold solution of cyclopropylcarbonyl³ (2.20 g., 0.031 mole) in 10 ml. of dry pyridine. The reaction mixture was allowed to stand at room temperature for one hour, and then was taken up in ether and washed with 1 N hydrochloric acid, 5% sodium carbonate solution, and finally with water. The ethereal solution was dried over anhydrous magnesium sulfate, and the ether was removed through a glass helix-packed column. The residue was fractionated through a micro column.¹⁰ The yield of pure cyclopropylcarbonyl cyclobutanecarboxylate was 2.4 g. (55%); b.p. 84.5° (12 mm.), n_D^{25} 1.4514. The infrared spectrum is given in Fig. 1.

Anal. Calcd. for $C_6H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.01; H, 9.09.

Cyclobutyl cyclobutanecarboxylate was prepared from cyclobutanol⁵ by the above method for cyclopropylcarbonyl cyclobutanecarboxylate in a yield of 66%; b.p. 75° (12 mm.), n_D^{25} 1.4524. The infrared spectrum is given in Fig. 1.

Anal. Calcd. for $C_6H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.94; H, 8.90.

Allylcarbonyl cyclobutanecarboxylate was similarly prepared from allylcarbonyl³ in 85% yield; b.p. 73–74° (12 mm.), n_D^{25} 1.4441. The infrared spectrum is given in Fig. 1.

Anal. Calcd. for $C_6H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.06; H, 9.31.

Reaction of Silver Cyclobutanecarboxylate with Cyclobutyl Bromide.—A mixture of cyclobutyl bromide¹² (3.7 g., 0.026 mole) and dry silver cyclobutanecarboxylate (5.4 g., 0.026 mole) was heated in an oil-bath at 120° for 48 hours. The volatile products were lyophilized into a Dry Ice trap, taken up in ether, washed with 5% sodium carbonate solution and then with water. The ethereal solution was dried over anhydrous magnesium sulfate, and the ether removed through a glass helix-packed column. The residue was fractionated through a micro column¹⁰ and yielded 2.8 g. (70%) of ester mixture; b.p. 77° (12 mm.), n_D^{25} 1.4501. The infrared spectrum is given in Fig. 1.

Anal. Calcd. for $C_6H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.26; H, 9.04.

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(11) C. Gould, G. Holzman and C. Niemann, *Ind. Eng. Chem., Anal. Ed.*, **19**, 204 (1947).

(12) Cyclobutyl bromide, b.p. 105–106°, n_D^{25} 1.4763, was prepared in yields up to 57% by the reaction of silver cyclobutanecarboxylate with bromine, using dichlorodifluoromethane as the reaction medium, as described by J. D. Roberts and V. C. Chambers, *THIS JOURNAL*, **73**, 3178 (1951).