

lation with an efficient spinning-band column gave 45 g. (60%) of  $\beta$ -phenylallyl chloride boiling at 88–89° at 5 mm.,  $n_D^{20}$  1.5545. Hatch and Patton<sup>2</sup> report an identical boiling point and  $n_D^{20}$  1.5550.

**Cyclopropane and Methylcyclopropane Preparation.**—Identical procedures were employed for the preparation of cyclopropane and methylcyclopropane. A 500-ml. three-neck flask was employed as the reaction flask.

One-half mole of allyl or  $\beta$ -methylallyl chloride was placed in 100 ml. of pure diglyme and the diborane generated from 10.1 g. of sodium borohydride and 52 g. of boron trifluoride etherate<sup>6</sup> was passed in with stirring at 0°. The system had been purged with dry nitrogen before the addition of diborane was commenced. Following the addition, the solution was allowed to stand at 0° for one hour and purged with dry nitrogen. A reflux condenser was attached to the outlet of the reaction flask which in turn was connected to a series of two Dry Ice-cooled traps. A pressure-equalized dropping funnel which contained a solution of 48 g. of sodium hydroxide in 200 ml. of water and carried a nitrogen inlet tube was attached to the reaction flask. The cooling bath was then removed from the reaction flask and the aqueous sodium hydroxide added slowly with vigorous stirring. The reaction mixture was allowed to warm to about 50°. The system was slowly swept with nitrogen after the addition of the

base solution. The methylcyclopropane (20.0 g., 72%) or cyclopropane (9.0 g., 43%) was collected in one –80° trap and identified by infrared and mass spectra. Additional purification was made by passing the products through a 5% solution of potassium permanganate to remove traces of oxidizable impurities.

**Procedure for the Preparation of Benzyl-, Phenyl- and *n*-Propylcyclopropane.**—The procedure employed in the preparation of high boiling substituted cyclopropanes was essentially the same as that described above for the lower boiling members of the series. These reactions were carried out on an 0.10-mole scale. The diborane employed was generated from 2.0 g. of sodium borohydride and 10.5 g. of boron trifluoride etherate.<sup>2</sup>

One-tenth mole of the appropriate allyl chloride was dissolved in 30 ml. of dry ethyl ether, cooled to 0° and treated with diborane as described above. Following the addition, the reaction mixture was maintained at 0° and a solution of 10 g. of sodium hydroxide in 40 ml. of water was added. The two-phase system was stirred at room temperature for 30 minutes and the organic layer separated, washed with water, dried and distilled with a small spinning-band column. Table I reports yields and boiling points.

HUNTSVILLE ALA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

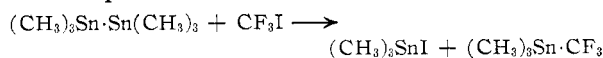
## Perfluoroalkyl Derivatives of Tin. I. Trimethyltrifluoromethyltin<sup>1</sup>

BY H. C. CLARK AND C. J. WILLIS

RECEIVED AUGUST 18, 1959

The reaction of hexamethylditin with trifluoroiodomethane gives trimethyltrifluoromethyltin. Differences in behavior between this compound and similar known compounds of other elements are related to the more electropositive nature of tin. Thermal decomposition of trimethyltrifluoromethyltin appears to proceed *via* difluoromethylene radicals, since pyrolysis alone or with tetrafluoroethylene gives perfluorocyclopropane. Reaction of equimolar amounts of trimethyltrifluoromethyltin and chlorine removes one methyl group to give dimethyltrifluoromethyltin chloride.

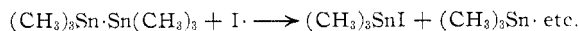
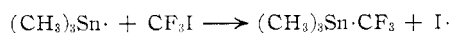
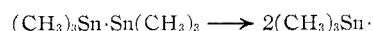
Comparatively few compounds are known in which a perfluoroalkyl group is linked to a metallic atom. In particular, knowledge is lacking of derivatives of the metallic elements of groups IIIA and IVA, for which very extensive ranges of organometallic compounds are known. We now report the first synthesis of a trifluoromethyl derivative of tin, trimethyltrifluoromethyltin, which may be prepared by using the high reactivity of hexamethylditin,  $(\text{CH}_3)_3\text{Sn}\cdot\text{Sn}(\text{CH}_3)_3$ . This compound will react readily with oxygen, sulfur, halogens or alkyl halides, in each case with cleavage of the intermetallic bond. It has now been found that reaction with trifluoroiodomethane will occur according to the equation



The reaction was carried out under pressure in the absence of light at 80°, using excess trifluoroiodomethane as solvent, and was complete in 24 hours. Trimethyltrifluoromethyltin is a colorless liquid, b.p. 101°, having a faint smell similar to that of tetramethyltin. Its boiling point shows an increase of 24° over that of tetramethyltin, a much larger increase than the 5° rise which accompanies the exchange of one methyl group for trifluoromethyl in trimethyl-phosphine, -arsine or -stibine.<sup>2</sup> This large increase may be due to the more polar nature of the trifluoromethyl compound of tin, which is

much more electropositive than the group V elements.

When the mechanism of the reaction of hexamethylditin with trifluoroiodomethane is considered it would be easy to suggest a radical mechanism with homolytic dissociation of the tin compound as the first step, *e.g.*



Such a process must be considered unlikely, however, in view of current opinion on the dissociation of hexamethylditin. Early workers,<sup>3</sup> on the basis of cryoscopic molecular weight measurements in dilute solution, regarded the molecule as largely dissociated into "trimethyltin." More recent magnetic measurements,<sup>4</sup> however, have shown that very little dissociation can be occurring, while as long ago as 1869 Ladenburg<sup>5</sup> found that the vapor density of hexamethylditin at 225° corresponded to the formula  $(\text{C}_2\text{H}_5)_6\text{Sn}_2$ . All workers agree that the complete absence of color in hexamethylditin or its solutions is strong evidence against its dissociation into radicals.

As an alternative reaction mechanism, an intermediate complex of hexamethylditin with trifluoroiodomethane may be postulated, which could

(1) This work was supported by the U. S. Office of Naval Research.

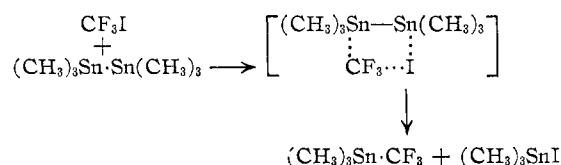
(2) R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3631 (1950).

(3) C. A. Kraus and W. V. Sessions, *THIS JOURNAL*, **47**, 2361 (1925).

(4) H. Morris and P. W. Selwood, *ibid.*, **63**, 2509 (1941).

(5) A. Ladenburg, *Ann. Suppl.*, **8**, 69 (1869).

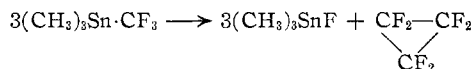
then decompose by breaking the intermetallic bond



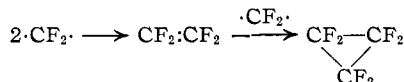
A better understanding of the mechanism of this interesting reaction may be obtained from work now in progress<sup>6</sup> on its application to some of the many reactive compounds containing metal-metal bonds formed by the elements of groups IV and V.

The hydrolytic stability of trimethyltrifluoromethyltin is, as might have been expected, very low. Immediate decomposition occurred on treatment with aqueous alkali in the cold, and fluoroform was quantitatively liberated. No immediate reaction was apparent on shaking with water at 20°, but prolonged contact or heating to 100° gave a high yield of fluoroform. This easy hydrolysis is comparable to that of the analogous antimony compound dimethyltrifluoromethylstibine, which is completely decomposed in three days by contact with aqueous alkali at 20°, although the corresponding compounds of the less electropositive elements arsenic and phosphorus,  $(\text{CH}_3)_2\text{As}\cdot\text{CF}_3$  and  $(\text{CH}_3)_2\text{P}\cdot\text{CF}_3$ , are less than 10% hydrolysed under these conditions.

Trimethyltrifluoromethyltin was found to be readily decomposed by heating. No sign of decomposition was noticed when it was distilled at 101°, but on heating to 150° in a sealed tube in the absence of air a white crystalline solid soon appeared. After maintaining at this temperature for 20 hours, over 90% of the trimethyltrifluoromethyltin had decomposed. The solid material was identified as trimethyltin fluoride, and the volatile products were found to consist almost entirely of perfluorocyclopropane, with about 1% of fluoroform and less than 1% of tetrafluoroethylene and silicon tetrafluoride. It hence appears that decomposition takes place according to the equation



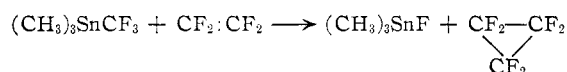
A smooth decomposition of this nature was unexpected, but the products may be simply accounted for. Attached to the tin atom are three electron-releasing methyl groups and an accepting trifluoromethyl group. Ready migration of a fluoride ion from the trifluoromethyl group to the tin atom may therefore occur, accompanied by elimination of a difluoromethylene radical. The difluoromethylene may then dimerize to tetrafluoroethylene, followed by further addition to form the three-membered ring



The surprising feature here is the almost quantitative yield of perfluorocyclopropane. This compound has been found before in reactions of this type, but

only as a minor constituent of the products. Ayscough and Emeleus<sup>7</sup> investigated the thermal decomposition of tris(trifluoromethyl)arsine and tris(trifluoromethyl)stibine and found tetrafluoroethylene and perfluorocyclopropane produced when the latter was pyrolyzed at 180–220°, but they only amounted to 10% of the products. Haszeldine<sup>8</sup> found 3% of perfluorocyclopropane among the products of the irradiation of tetrafluoroethylene with pentafluoroiodoethane, while Atkinson<sup>9</sup> found that it was produced in the irradiation of tetrafluoroethylene in the presence of mercury; all workers agree in suggesting that the three-membered ring is produced by the addition of difluoromethylene to tetrafluoroethylene.

To confirm this last point, and also to investigate the synthetic possibilities of this reaction, a sample of trimethyltrifluoromethyltin was pyrolyzed in the presence of excess tetrafluoroethylene in the vapor phase at 150°. It was found that smooth addition occurred to give a virtually quantitative yield of perfluorocyclopropane according to the equation



The only other volatile product found in this reaction was a small amount of perfluorocyclobutane; this probably arises from the thermal dimerization of tetrafluoroethylene, known to occur readily at 200°. Further applications of this novel method of producing fluorinated three-membered rings are being investigated.

Although the presence of three methyl groups in trimethyltrifluoromethyltin may contribute to its low thermal stability the primary reason for the ready breakdown is probably the relatively electropositive nature of the tin atom, which would facilitate the elimination of a fluoride ion from the trifluoromethyl group. The corresponding compounds of arsenic and phosphorus, for example, are stable at 240°. This result suggests, therefore, that it will prove difficult or impossible to prepare trifluoromethyl derivatives of the more electropositive elements by high-temperature reactions with trifluoroiodomethane, a method widely used for the group V elements.

Studies on the breakdown of perfluoroalkyl derivatives of magnesium<sup>10</sup> and zinc<sup>11</sup> have been reported but are not strictly comparable with the present work, since the magnesium and zinc compounds are made and studied in solution, where decomposition usually occurs by hydrogen abstraction from the solvent to give fluoroform (from trifluoromethyl derivatives) or heptafluoropropane (from heptafluoropropyl derivatives). However, rapid thermal decomposition of trifluoromethylmagnesium iodide was found to give tetrafluoroethylene and polymeric material, an anionic polymerization mechanism being proposed for the latter.

(7) P. B. Ayscough and H. J. Emeleus, *J. Chem. Soc.*, 3381 (1954).

(8) R. N. Haszeldine, *ibid.*, 3761 (1953).

(9) B. Atkinson, *ibid.*, 2684 (1952).

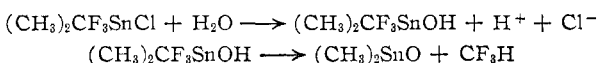
(10) R. N. Haszeldine, *ibid.*, 1273 (1954).

(11) R. N. Haszeldine and E. G. Walachewski, *ibid.*, 3606 (1953); W. T. Miller, E. Bergman and A. H. Fainberg, *THIS JOURNAL*, **79**, 4159 (1957).

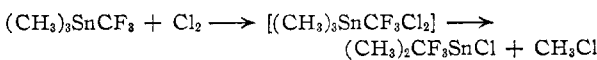
(6) W. R. Cullen, unpublished results.

Trifluoromethyl compounds of zinc are not known, but pyrolysis of heptafluoropropyl zinc iodide gives some perfluoropropene. It appears, then, that cyclic compounds will only be produced by such decompositions in the absence of solvent.

The halogens react readily with tetraalkyl tin compounds, giving alkyl halides and trialkyltin halides. A considerable number of compounds have been studied to determine which groups are preferentially removed in mixed alkyl or aryl tin compounds. Although mixed alkyl-perfluoroalkyl compounds of the group V elements have been known for some years, no studies have been reported to determine whether methyl or trifluoromethyl groups are more easily removed by the action of halogens. It was of interest, therefore, to determine the nature of the products from the reaction of trimethyltrifluoromethyltin with an equivalent amount of halogen. It was found that ready reaction occurred between trimethyltrifluoromethyltin and chlorine when equivalent quantities were mixed at  $-50^\circ$  and slowly allowed to warm to room temperature, although reaction was much slower than with tetramethyltin and a yellow color persisted for 24 hours. The volatile products were found to be mainly methyl chloride containing about 5% trifluorochloromethane, the other product being a solid, purified by vacuum sublimation to give dimethyltrifluoromethyltin chloride, m.p.  $46-47^\circ$ . The last compound had an extremely pungent, irritant vapor, similar to the trimethyltin halides but if anything more unpleasant. It also showed very low thermal stability and decomposed at  $80^\circ$ ; some perfluorocyclopropane was again formed. Hydrolytic stability of the chloride was low and heating with excess alkali gave fluoroform, but it dissolved readily in water to give an apparently stable acid solution which could be titrated with aqueous alkali to an end-point when one equivalent of alkali had been added; some decomposition then began. This acidity is clearly due to ionization of the chlorine, the chloride being the salt of a weak base and strong acid.

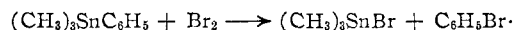


The elimination of the relatively electropositive methyl group instead of the electronegative trifluoromethyl group in the chlorination could be explained by postulating a mechanism involving an intermediate hexavalent tin compound, *e.g.*



It might be expected here that the electronegative chlorine would combine with the more electropositive methyl group, eliminating a molecule of methyl chloride. In direct conflict with such a suggestion, however, is a large body of work on mixed alkyl-aryl tin compounds<sup>12</sup> such as trimethylphenyltin, which reacts with bromine in carbon tetrachloride solution to cleave the tin-phenyl bond<sup>13</sup>

(12) J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, Middlesex, England, 1955.



From this and similar work the following order of "ease of cleavage" has been drawn up, the most easily removed groups being given first: tolyl, phenyl, benzyl, methyl, ethyl, propyl, butyl.

The groups in this list fall in order of decreasing electronegativity, and some workers have suggested the empirical rule that the more electronegative group is preferentially removed. The results now available from trimethyltrifluoromethyltin suggest that the electronegative nature of alkyl or aryl groups attached to a tin atom is not the factor determining which is more easily removed. It may rather be the strength of the tin-carbon bond which is the important factor. It will therefore be of interest to carry out studies on further trifluoromethyl derivatives of tin as they become available, in particular the fully fluorinated compound  $(\text{CF}_3)_4\text{Sn}$ .

### Experimental

Volatile compounds were manipulated in a conventional vacuum system, and purified by trap-to-trap distillation. Molecular weights were determined by Regnault's method.

**Hexamethylditin.**—Tetramethyltin was made by the method of Edgell and Ward.<sup>14</sup> The Grignard reagent was made from magnesium turnings (50 g.) and methyl iodide (225 g.) in butyl ether, and stannic chloride (74.5 g.) was added slowly. After reflux the tetramethyl tin was separated by distillation and redistilled through an efficient column to give a yield of 45.6 g. (89%), b.p.  $76-77^\circ$ . The tetramethyltin was brominated with stannic bromide to give trimethyltin bromide according to Luijten and van der Kerk.<sup>12</sup> Stannic bromide (77.7 g.) was slowly added to tetramethyltin (95 g.). The initial heat of the reaction caused the temperature of the liquid to rise to  $85^\circ$ ; after addition was complete the mixture was heated to  $120^\circ$ , when the reflux began. After heating for three hours the temperature of the liquid had risen to  $155^\circ$  and distillation gave trimethyltin bromide (153 g., 89%, b.p.  $160-165^\circ$ ) which solidified on cooling. Hexamethylditin was then prepared from the bromide by the action of sodium in liquid ammonia, the method of Kraus and Sessions.<sup>3</sup> Trimethyltin bromide (40 g.) in anhydrous liquid ammonia (200 ml.) was added to sodium (4.1 g.) in liquid ammonia (100 ml.). The ammonia was allowed to evaporate, then the residue extracted with ether, the ether extract washed with water, dried over sodium sulfate and distilled to give hexamethylditin (16 g., 71%, b.p.  $181-182^\circ$ ) which solidified on cooling.

**Trimethyltrifluoromethyltin.**—Hexamethylditin (15.7 g., 48 mmoles) was introduced into a Pyrex Carius tube (100 ml.) and after freezing and evacuating the tube, trifluoroiodomethane (28.9 g., 153 mmoles) was condensed on. The trifluoroiodomethane was a redistilled commercial sample, b.p.  $-23^\circ$ . After heating the tube to  $80^\circ$  for 20 hours fractionation of the contents gave unchanged trifluoroiodomethane (19.2 g., 98 mmoles; mol. wt. found 194 calcd. 196), a fraction boiling  $100-104^\circ$  and trimethyltin iodide (10.5 g., 36 mmoles, b.p.  $165-169^\circ$ ). The second fraction was redistilled to give trimethyltrifluoromethyltin, b.p.  $100-101^\circ$  (9.0 g., 39 mmoles). The infrared spectrum showed the absorption bands: vapor phase: 3055(w), 2995(m), 2915(m), 2395(vw), 2355(vw), 2220(vw), 2125(vw), 1265(vw), 1217(w), 1200(w), 1158(vs), 1093(w), 1071(vs), 814(m), 782(s), 725(m); liquid phase: 3000(m), 2920(m), 2340(m), 1213(w), 1150(vs), 1040(vs), 784(s), 729(m).

*Anal.* Calcd. for  $\text{C}_3\text{H}_3\text{SnCF}_3$ : C, 28.9; Sn, 51.0; mol. wt., 233. Found: C, 29.1; Sn, 50.3; mol. wt., 235.

**Thermal Decomposition of Trimethyltrifluoromethyltin.**—Trimethyltrifluoromethyltin (1.45 g.) in an evacuated Pyrex tube (5 ml.) was heated to  $150^\circ$  for 20 hours, when the liquid had disappeared and a white crystalline solid was present. Fractionation of the volatile products gave unchanged trimethyltrifluoromethyltin (0.096 g., 7%) identified spectro-

(13) R. H. Bullard and W. V. Robinson, *THIS JOURNAL*, **49**, 1368 (1927).

(14) W. V. Edgell and C. H. Ward, *ibid.*, **76**, 1169 (1954).

scopically; a fraction condensing at  $-196^{\circ}$  (0.015 g.) shown spectroscopically to contain fluoroform, perfluorocyclopropane, tetrafluoroethylene and a trace of silicon tetrafluoride; and a fraction condensing at  $-132^{\circ}$  (0.272 g.) shown by spectroscopic examination and molecular weight measurement to be nearly pure perfluorocyclopropane (mol. wt. found 148, calcd. 150). The infrared spectrum of this fraction showed strong bands at 1275 and 864  $\text{cm}^{-1}$ . These have been identified as the characteristic bands of perfluorocyclopropane. The amount produced represented a yield of over 95% based on trimethyltrifluoromethyltin destroyed.

The white crystalline solid produced (1.04 g.) decomposed at  $250^{\circ}$  without melting. It was insoluble in water but dissolved in 50% sulfuric acid; distillation of the resulting solution followed by precipitation of the fluoride as lead chlorofluoride in the usual way identified the solid as trimethyltin fluoride.

This represents a yield of 98% based on the trimethyltrifluoromethyltin destroyed.

*Anal.* Calcd. for  $\text{C}_3\text{H}_3\text{SnF}$ : F, 10.4. Found: F, 10.5, 10.8.

**Pyrolysis of Trimethyltrifluoromethyltin with Tetrafluoroethylene.**—Trimethyltrifluoromethyltin (1.40 g.) and tetrafluoroethylene (2.00 g.) in an evacuated Pyrex tube (100 ml.) were heated to  $150^{\circ}$  for 15 hours. At the end of this time a white solid had appeared in the tube, and fractionation of the volatile products gave unchanged tetrafluoroethylene (1.27 g.; mol. wt. found 100, calcd. 100) unchanged trimethyltrifluoromethyltin (0.05 g., 4%) and perfluorocyclopropane (0.92 g.; mol. wt. found 153, calcd. 150) shown spectroscopically to contain a small amount of perfluorocyclobutane.

**Hydrolysis of Trimethyltrifluoromethyltin.**—Trimethyltrifluoromethyltin (0.1880 g., 0.808 mmole) and 10% aqueous sodium hydroxide (5 ml.) were heated to  $75^{\circ}$  for 15 hours in a Pyrex tube (20 ml.) Fractionation of the products gave fluoroform (0.0568 g., 0.811 mmole; mol. wt. found 70, calcd. 70) identified spectroscopically. When trimethyltrifluoromethyltin (0.232 g.) was added to water (0.177 g.) at

$20^{\circ}$  in a Pyrex tube (10 ml.) the two liquids were immiscible and no reaction was immediately apparent, but after heating to  $100^{\circ}$  for 15 hours the tin compound had decomposed and fluoroform (0.065 g., 93%), was found. A similar tube containing trimethyltrifluoromethyltin (0.273 g.) and water (0.932 g.) was kept at  $20^{\circ}$  for 6 days with intermittent shaking, when fluoroform (0.077 g., 95%) was found.

**Reaction of Trimethyltrifluoromethyltin with Chlorine.**—Trimethyltrifluoromethyltin (7.27 g., 31.2 mmole) and chlorine (2.21 g., 31.2 mmole) in an evacuated Pyrex tube (50 ml.) were allowed to warm up from  $-196$  to  $-46^{\circ}$  and placed in a slush-bath at this temperature; the bath was then allowed to warm up slowly and kept at  $20^{\circ}$  for 24 hours, when the yellow color of the chlorine had gone. Fractionation of the volatile products gave a fraction condensing at  $-196^{\circ}$  (0.18 g.) shown spectroscopically to contain fluoroform (4% yield) and chlorotrifluoromethane, (3% yield) a fraction condensing at  $-132^{\circ}$  (1.59 g.; mol. wt. found 52, calcd. 50.5) identified spectroscopically as methyl chloride and a fraction condensing at  $-78^{\circ}$  which consisted of unchanged trimethyltrifluoromethyltin (0.58 g., 8%). The solid remaining in the reaction tube was purified by vacuum sublimation and identified as dimethyltrifluoromethyltin chloride, m.p.  $46-47^{\circ}$ .

*Anal.* Calcd. for  $\text{C}_2\text{H}_4(\text{CF}_3)_2\text{SnCl}$ :  $\text{CF}_3$ , 27.3; Sn, 46.9; Cl, 14.0; equiv. wt., 253. Found:  $\text{CF}_3$ , 25.3; Cl, 13.9; Sn, 46.6; equiv. wt., 247.

In view of the slightly low result for the  $\text{CF}_3$  analysis by alkaline hydrolysis, which was reproducible and unchanged by resublimation of the sample, the solution was tested for fluoride ion after hydrolysis, but none was found. The equivalent was determined by titration with 0.1 N sodium hydroxide solution, using bromthymol blue as indicator. The infrared spectrum of dimethyltrifluoromethyltin chloride showed the absorption bands (Nujol mull): 2910(m), 2850(m), 1616(w), 1212(w), 1149(vs), 1070(vs), 790(s), 724(m). An attempt was made to estimate the boiling point of the chloride by vapor pressure measurements, but extensive decomposition occurred at  $70-80^{\circ}$ .

VANCOUVER 8, B. C., CANADA

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

## Intramolecular Carbon Isotope Effect in the Decarboxylation of Malonic Acid in Dioxane Solution

By PETER E. YANKWICH AND RICHARD M. IKEDA

RECEIVED JUNE 24, 1959

The intramolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solution was studied between 89 and  $129^{\circ}$ . Through comparison of the results with those obtained earlier for the intermolecular isotope effect in the same solvent and those obtained from studies of both isotope effects in quinoline solutions, values have been obtained for the various complexing equilibrium contributions to the over-all isotope fractionation which agree well with values reported previously and with predictions of absolute and relative magnitude made by Bigeleisen and Wolfsberg. The very high temperature dependence of the isotope effect is indicative of a temperature-independent factor in the isotopic rate constant ratio which is certainly not much greater than unity, and which appears to be somewhat less than unity on the basis of calculations with two very different models. There seems to be no obvious explanation for this deviation from theoretical expectation.

### Introduction

Recently<sup>1</sup> we reported measurements over the temperature range 40 to  $99^{\circ}$  of the intermolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solution. Comparison with earlier results obtained on quinoline solutions indicated that the structural effect, if any, of solvent complexing was small compared with the equilibrium effect; further, good correspondence was found between values for this equilibrium effect calculated on two bases: 1, comparison of the intermolecular isotope effects in quinoline<sup>2</sup> and

dioxane solutions of the free acid; and 2, comparison in terms of simpler models of the intermolecular<sup>3</sup> and intramolecular<sup>4</sup> isotope effects in the decarboxylation in quinoline solutions of the monoanion of malonic acid.

In the investigation to be reported here, the intramolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solutions was studied over the temperature interval  $89-129^{\circ}$ . Since the effect of the reaction coordinate motion is expected to be somewhat different on the observed intramolecular isotope effect than on the

(1) P. E. Yankwich and R. M. Ikeda, *THIS JOURNAL*, **81**, 5054 (1959).

(2) P. E. Yankwich and R. L. Belford, *ibid.*, **75**, 4178 (1953).

(3) P. E. Yankwich and H. S. Weber, *ibid.*, **77**, 4513 (1955).

(4) P. E. Yankwich and H. S. Weber, *ibid.*, **78**, 564 (1956).