Analysis of Products. A mixture of aliphatic acid (10 mmol), bromine (10 mmol), chlorosulfonic acid (0.5 mL), and 1,2-dichloroethane (50 mL) was heated at 85 °C for 2 h.

After unreacted bromine and 20 mL of 1,2-dichloroethane were distilled off, methanol (30 mL) was added to the mixture and the solution was refluxed for 10 h. The resulting ester of the α-bromo acid was identified and estimated by means of GLC using a Yanagimoto GCG 550 gas chromatograph equipped with a copper column packed with PEG 20 M 10% on Chromosorb WAW 60–80 mesh by employing methyl caprate as an internal standard.

After removal of methanol by distillation from the ester solution the residual mixture was washed with water, dried (Na_2SO_4), and distilled in vacuo. The isolated ester of α-bromo acid was identified by NMR and IR spectroscopies. NMR and IR spectra were measured with a 60 MHz Hitachi R-24B NMR spectrometer at 35 °C and a Perkin-Elmer Model 337 spectrophotometer, respectively.

Acknowledgments. We are grateful to Mitsubishi Chemical Industry Co. and the Toa Gosei Co. for their gift of materials and also to Mr. M. Inaishi for his helpful assistance.

Registry No.—Chlorosulfonic acid, 7790-94-5.

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$$(CH_3)_2CHCO_2H \xrightarrow{P,\ Br_2} (CH_3)_2CBrCOBr \xrightarrow{Zn} (CH_3)_2C{=}C{=}O$$
$$\xrightarrow[EDC]{Cl_2} (CH_3)_2CClCOCl \xrightarrow{CH_3OH} (CH_3)_2CClCO_2CH_3$$

Resulting methyl α-chloroisobutyrate was analyzed by GLC (12%). The analogous reaction was observed with the reaction of dimethylketene with Br_2.
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Carbanion Halogenations with Carbon Tetrahalides. α-Halo Esters

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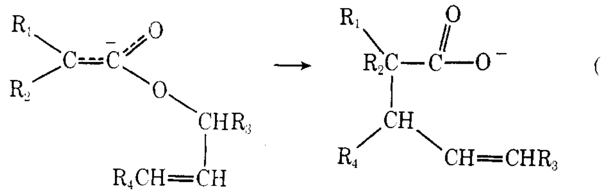
Received March 7, 1978

Carbanions generated by treatment of saturated or unsaturated esters with lithium diisopropylamide in THF at −78 °C react rapidly with carbon tetrahalides to produce α-halo esters in high yields (75–95%). Competitive bromination and chlorination of these carbanions with bromotrichloromethane are also described. These halogenations can be rationalized in terms of a radical anion–radical pair mechanism recently proposed for similar halogenations of carbanions derived from ketones or sulfones.

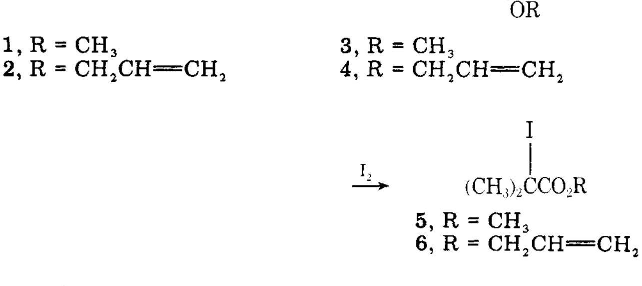
The regiospecific thermal rearrangement of enolate carbanions derived from allylic esters (eq 1), which we first described many years ago,[1] has proven to be of general synthetic usefulness. In certain cases, it is advantageous to convert the enolate anion into its O-trialkylsilyloxy derivative prior to rearrangement.[2]



(1)

During the course of a recent study relating to this symmetry-allowed [3.3] sigmatropic rearrangement, we required a quantitative method for determining the amount of carbanion formed when allylic esters of isobutyric acid were treated with 1 equiv of lithium diisopropylamide (LDA) in THF at −78 °C.

The quantitative iodination of ester carbanions with elemental iodine, which may be used with saturated or unsatu-



1, R = CH_3
2, R = $CH_2CH{=}CH_2$
3, R = CH_3
4, R = $CH_2CH{=}CH_2$
5, R = CH_3
6, R = $CH_2CH{=}CH_2$

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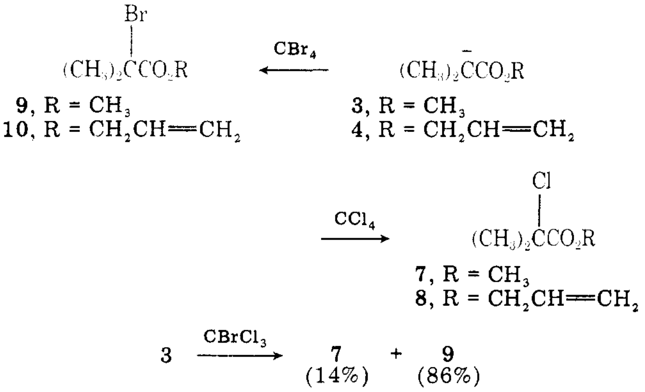
rated esters as described by Rathke et al.,[3] proved to be satisfactory in every way. In our examples, the profound change in the NMR spectra, which involves the disappearance of the methyl doublets in **1** and **2** and their replacement by a singlet in **5** and **6**, made this method very precise.

Using carbanions from saturated esters, Rathke et al.[3] also employed bromine (but not chlorine) with comparable results, but our findings are at variance with those reported with this halogen. In spite of the fact that our experience with iodination left no doubt that the transformation **1** → **3** was quantitative, treatment of **3** or **4** with exactly 1 equiv of bromine in THF produced the expected α-bromo esters contaminated by considerable amounts of the starting esters **1** or **2**.

We surmised that this strange result could be due to the reconversion of **3** into **1** (or **4** into **2**) by HBr generated from the photochemical bromination of the solvent (THF) prior to addition. In response to this proposal, a solution of bromine in carbon tetrachloride was added to **3** in THF (−78 °C). The crude product, worked up as before, contained no starting ester (**1**) but was shown (GLC and NMR) to consist of a mixture of the α-chloro and α-bromo esters **7** and **9**, respectively, with the former predominating in large excess. This result, which indicated that carbon tetrachloride is an effective chlorinating agent of ester carbanions under these conditions, has now been repeatedly demonstrated with several examples. Indeed, when the carbanions **3** or **4** are treated with carbon tetrachloride (1 equiv) at −78 °C and the mixture is allowed to warm to room temperature, the corresponding α-chloro esters (**7** or **8**) were formed in high yields (82 or 91%, respectively). Under comparable conditions, carbon tetrabromide produced the corresponding α-bromo esters (**9** or **10**, respectively). When the carbanion **3** was treated with bromotrichloromethane (1 equiv), the α-chloro and α-bromo esters (**7** and **9**) were formed in relative yields of 14 and 86%, respectively (as determined by NMR and GLC). These transformations are summarized below.



$(CH_3)_2CBrCO_2R \xleftarrow{CBr_4} (CH_3)_2\bar{C}CO_2R \xrightarrow{CCl_4} (CH_3)_2CClCO_2R$

9, R = CH_3
10, R = $CH_2CH{=}CH_2$

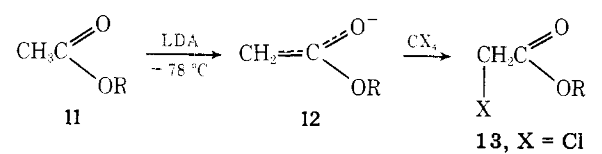
3, R = CH_3
4, R = $CH_2CH{=}CH_2$

7, R = CH_3
8, R = $CH_2CH{=}CH_2$

$$3 \xrightarrow{CBrCl_3} \underset{(14\%)}{7} + \underset{(86\%)}{9}$$

Erickson and Kornblum,[4] in a very recent study, have demonstrated that carbanions derived from primary nitroparaffins can be monohalogenated in excellent yields (82–94%) using elemental halogens. In practice, however, the metering of exactly 1 equiv of chlorine is not a simple technique.

Where applicable, we believe that the use of carbon tetrachloride has much to recommend it, especially when the carbanions undergoing chlorination contain carbon–carbon double bonds. We have now demonstrated that carbanions derived from primary esters can be selectively monohalogenated using carbon tetrahalides. Thus, when allyl acetate (**11**) was converted into its carbanion (**12**) and the latter treated with carbon tetrachloride (1 equiv) at −78 °C, allyl α-chloroacetate (**13**) was formed to the extent of 74%, and no α,α-dichloroacetate could be detected. The absence of dihalogenated product indicates that the rate of halogenation of the carbanion (**12**) is much greater than the rate of proton transfer between **12** and the monochloro ester (**13**).



11 **12** **13**, X = Cl
14, X = Br

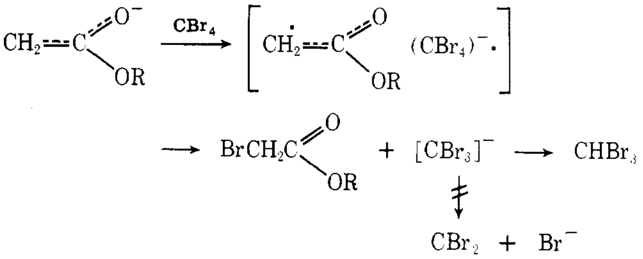
R = $CH_2CH{=}CH_2$

Similarly, **12** undergoes monobromination (ca. 75%; GLC and NMR) when treated with carbon tetrabromide. Unfortunately, in this case the pure allyl α-bromoacetate (**14**) was not easily separated by distillation, and it decomposed during attempts to separate it by column chromatography.

During the last decade, several reports have appeared describing the halogenation of carbanions with polyhaloalkanes. These include carbanions derived from diarylmethanes,[5] alkyl phosphonates,[6] ketones,[7] sulfones,[7,8] N-substituted amides and imides,[9] esters[9] (one example), and lactones[10] (one example). In other cases, carbanions derived from esters,[11] nitriles,[11] or 2-nitroalkanes[12] undergo oxidative coupling (presumably via the intermediate halogenated derivatives) to form dimeric products.

Extensive studies have been reported by Meyers et al.[7] using the system KOH (powdered)–*t*-BuOH–CCl_4, principally with ketones and sulfones. The reaction proceeds rapidly at room temperature, and the exact nature of the product(s) isolated depends on the reactivity of the first-formed halogenated ketone (or sulfone) under the conditions employed. These investigators have also studied competitive bromination vs. chlorination using bromotrichloromethane.

Our results are easily rationalized in terms of the radical anion–radical pair mechanism proposed by Meyers,[7] with the exception that the CX_3^- moiety, formed by the collapse of the radical anion–radical pair, does not decompose appreciably under the conditions which we employ to form a dihalocarbene and halide ion. For example, with all brominations of ester carbanions which we have effected with CBr_4, bromoform was always formed as a substantial product as illustrated below.



The apparent absence of dihalocarbenes in our system also explains why we were unable to detect any dihalocyclopropane derivatives in products derived from unsaturated esters.

Experimental Section

Tetrahydrofuran, carbon tetrachloride, and diisopropylamine were purified by standard methods and stored over appropriate drying agents. Carbon tetrabromide (Matheson, Coleman and Bell), bromotrichloromethane (Eastman Kodak), and *n*-BuLi (1.6 M solution in hexane) (Aldrich) were used without further purification. Allyl acetate (Matheson, Coleman and Bell) was distilled and stored over molecular sieves. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

NMR spectra were recorded on a Varian A-56/60 spectrometer, and all chemical shifts are given in ppm downfield from tetramethylsilane (δ scale). Analytical GLC analyses were recorded on a Varian 204-1B instrument fitted with flame ionization detectors using helium as a carrier gas with a flow of 40 mL/min and hydrogen with a flow rate of 40 mL/min. The column used was a 0.25 in × 10 ft stainless steel tube containing 5% QF-1 on Chromosorb W (60–80 mesh). Peaks were integrated on a Varian 477 integrator.[13]

Lithium Diisopropylamide. A 1.6 M solution of *n*-BuLi in hexane (6.875 mL, 11 mmol) was added to a solution of diisopropylamine (1.113 g, 11 mmol) in THF (2 mL) at 0 °C under argon. The mixture was stirred for 15 min at 0 °C and cooled to −78 °C before using it for the preparation of ester carbanions.

Allyl Isobutyrate (2). A solution of isobutyryl chloride (34.84 g, 327 mmol) in dry ether (30 mL) was added dropwise over a period of 1 h to a stirred solution of allyl alcohol (18.99 g, 327 mmol), pyridine (25.87 g, 327 mmol), and dry ether (50 mL) at 0 °C. The mixture was stirred for an additional 30 min and left in a refrigerator overnight. It was poured onto ice, the layers separated, and the aqueous layer was extracted with ether (2 × 30 mL). The combined organic layers were washed with cold HCl (40 mL, 2 M), saturated sodium bicarbonate solution (40 mL), and water (2 × 40 mL) and dried ($MgSO_4$). Evaporation of the solvent and distillation gave 31.43 g (75%) of **2:** bp 133–134 °C (lit.[14] bp 133 °C); NMR (CCl_4) δ 1.15 (d, 6 H), 2.52 (septet, 1 H), 4.52 (d, 2 H), 5.18 (m, 1 H), 5.38 (m, 1 H), 5.95 (m, 1 H).

Allyl α-Iodoisobutyrate. Allyl isobutyrate (1.28 g, 10 mmol) was added dropwise and with stirring to a solution of lithium diisopropylamide (11 mmol) in THF at −78 °C under argon. The reaction mixture was stirred for 30 min, and a solution of iodine (2.54 g, 10 mmol) in THF (20 mL) was added dropwise over a period of 10 min at −78 °C. The brown color of iodine disappeared immediately on addition, and a light yellow precipitate formed. The mixture was allowed to warm to room temperature and then was stirred for 1 h, during which time the color changed to dark brown. Cold HCl (20 mL, 1 M) was added, the layers separated, and the organic layer was washed with saturated sodium bicarbonate (20 mL) and water (50 mL) and dried ($MgSO_4$). The solvent was removed on a rotary evaporator to give a dark brown liquid (2.52 g, 99%) whose NMR spectrum was indistinguishable from the pure product. Distillation, with a considerable mechanical loss, gave 1.21 g (47.6%) of pure allyl α-iododoisobutyrate as a colorless liquid which becomes colored on standing: bp 28 °C (0.01 mm); NMR ($CDCl_3$) δ 2.09 (s, 6 H), 4.61 (d, 2 H), 5.24 (m, 1 H), 5.48 (m, 1 H), 5.98 (m, 1 H).

Anal. Calcd for $C_7H_{11}IO_2$: C, 33.09; H, 4.36; I, 49.95. Found: C, 32.79; H, 4.49; I, 48.30.

Methyl α-Iodoisobutyrate. Using a similar technique, methyl isobutyrate (2.04 g, 20 mmol) was converted into its anion with LDA and halogenated with iodine (5.08 g, 20 mmol) to give 4.32 g (95%) of a dark brown product whose NMR spectrum was indistinguishable from the distilled product. Distillation gave 4.02 g (88.1%) of the expected ester as a light brown liquid: bp 55–57 °C (13.4 mm) [lit.[15] bp 64 °C (12 mm)]; NMR (CCl_4) δ 2.07 (s, 6 H), 3.76 (s, 3 H).

α-Halogenation of Methyl Isobutyrate with Bromine in Carbon Tetrachloride. A. Methyl isobutyrate (2.04 g, 20 mmol) was added dropwise to a stirred solution of lithium diisopropylamide (22 mmol) in THF at −78 °C under argon. The mixture was stirred for 20 min, and a solution of bromine (3.52 g, 22 mmol) in carbon tetrachloride (10 mL, 15.94 g, 103.5 mmol) was added dropwise with stirring over a period of 10 min at −78 °C. The bromine color disappeared instantaneously. The mixture was allowed to warm to room temperature, a light yellow precipitate appeared, and stirring was continued for 1 h. Cold HCl (20 mL, 1 M) was added, the layers separated, and the carbon tetrachloride layer was washed successively with saturated sodium bicarbonate (20 mL) and water (40 mL). It was dried ($MgSO_4$) and the excess carbon tetrachloride removed on a rotary evaporator at low temperature. The brown liquid residue (2.62 g) was analyzed by GLC and consisted of a mixture of α-halo esters (95.2%) plus nonester impurities (4.8%). The ratio of methyl α-chloroisobutyrate (**7**) to methyl α-bromoisobutyrate (**9**) was 87.2:12.8.

B. The above experiment was repeated using bromine (3.2 g, 20 mmol) and carbon tetrachloride (3.08 g, 20 mmol). The brown product (3.05 g) was analyzed by GLC, which showed that it consisted of **7** and **9** in a ratio of 58.35:41.65. Only 1.5% of the crude product represented nonester impurities.

Methyl α-Chloroisobutyrate (7). Methyl isobutyrate (2.04 g, 20 mmol) was added to a stirred solution of lithium diisopropylamide (22 mmol) in THF at −78 °C under argon. The mixture was stirred for 20 min, and carbon tetrachloride (3.38 g, 22 mmol) in THF (2 mL) was added dropwise over a period of 5 min at −78 °C. The mixture was allowed to warm to room temperature and was stirred for an additional 1 h, during which time a light yellow precipitate formed. Cold HCl (20 mL, 1 M) was added, and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with saturated bicarbonate (20 mL) and water (30 mL) and dried ($MgSO_4$). Removal of the solvent on a rotary evaporator at low temperature gave 2.24 g (83%) of the α-chloro ester (98% of **7** by GLC). Distillation, with a large mechanical loss, gave 1.01 g (37%) of pure **7:** bp 35–36 °C (16 mm) (lit.[16] bp 133–135 °C); NMR (CCl_4) δ 1.75 (s, 6 H), 3.76 (s, 3 H).

Allyl α-Chloroisobutyrate (8). In a manner similar to that described for **7**, allyl isobutyrate (2.56 g, 20 mmol) was converted to its anion with LDA and treated with carbon tetrachloride (3.38 g, 22 mmol). The crude product (3.1 g; 95% pure by GLC) was distilled with a considerable mechanical loss to give 1.52 g (46.9%) of pure **8:** bp 49–51 °C (13.5 mm); NMR (CCl_4) δ 1.75 (s, 6 H), 4.62 (d, 2 H), 5.22 (m, 1 H), 5.47 (m, 1 H), 5.97 (m, 1 H).

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82; Cl, 21.80. Found: C, 51.60; H, 6.76; Cl, 22.07.

Methyl α-Bromoisobutyrate (9). Methyl isobutyrate (1.02 g, 10 mmol) was converted to its anion as described above and treated with carbon tetrabromide (3.32 g, 10 mmol) dissolved in THF (16 mL). The crude product (1.89 g), aside from an absorption for $CHBr_3$, had an NMR spectrum identical with pure **9.** Distillation gave 1.43 g (79.4%) of pure **9:** bp 40–41 °C (16 mm) [lit.[17] bp 52.2 °C (21 mm)]; NMR (CCl_4) δ 1.90 (s, 6 H), 3.76 (s, 3 H).

Allyl α-Bromoisobutyrate (10). In a manner similar to that described above, allyl isobutyrate (1.28 g, 10 mmol) was converted to its anion and treated with carbon tetrabromide (3.32 g, 10 mmol) dissolved in THF (16 mL). The crude product (2.1 g; 95% pure by NMR) was distilled to give 1.60 g (77.3%) of pure **10:** bp 50–51 °C (12 mm); NMR (CCl_4) δ 1.92 (s, 6 H), 4.66 (d, 2 H), 5.29 (m, 1 H), 5.52 (m, 1 H), 6.01 (m, 1 H).[18]

Although this compound has been prepared[19] from α-bromoisobutyryl bromide and allyl alcohol, its physical properties have not been reported.

α-Halogenation of Methyl Isobutyrate with Bromotrichloromethane. In the usual manner, methyl isobutyrate (1.02 g, 10 mmol) was converted to its anion at −78 °C under argon and treated with bromotrichloromethane (2.18 g, 11 mmol). The crude product (1.68 g), isolated as described above, was analyzed by GLC and consisted of methyl α-chloroisobutyrate (**7**) and methyl α-bromoisobutyrate (**9**) in a ratio of 14.26:85.74, respectively. A 9% amount of the crude product represented other impurities. Within experimental error, the NMR data were in accord with those obtained by GLC.

Allyl α-Chloroacetate (13). As described above, allyl acetate (2.0 g, 20 mmol) was converted into its anion with LDA (22 mmol) at −78 °C under argon and treated with carbon tetrachloride (3.38 g, 22 mmol). The crude product (2.01 g) was analyzed by GLC and shown to contain 98% of **13.** Distillation, with a considerable mechanical loss, gave 1.32 g (49%) of allyl chloroacetate (**13**): bp 42–43 °C (13 mm) [lit.[20] bp 162–163.5 °C (766 mm)]; NMR (CCl_4) δ 4.03 (s, 2 H), 4.58 (d, 2 H), 5.19 (m, 1 H), 5.37 (m, 1 H), 5.91 (m, 1 H).

Registry No.—**1**, 547-63-7; **2**, 15727-77-2; **3**, 67194-51-8; **4**, 67194-52-9; **5**, 67194-53-0; **6**, 67194-54-1; **7**, 22421-97-2; **8**, 67194-55-2; **9**, 23426-63-3; **10**, 40630-82-8; **11**, 591-87-7; **12**, 67194-56-3; **13**, 2916-14-5; isobutyryl chloride, 79-30-1; allyl alcohol, 107-18-6; carbon tetrachloride, 56-23-5; carbon tetrabromide, 558-13-4; bromotrichloromethane, 75-62-7.

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