extracted with ether, the dried extract was treated with ethereal HCl (100 ml), and ether was removed. The residue was treated with 15% aqueous NaOH and extracted with ether. The dried extract was concentrated and analyzed by GLC (20% Carbowax 20M, 150 °C, 30 ml/min He). Pyridine (98%, t_R 1.5 min) and 3-bromopyridine (2%, t_R 4.87 min) were detected.

2. 3-*n*-Butylpyridine. Pyridine (0.02 mol) was added at −100 °C to a solution of 3-lithiopyridine (0.02 mol), prepared as described above. The solution was allowed to warm to 32 °C, then processed essentially as described in the IIIB1 aliquot. Analysis (GLC, as shown above) showed 3-*n*-butylpyridine (t_R 2.25 min) and pyridine (t_R 1.5 min). Distillation of the crude product gave 1.62 g (60%) of pure 3-*n*-butylpyridine [bp 46–48 °C (1.5 Torr), lit.[17] bp 82–83 °C (10 Torr); NMR ($CDCl_3$) δ 0.9 (t, 3), 1.1–1.7 (m, 4), 2.5 (t, 2), 7.1–7.4 (m, 2), 8.4 (m, 2)].

3. 3-Pyridyldiphenylcarbinol. 3-Lithiopyridine (**13**, 0.022 mol) was treated at −100 °C with benzophenone (0.022 mol). The mixture was allowed to warm to 32 °C and THF was removed (rotary evaporator). Dilute H_2SO_4 (10 ml of 10%) was added and unreacted benzophenone (0.009 mol) was removed by filtration. The acid solution was made basic (KOH) and extracted with chloroform. The product (3.44 g) obtained from the dried chloroform was recrystallized from petroleum ether (bp 30–60 °C) to give 2.82 g (54% yield) of 3-pyridyldiphenylcarbinol (mp 111–114 °C, lit. 115 °C[18]).

4. Reaction of 3-Lithiopyridine (13) with 2-Bromopyridine at −100 °C. A mixture of **13** (0.02 mol), prepared as described above, and 2-bromopyridine (0.02 mol) was stirred at −100 °C for 40 min. The entire mixture was added to 10% HCl (200 ml) and processed essentially as described in IIIA aliquot. Analysis (GLC as in IIIA, 140 °C) showed the ratio of 2-bromopyridine (t_R 9.75 min) to 3-bromopyridine (t_R 6.00 min) to be 96/4. The yield of recovered 2-bromopyridine, determined by adding *o*-bromoanisole (t_R 10.75 min) and making corrections for the relative response factors of each, was 73%.

When the mixture of **13** and **10** was allowed to warm to 32 °C a black tar was obtained which was not processed.

C. Reactions of 2-Bromopyridine (10). 1. 2-Lithiopyridine (14) was prepared and analyzed as described for **13** in section IIIB. Analysis of aliquots (20 min, GLC, 130 °C) showed pyridine (t_R 2.12 min) and no unchanged 2-bromopyridine (t_R 5.62 min).

2. 2-Benzoylpyridine. A solution of **14** (0.0344 mol) was treated after 20 min with methyl benzoate (0.04 mol); the mixture was allowed to warm to room temperature, THF was removed (rotary evaporator), and the residue was partitioned between ether and water. The ether layer was distilled to give 4.46 g (71% yield) of 2-benzoylpyridine [bp 125–135 °C (0.3 Torr); picrate mp 129–130 °C, lit.[19] 124–127 °C].

3. Reaction of 2-lithiopyridine with 3-bromopyridine at −100 °C was carried out as in section IIIB4 (GLC, 6 ft × 0.25 in. 20% Carbowax 20M on Chromosorb W 30/60, 30 ml/min He). Aliquots taken at 20 and 60 min gave identical ratios of 2-bromopyridine (t_R 8.12 min) to 3-bromopyridine (t_R 4.37 min) of 79/21. Some condensation occurred as evidenced by the dark color of the crude product.

Registry No.—**1a**, 615-59-8; **1b**, 3460-18-2; **1c**, 60573-63-9; **1d**, 610-71-9; **1e**, 3638-73-1; **4**, 60573-64-0; **5**, 60573-65-1; **6**, 60573-66-2; **7**, 60573-67-3; **8**, 624-28-2; **10**, 109-04-6; **12**, 626-55-1; **13**, 60573-68-4; **14**, 17624-36-1; *n*-butyllithium, 109-72-8; 2-bromo-5-butyltoluene, 60573-69-5; 5-bromo-2-butyltoluene, 60573-70-8; benzophenone, 119-61-9; cyclohexanone, 108-94-1; 2-bromo-*N,N*-dimethylaniline, 698-00-0; 3-bromo-*N,N*-dimethylaniline, 16518-62-0; pyridine, 110-86-1; 3-*n*-butylpyridine, 539-32-2; methyl benzoate, 93-58-3; 2-benzoylpyridine, 91-02-1.

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(5) Anions of atoms attached directly to the aromatic ring are known to inhibit halogen–metal exchange: (a) for CH^- cf. W. E. Parham and L. D. Jones, *J. Org. Chem.*, **41**, 1187 (1976); (b) for phenoxides, halogen exchange is generally conducted at 32 °C, cf. H. Gilman, C. E. Arntzen, and F. E. Webb, *J. Org. Chem.*, **10**, 374 (1945); (c) *p*-bromoaniline undergoes exchange at reflux in ether, cf. H. Gilman and G. C. Gainer, *J. Am. Chem. Soc.*, **69**, 1946 (1947).
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(8) The aromatic proton (δ 8.2) ortho to both bromine and carbonyl in methyl *m*-bromobenzoate is deshielded to a greater extent than those adjacent to only bromine or carbonyl. There is no absorption at δ 8.2 in methyl *o*-bromobenzoate.
(9) A slow reaction occurs at −100 °C, expectedly more rapid at higher temperatures to give tarry condensation products.
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Reactions of Lithio Derivatives of Carboxylic Acids. 1. 3-Methyl-2-butenoic Acids[1]

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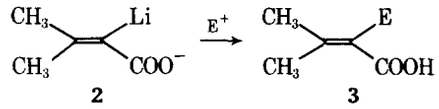
Halogen–metal exchange with 2-bromo-3-methyl-2-butenoic acid at −100 °C leads to a stable lithiovinyl intermediate which reacts with a variety of electrophiles to afford 2-alkylated derivatives in good yields. Reaction of 3-methyl-2-butenoic acid with *n*- and *tert*-butyllithium followed by protonation or alkylation is discussed.

Since 2-bromo-2-alkenoic acids are readily available from 2-alkenoic acids,[3] then possible reaction as shown in Scheme I (**1** → **2** → **3**) appeared attractive as a general method for synthesis of 2-substituted 2-alkenoic acids. The previous observation that salts of bromobenzoic acids[4a] and bromoarylalkanoic acids[4b] form stable lithium intermediates by halogen–metal exchange provided a firm precedent for this sequence; however, it remained to be established[3,5] whether proton removal from allylic (γ) positions (i.e., **1** → **6**) or lithium interchange (i.e., **2** ⇄ **4**) would impose a synthetically unacceptable limitation on such a sequence.

2-Bromo-3-methyl-2-butenoic acid (**1**)[3] was chosen as a model and halogen–metal exchange was conducted in tetrahydrofuran at −100 °C with *n*-butyllithium. The progress of

Table I. Reaction of Lithio Derivative 2 with Electrophiles (E^+)

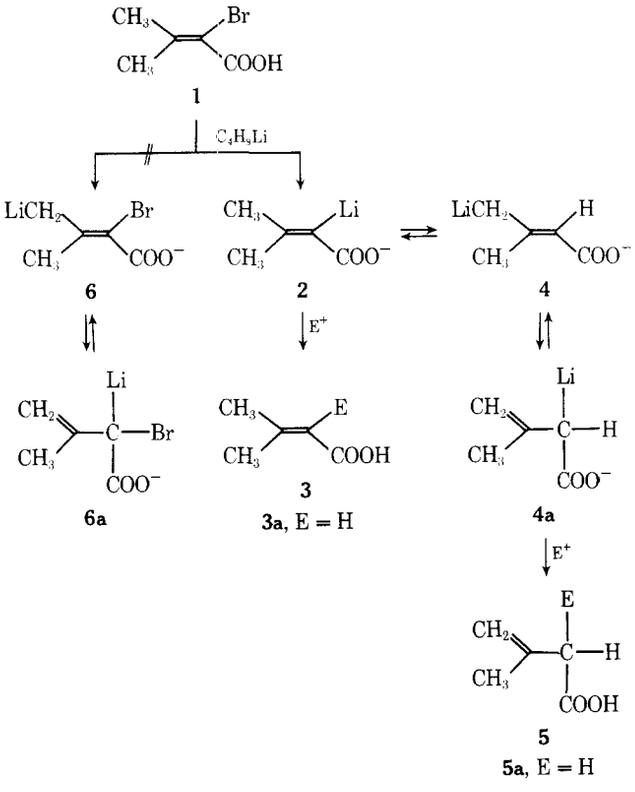


2 3

Electrophile	Product(s)	E	Isolated yield, %	Mp, °C	Ir (acid $\nu_{C=O}$), cm^{-1}
H_2O	3a, 5a	H	98[a]	45–55[b]	1695[c,d]
CH_3OD[e]	3b	D[f]	94[g]	64–66	1695[h]
CH_3CH_2I	3c	CH_2CH_3	79	42.5–44[i]	1686[c]
	3d		30	156.5–157.5 dec	1701[j]
$C_6H_5COC_6H_5$	3e	$C(OH)(C_6H_5)_2$	64	143–144 dec	1692[j]
C_6H_5NCO	3f	$CONHC_6H_5$	58	181.5–182.5 dec	1686[j]
CH_3SSCH_3	3g	SCH_3	59	80–81	1689[h]
$C_6H_5SSC_6H_5$	3h	SC_6H_5	61	85–86	1684[h]

[a] See note 5. [b] Lit.[6] mp of 3a is 69.5–70° C. [c] Melt. [d] Agrees with ref[7] value for 3a. [e] 99% D. [f] Ca. 95% D by NMR. Anal. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.18; H, 7.99. [g] See note 8. [h] CCl_4 solution. [i] See Experimental Section. [j] KBr pellet.

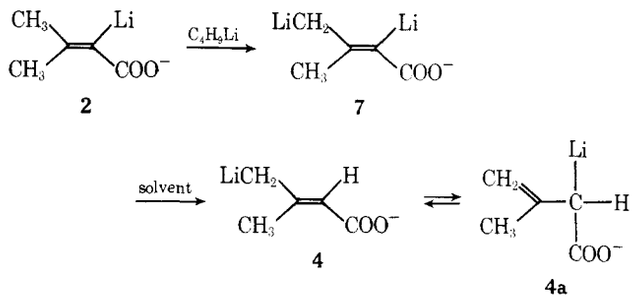
Scheme I



reaction was followed by examining aliquots which were quenched with water (identical results were obtained with saturated aqueous NH_4Cl or 10% aqueous HCl) and analyzed (by NMR) for unchanged **1** and reduced acids **3a** and/or **5a**. Halogen–metal exchange was rapid and complete when the first aliquot was taken 15 min after addition of 2 molar equiv of *n*-butyllithium per mole of acid (at −100 °C). When less than 2 molar equiv of *n*-butyllithium was employed (i.e., 1.8), the product acids (isolated in 98% yield) were 3-methyl-2-butenoic acid (**3a**) and unchanged **1** (ratio **3a**/**1** = 75/25). When a 10% excess (i.e., 2.2 equiv) of *n*-butyllithium was employed, the product (isolated in 98% yield) contained mostly **3a** but was contaminated with about 10% **5a**. We were unable to eliminate either small quantities of **1** or **5a** and therefore conducted subsequent experiments with 2.0 equiv of *n*-butyllithium (ratio **3a**/**5a** = 95/5). We found no evidence (other than unchanged **1**) for the formation of **6** or **6a**. The lithio derivative **2** reacted with various electrophiles (E^+) to give fair to good yields of 2-substituted 3-methyl 2-butenoic acids (**3**). The results are summarized in Table I.

The exact process by which **5** is formed remains obscure since there are a number of logical routes for its formation.[3] The fact that the ratio **3a**/**5a** does not change significantly when a solution of the lithio derivative **2** is aged at −100 or −70 °C (6 h) shows that **4** is not formed by direct conversion of **2** to **4**, or, alternatively, if there is an equilibrium between **2** and **4** it is reached rapidly and greatly favors **2**. The absence of isomer **5a**, unless a slight excess of *n*-butyllithium is employed, implicates the trianion **7** (Scheme II) as an intermediate.

Scheme II



Rapid decay of the trianion, precedented by observation with *o*- and *p*-bromophenylacetic acids,[4b] defines one reasonable path for the formation of **5a**. It is not implied that metalation occurs preferentially at either the cis or trans methyl group; however, only trans-alkylated product (**9**, Scheme III) was isolated.

A study of the reaction of **1** with *tert*-butyllithium was made in an attempt to obviate formation of *n*-butyl bromide formed during halogen–metal exchange with *n*-butyllithium. This would be advantageous since it would permit alkylation of **2** with less reactive electrophiles than were employed above. Reaction of **1** with 3 molar equiv of *tert*-butyllithium, however, led to appreciable isomerization to **5a** (ratio **3a**/**5a** = 68/32) after 15 min at −100 °C. These results are not surprising in retrospect since *tert*-butyllithium is a stronger base and possibly more prone to lead to trilithio derivatives. Alternatively, **2** could compete with *tert*-butyllithium in dehydrohalogenation of the *tert*-butyl bromide formed, thereby leading to **3a** and, subsequently, to **5a**.

Katzenellenbogen[10] prepared the lithio derivative **4** (**4a**)

Table II. Lithiation of 3-Methyl-2-butenoic Acid at −100 °C

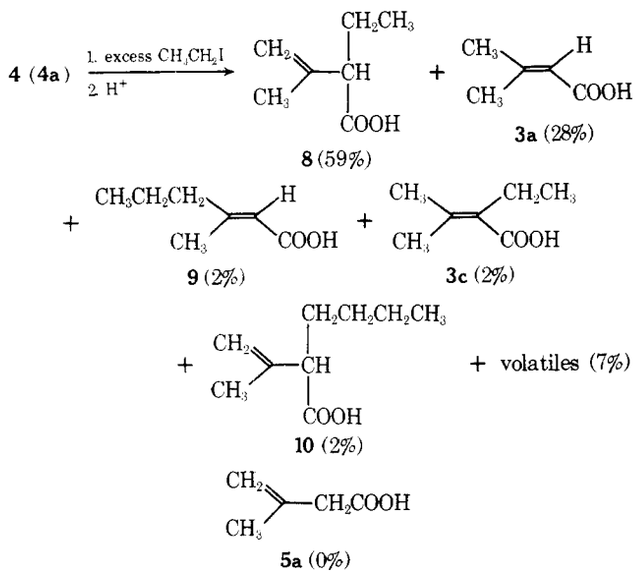
Reaction time, h	Equiv C_4H_9Li	% **5a** in product[a]	
		n-C_4H_9Li	t-C_4H_9Li
0.25	2.0	51	65
1.0	2.0	53	75
2.0	2.0	59	75
2.25	3.0[b]	63	75
3.0	3.0	71	79
4.0	3.0	73	80

[a] After quenching in water; remainder was **3a**. [b] After adding an additional 1 equiv of butyllithium in the same experiment.

by reaction of **3a** with lithium diisopropylamide (LDA) and showed that it undergoes alkylation to give almost exclusively derivatives of **5**. While one would expect **4** (**4a**) to protonate in a fashion analogous to alkylation, neither this result nor the direct formation of **4** (**4a**) by use of alkyllithium has been reported. The results shown in Table II show that after 1 h the product ratio is not highly time dependent and is not influenced significantly by additional alkyllithium. While these results suggest that **4** (**4a**) is protonated to **3a**/**5a** up to the ratio 20/80, results described below for alkylation of the reaction mixture do not support such a conclusion.

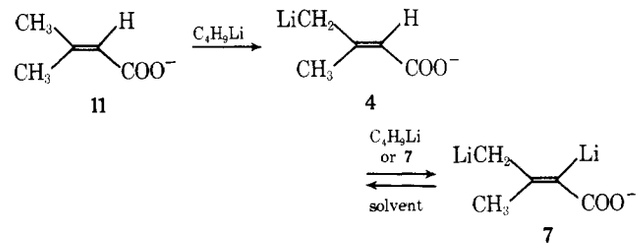
Alkylation of the lithio derivative mixture with excess ethyl iodide added 15 min after addition of 2.0 equiv of n-butyllithium (at −100 °C, see Experimental Section) afforded a mixture of acids which was analyzed by GLC[11] and NMR. The results are shown in Scheme III.

Scheme III



Compounds **3a**, **3c**, **8**, **9**, and **10** were isolated (GLC) and characterized by NMR and combustion analysis. Formation of alkylated products **8** and **10** (evidently some n-butyl iodide was formed under the reaction conditions) corroborates Katzenellenbogen's results; only 2% of γ-alkylated product **9** was obtained. The fact that no **5a** was formed (NMR analysis of the GLC fraction containing **3a**) confirms that alkylation of **4** (**4a**) was complete. Therefore it is unreasonable to conclude that the high recovery of **3a** was a consequence of incomplete alkylation of **4** (**4a**) and it is strongly suggested that the unmetalated carboxylate salt of **3a** (i.e., **11**, Scheme IV) was present in the reaction mixture and, analogously, in the reaction products from the protonation experiments. Incomplete metalation of **11** suggests that metalation of **4** (**4a**) to **7** is competitive with initial metalation of **11** (Scheme IV).

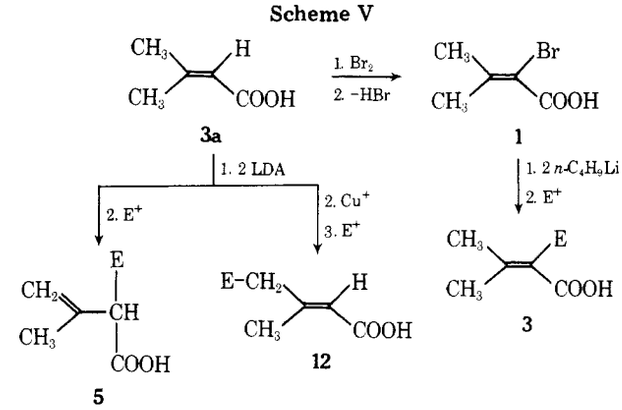
Scheme IV



Failure to isolate dialkylated products is consistent with rapid anion decay of the trianion **7** to **4** (**4a**). Such decay of trianions is precedented.[4b]

In summary, halogen–metal exchange in acids of type **1** affords reasonable yields of derived acids of type **3**. This work complements that of Katzenellenbogen and co-workers;[10] consequently it is now possible (Scheme V) to alkylate acids

Scheme V



of type **3a** either at the 2 position, as described herein to give acids of type **3**, at the 4 position through the copper dienolate[10] to give acids of type **12**, or at the 2 position to give isomerized acids of type **5**.

Experimental Section

All reactions involving organolithium reagents were conducted under an atmosphere of nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride or n-butyllithium[12] prior to use. Reaction temperatures of −100 °C were achieved with a diethyl ether–liquid nitrogen bath. All organic residues were dried with anhydrous magnesium sulfate. NMR data were obtained from a JEOL Model JNM-MH-100 100-MHz spectrometer using 1–2% tetramethylsilane as an internal standard; IR data were obtained from a Perkin-Elmer Model 137 spectrometer; GLC analyses were performed with a Varian Model 910 gas chromatograph (thermal conductivity detector). Microanalyses were performed by MHW Laboratories, Garden City, Mich. All melting points were determined on a Mel-Temp heating block apparatus and are corrected.

General Procedure for Halogen–Metal Exchange. 2-Bromo-3-methyl-2-butenoic acid[3] (**1**, 4.48 g, 0.025 mol, mp 88–90 °C, lit.[3] mp 91.5 °C) and tetrahydrofuran (200 ml) were introduced, under nitrogen, into a 250-ml three-neck flask equipped with a low-temperature thermometer, pressure-equalizing addition funnel, nitrogen inlet, and mechanical stirrer. The reaction mixture was cooled to −100 °C and n-butyllithium (20 ml, 0.050 mol, 2.5 M solution in hexane) was added at a rate such that the temperature did not exceed −90 °C. Fifteen minutes after the addition of n-butyllithium was complete (examination of aliquots showed that formation of **2** was complete at this time), a solution of the electrophile in tetrahydrofuran (25 ml) was added at a rate such that the temperature did not exceed −90 °C. After an additional 15 min at about −90 °C, the reaction mixture was allowed to warm to room temperature (3 h) and poured into water (50 ml). Solvents were removed (rotary evaporation) and the mixture was extracted with two 30-ml portions of ether (to remove neutral material). The aqueous solution was cooled (0 °C) and made acidic (concentrated hydrochloric acid), and the crude product was isolated (solids by filtration; oils by extraction with five 30-ml portions of ether). The crude products were purified by either recrystallization or preparative GLC.[11]

A. 2-Ethyl-3-methyl-2-butenoic acid (3c) was obtained from **2** and ethyl iodide (19.5 g, 0.125 mol). Concentration of the acid-containing organic extracts afforded 2.60 g of colorless, semicrystalline material (mp 25–40 °C). Spectral analysis (NMR) of this material showed it to be a mixture of **3c** (97%, 79% yield) and 2-ethyl-3-methyl-3-butenoic acid (**8**, 3%, 2% yield). This material was purified by preparative GLC to afford pure **3c** as white needles [mp 42.5–44 °C, lit.[13] mp 49.5 °C; NMR ($CDCl_3$) δ 1.02 (t, 3, CH_2CH_3), 1.84 (s, 3, CH_3), 2.08 (s, 3, CH_3), 2.34 (quartet, 2, CH_2CH_3), 12.0 (s, 1, OH)]. Attempts to purify the mixture of crude acids by either recrystallization or sublimation were of limited success.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.60; H, 9.23.

B. 2-(1-Hydroxycyclohexyl)-3-methyl-2-butenoic acid (3d) was obtained from **2** and cyclohexanone (2.45 g, 0.025 mol). The precipitate (3.83 g, mp 106–113 °C dec) obtained upon acidification of the alkaline solution was recrystallized from chloroform to afford 1.48 g (30% yield) of nearly pure **3d** as white needles, mp 135–137.5 °C dec. Two further recrystallizations afforded an analytically pure sample: mp 156.5–157.5 °C dec; NMR (acetone-d_6) δ 1.70 (s, 3, CH_3), 1.98 (s, 3, CH_3), 1.0–2.2 (m, 10, ring CH_2's), 4.2 (broad s, 2, OH's).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.69; H, 9.13.

C. 2-(Hydroxydiphenylmethyl)-3-methyl-2-butenoic acid (3e) was obtained from **2** and benzophenone (9.11 g, 0.050 mol). The precipitated crude product (6.03 g) was recrystallized from a 1:1 mixture of methylene chloride and hexane to afford 4.52 g (64% yield) of nearly pure **3e** [in two crops, mp 131–134 °C dec (sealed tube) and 121–126 °C dec (sealed tube)]. A second recrystallization afforded an analytically pure sample as finely divided white crystals: mp 143–144 °C dec (sealed tube); NMR (acetone-d_6) δ 1.46 (s, 3, CH_3), 1.88 (s, 3, CH_3), 5.30 (broad s, 2, OH's), 7.1–7.8 (m, 10, ArH).

Anal. Calcd for $C_{18}H_{18}O_3$: 76.57; H, 6.42. Found: C, 76.59; H, 6.44.

D. 2-(*N*-Phenylcarbamoyl)-3-methyl-2-butenoic acid (3f) was obtained from **2** and phenyl isocyanate (3.28 g, 0.0275 mol). The precipitated crude product (3.94 g) was recrystallized from water to afford 3.15 g (58% yield) of nearly pure **3f**, mp 174.5–176.5 °C dec (sealed tube). A second recrystallization afforded an analytically pure sample as yellowish needles: mp 181.5–182.5 °C dec (sealed tube); NMR (CF_3CO_2H) δ 2.22 (s, 3, CH_3), 2.40 (s, 3, CH_3), 7.42 (m, 5, ArH), 9.1 (broad s, 1, NH).

Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.76; H, 5.94; N, 6.26.

E. 2-Methylthio-3-methyl-2-butenoic acid (3g) was obtained from **2** and dimethyl disulfide (2.60 g, 0.0275 mol). Concentration of the acid-containing organic extracts afforded 3.45 g of crude product (mp 52–70 °C); this was recrystallized from hexane to afford 2.04 g (59% yield) of analytically pure **3g** [mp 80–81 °C; NMR ($CDCl_3$) δ 2.12 (s, 3, CH_3), 2.14 (s, 3, CH_3), 2.26 (s, 3, CH_3), 12.0 (s, 1, OH)] as finely divided white crystals.

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89; S, 21.93. Found: C, 49.14; H, 6.84; S, 21.76.

F. 2-Phenylthio-3-methyl-2-butenoic acid (3h) was obtained from **2** and diphenyl disulfide (6.00 g, 0.0275 mol). Concentration of the acid-containing organic extracts afforded 4.46 g of crude product (mp 58–71 °C); this was recrystallized from hexane to afford 2.73 g (61% yield) of analytically pure **3h** [mp 85–86 °C; NMR ($CDCl_3$) δ 2.16 (s, 3, CH_3), 2.20 (s, 3, CH_3), 7.16 (s, 5, ArH), 12.0 (s, 1, OH)] as finely divided white crystals.

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.39. Found: C, 63.60; H, 5.71; S, 15.12.

Reaction of 3-Methyl-2-butenoic Acid (3a) with Butyllithium. A. Isomerization to 5a. Reaction of **3a** (2.50 g, 0.025 mol, mp 65–67 °C, lit.[6] mp 69.5–70 °C) in dry tetrahydrofuran (200 ml) with butyllithium [initially 0.050 mol of *n*- (2.5 M solution in hexane) or *tert*- (1.6 M solution in pentane) butyllithium] was carried out analogously to the general procedure described for **1**. Aliquots were quenched in water, made acidic, extracted with ether, concentrated, and analyzed by NMR. After 2 h of reaction in the presence of 2.0 equiv of butyllithium at −100 °C, a third molar equivalent of butyllithium was added to the reaction mixture at −100 °C and additional aliquots were examined (see Table II in discussion). The product acids **3a** and **5a** could not be separated by preparative GLC.

B. Reaction of the Lithio Derivative of 3a with Ethyl Iodide. Reaction of **3a** (2.50 g, 0.025 mol) in dry tetrahydrofuran (200 ml) with *n*-butyllithium (0.050 mol) and ethyl iodide (19.5 g, 0.125 mol) was carried out analogously to the procedure described in A for the preparation of **3c**. Concentration of the acid-containing organic extracts afforded 2.47 g of yellowish liquid. Analysis of this material by preparative GLC afforded analytically pure samples of the component acids [listed in order of their elution; the composition of a volatile fraction (7%) was not determined].

3-Methyl-2-butenoic acid (3a) (28%, 28% yield) was obtained as white needles [mp and mmp 65–67 °C, lit.[6] 69.5–70 °C; NMR ($CDCl_3$) δ 2.00 (s, 3, CH_3), 2.24 (s, 3, CH_3), 5.86 (m, 1, vinyl H), 12.0 (s, 1, OH)].

2-Ethyl-3-methyl-3-butenoic acid (8) (59%, 59% yield) was obtained as a colorless liquid [NMR ($CDCl_3$) δ 0.92 (t, 3, CH_2CH_3), 1.80 (s, 3, CH_3), 1.81 (m, 2, CH_2CH_3), 3.00 (t, 1, methine H), 5.00 (m, 2, *gem*-CH_2), 12.0 (s, 1, OH)].

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.75; H, 9.61.

2-Ethyl-3-methyl-2-butenoic acid (3c) (2%, 2% yield) was obtained as white needles (mp 42.5–44 °C, lit.[13] mp 49.5 °C; NMR data are reported above).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.41; H, 9.33.

(*E*)-3-Methyl-2-hexenoic acid (9) (2%, 2% yield) was obtained as white needles [mp 33.5–36 °C; NMR ($CDCl_3$) δ 0.94 (t, 3, $CH_2CH_2CH_3$) 1.56 (sextet, 2, $CH_2CH_2CH_3$), 2.19 (t, 2, $CH_2CH_2CH_3$), 2.20 (s, 3, CH_3), 5.82 (m, 1, vinyl H), 12.0 (s, 1, OH)].

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.57; H, 9.41.

2-*n*-Butyl-3-methyl-3-butenoic acid (10) (2%, 1% yield) was obtained as a colorless liquid [NMR ($CDCl_3$) δ 0.92 (t, 3, $CH_2CH_2CH_2CH_3$), 1.2–1.5 (m, 4, $CH_2CH_2CH_2CH_3$), 1.5–2.0 (m, 2, $CH_2CH_2CH_2CH_3$), 1.84 (s, 3, CH_3), 3.10 (t, 1, methine H), 5.02 (m, 2, *gem*-CH_2), 12.0 (s, 1, OH)].

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.30; H, 10.59.

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Registry No.—**1**, 1578-14-9; **2**, 60582-20-9; **3a**, 541-47-9; **3b**, 60582-29-8; **3c**, 60582-21-0; **3d**, 60582-22-1; **3e**, 60582-23-2; **3f**, 60582-24-3; **3g**, 60582-25-4; **3h**, 60582-26-5; **5a**, 1617-31-8; **8**, 60582-27-6; **9**, 27960-21-0; **10**, 60582-28-7; *n*-butyllithium, 109-72-8; *tert*-butyllithium, 594-19-4; ethyl iodide, 75-03-6; cyclohexanone, 108-94-1; benzophenone, 119-61-9; phenyl isocyanate, 103-71-9; dimethyl disulfide, 624-92-0; diphenyl disulfide, 882-33-7.

References and Notes

(1) Supported by the U.S. Army Research Office through Grant DAHCO4 74 GD128.
(2) This article is dedicated with deep appreciation to the late Professor Parham, deceased May 21, 1976.
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