data of the constituents are as follows.

2,6-Dimethyl-2-cyclohexenone (8): t_R = 4.4 min; IR (neat) 1670 cm^{-1} (C=O); ^1H NMR (100 MHz) δ 1.02 (d, 3, J = 7 Hz, CH_3), 1.20–2.55 (m, 5, CH_2, CH), 1.79 (complex s, 3, CH_3), 6.70 (m, 1, HC=C).

2,6-Dimethyl-2-methoxycyclohexanone 1c (n = 3, R^1 = R^2 = Me): t_R = 4.4 min; IR (neat) 2812, 1700 (C=O), 1170, 1080, 1015, 994 cm^{-1}; ^1H NMR (100 MHz) δ 1.17 (d, 3, J = 7 Hz, CH_3), 1.10–2.40 (m, 7, CH_2, CH), 1.21 (s, 3, CH_3), 3.14 (s, 3, OCH_3).

Methyl 2-methyl-5-oxopentanoate (9): t_R = 10.4 min; IR (neat) 2720, 1730, (COO), 1720 cm^{-1} (C=O); ^1H NMR (100 MHz) δ 1.20 (d, 3, J = 7.5 Hz, CH_3), 1.72–2.10 (m, 2, CH_2), 2.40–2.65 (m, 3, CH_2, CH), 3.68 (s, 3, OCH_3), 9.76 (t, 1, J = 1 Hz, CHO).

Dimethyl 2-methylglutarate (10): t_R = 17 min; IR (neat) 1745 cm^{-1} (COO); ^1H NMR (100 MHz) δ 1.19 (d, 3, J = 7 Hz, CH_3), 1.70–2.64 (m, 5, CH_2, CH), 3.68 (s, 6, OCH_3).

Methyl (3*R*)-6-Hydroxy-3,7-dimethyl-7-octenoate (14). To a methanolic solution of **12** (60 mg, 0.3 mmol) and 0.4 M $CeCl_3 \cdot 7H_2O$ (0.75 mL, 0.3 mmol) was added $NaBH_4$ (11.4 mg, 0.3 mmol) at 0 °C. The mixture was stirred for 5 min, quenched with cold aqueous 10% AcOH, and extracted with AcOEt–benzene (1:1). The extract was worked up in the usual manner to give 59.4 mg (99%) of **14**: bp 95–97 °C (2 mm); $[\alpha]_D^{10}$ +8.8° (c 1.6); IR (neat) 3440 (OH), 3070, 1735 (COO), 1640 (C=C), 1199, 1151, 1088, 1000, 892 cm^{-1}; ^1H NMR (60 MHz) δ 0.95 (d, 3, J = 6 Hz, CH_3), 1.10–2.43 (m, 8, CH_2, CH, OH), 1.71 (br s, 3, CH_3), 3.68 (s, 3, OCH_3), 4.05 (t, 1, J = 6 Hz, CHO), 4.85–4.93 (m, 2, H_2C=C); ^{13}C NMR δ 17.4, 17.5 (q, C-7 Me), 19.7 (q, C-3 Me), 30.3, 30.4 (d, C-3), 32.2 (t), 32.5 (t), 41.5 (t, C-2), 51.4 (q, OMe), 75.6, 75.9 (d, C-6), 110.9, 111.1 (t, C-8), 147.5, 147.6 (s, C-7), 173.7 (s, C-1). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.92; H, 10.29.

Methyl (3*R*)-6-Chloro-3,7-dimethyl-7-octenoate (15) and Methyl (3*R*)-8-Chloro-3,7-dimethyl-6-octenoate (16). To a solution of **14** (95 mg, 0.48 mmol) and Et_3N (220 mg, 1.92 mmol) in DMF (3 mL) was added MsCl (97 mg, 0.96 mmol) at 0 °C. The mixture was stirred for 8 h at 45–50 °C, poured into cold aqueous $NaHCO_3$, and extracted with AcOEt–benzene (1:1). The extract was worked up in the usual manner and the crude product was chromatographed (SiO_2, hexane-AcOEt 10:1) to give 91 mg (88%) of a 42:58 mixture of **15** and **16**: bp 117–119 °C (16 mm); $[\alpha]_D^{17}$ +11.1° (c 0.97); IR (neat) 3075, 1735 (COO), 1640 (C=C), 1284, 1198, 1170, 1085, 1006, 904 cm^{-1}; ^1H NMR (60 MHz) δ 0.95 (d, 3, J = 6 Hz, CH_3), 1.10–2.40 (m, CH_2, CH), 1.72, 1.79 (br s, 3, CH_3), 3.63 (s, 3, OCH_3), 3.99 (s, CH_2Cl), 4.32 (t, J = 7 Hz, CHCl), 4.85, 4.96 (m, H_2C=C), 5.46 (t, J = 7 Hz, HC=C). Anal. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76. Found: C, 60.75; H, 8.75.

Methyl (3*R*,5*E*)-3,7-Dimethyl-5,7-octadienoate (17). A solution of **15** and **16** (30 mg, 0.14 mmol) in DBU (43 mg, 0.28 mmol) was heated for 30 min at 100 °C. The mixture was extracted with ether–benzene (2:1), and the extract was washed with cold aqueous 5% HCl and brine, dried (Na_2SO_4), and concentrated to give 21 mg (84%) of **17** after chromatography (SiO_2; hexane–ether, 10:1): bp 104–106 °C (16 mm); $[\alpha]_D^{17}$ +19.8° (c 0.83); IR (neat) 3055, 3010, 1735 (COO), 1605 (C=C), 1245, 1198, 1150, 1012, 962, 880 cm^{-1}; ^1H NMR (100 MHz) δ 0.96 (d, 3, J = 6 Hz, CH_3), 1.83 (t, 3, J = 1 Hz, CH_3), 1.60–2.50 (m, 5, CH_2, CH), 3.64 (s, 3, OCH_3), 4.88 (br s, 2, H_2C=C), 5.61 (dt, 1, J = 15, 7 Hz, HC=C), 6.15 (d, 1, J = 15 Hz, HC=C). ^{13}C NMR δ 18.7 (q, C-7 Me), 19.8 (q, C-3 Me), 30.7 (d, C-3), 40.0 (t, C-4), 41.0 (t, C-2), 51.4 (q, OMe), 114.8 (t, C-8), 128.1 (d, C-5), 134.9 (d, C-6), 142.0 (s, C-7), 173.6 (s, C-1). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.56; H, 10.15.

(3*R*,5*E*)-3,7-Dimethylocta-5,7-dien-1-ol (18). To a suspension of $LiAlH_4$ (21 mg, 0.55 mmol) in THF (4 mL) was added a solution of **17** (50 mg, 0.27 mmol) in THF (1 mL). The mixture was stirred for 1 h at room temperature, quenched with AcOEt and cold aqueous $NaHCO_3$, and worked up in the usual manner to give 40 mg (96%) of **18**: bp 131–133 °C (16 mm) [lit.[18] bp 100 °C (4 mm)]; $[\alpha]_D^{17}$ +6.7° (c 0.9); IR (neat) 3300 (OH), 3065, 3010, 1372, 1050, 960, 880 cm^{-1}; ^1H NMR (60 MHz) δ 0.92 (d, 3, J = 6 Hz, CH_3), 1.10–2.35 (m, 6, CH_2, CH, OH), 1.84 (br s, 3, CH_3), 3.67 (t, 2, J = 6.5 Hz, CH_2O), 4.85 (br s, 2, H_2C=C), 5.60 (dt, 1, J = 15, 7.5 Hz, HC=C), 6.16 (d, 1, J = 15 Hz, HC=C).

(+)-Rose Oxide (19). A solution of **18** (50 mg, 0.32 mmol) in 30% H_2SO_4 (1 mL) was stirred for 4 h at 17–18 °C. The mixture was worked up in the usual manner followed by chromatography (SiO_2; hexane–ether, 10:1) to give 48 mg (96%) of **19**: bp 68–70 °C (15 mm) [lit.[18] bp 72–73 °C (15 mm)]; $[\alpha]_D^{29}$ +39° (c 0.9) (lit.[14] $[\alpha]_D^{20}$ +38.1°).

Registry No. 1a (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 74285-12-4; **1a** (n = 3; R^1 = Me; R^2 = H), 16963-12-5; **1a** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 79664-86-1; **1a** (n = 3; R^1 = R^2 = Me), 56829-74-4; **1a** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-87-2; **1a** (n = 9; R^1 = R^2 = H), 26307-31-3; **1b** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 79664-88-3; **1b** (n = 3; R^1 = R^2 = Me), 66633-36-1; **1b** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-89-4; **1b** (n = 9; R^1 = Me; R^2 = H), 74285-14-6; **1b** (n = 9; R^1 = R^2 = H), 19025-38-8; **1c** (n = 3; R^1 = R^2 = Me), 79664-90-7; **2** (n = 3; R^1 = Me; R^2 = H), 2046-21-1; **2** (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 6093-95-4; **2** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 79664-91-8; **2** (n = 3; R^1 = R^2 = Me), 2570-90-3; **2** (n = 4; R^1 = n-C_5H_{11};R^2 = H), 54527-02-5; **2** (n = 9; R^1 = Me; R^2 = H), 74285-16-8; **2** (n = 9; R^1 = R^2 = H), 2009-59-8; **3** (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 24851-93-2; **3** (n = 3; R^1 = R^2 = Me), 6203-89-0; **3** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-92-9; **3** (n = 9; R^1 = Me; R^2 = H), 79664-93-0; **3** (n = 9; R^1 = H; R^2 = Me), 79664-94-1; **3** (n = 3; R^1 = Me; R^2 = H), 1196-73-2; **3** (n = 3; R^1 = n-C_5H_{11}; R^2 = H), 73746-55-1; **4** (n = 2; R^1 = n-C_5H_{11}; R^2 = H), 4819-67-4; **4** (n = 3; R^1 = R^2 = Me), 2816-57-1; **4** (n = 4; R^1 = n-C_5H_{11}; R^2 = H), 79664-95-2; **4** (n = 9; R^1 = Me; R^2 = H), 16837-94-8; **5**, 53771-94-1; **6a**, 57426-90-1; **6b**, 74219-28-6; **7**, 63175-00-8; **8**, 40790-56-5; **9**, 79664-96-3; **10**, 14035-94-0; *cis*-**11**, 35736-68-6; *trans*-**11**, 35736-67-5; **12**, 79664-97-4; **13**, 79664-98-5; **14**, 73374-55-7; **15**, 79664-99-6; **16**, 79665-00-2; **17**, 79665-01-3; **18**, 79731-38-7; *cis*-**19**, 4610-11-1; *trans*-**19**, 5258-10-6; 2-acetyl-2-pentylcyclopentanone, 79665-02-4; 3,4-epoxy-*p*-menth-3-yl acetate, 79665-03-5; *dl*-10-camphorsulfonic acid, 5872-08-2; methyl 12,12-dimethoxydodecanoate, 1931-67-5.

Metallo Aldimines. 3. Coupling of Lithium Aldimines with Aryl, Vinyl, and Acetylenic Halides[1]

Maurice J. Marks and Harry M. Walborsky*

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

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tert-Butyllithium aldimine, an acyl anion equivalent derived from 1,1,3,3-tetramethylbutyl isocyanide (TMBI) and *tert*-butyllithium, couples with aryl, vinyl, and acetylenic halides to give the corresponding ketimine which upon hydrolysis affords the corresponding ketones. These coupling reactions appear to result from halogen–metal exchange followed by addition–elimination to give the observed products.

Metallo aldimines, resulting from the addition of organometallic reagents to isocyanides (eq 1), have been shown to be very versatile acyl anion equivalents.[2] They were treated with primary alkyl halides, carbon dioxide,

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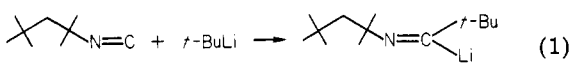

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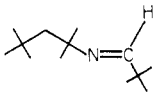
ethyl chloroformate, trimethysilyl chloride, nonenolizable aldehydes, propylene oxide, and water to give, after hydrolysis, the corresponding carbonyl compound[3] (Scheme I). Although only alkyllithiums react with TMBI in high yield to give lithium aldimine 1, they rank with lithiated 1,3-dithianes[4] and vinyl ethers[5] as versatile masked acyl anions.

Results and Discussion

In reactions unique among acyl anion equivalents,[5b] lithium aldimine 1 couples with aryl, vinyl, and acetylenic halides which upon hydrolysis yield the corresponding ketones (Scheme II).

As can be seen from Table I, aryl halides such as bromo- or iodobenzene, but not chlorobenzene, react to give high yields of imine. Moderate yields are obtained with *o*-bromotoluene and *o*-bromoanisole. The major byproduct in these reactions is aldimine 4. The lithium aldimines 1 are sufficiently basic intermediates to abstract protons from the added electrophile.[6]



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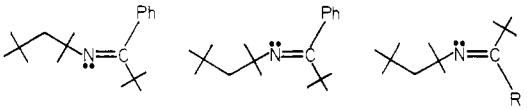
Due to severe steric interaction of a *t*-Bu group and the 1,1,3,3-tetramethylbutyl (TMB) group one would predict the 2 would exist largely if not entirely in the *Z* configuration rather than the *E* configuration. The ^{1}H NMR spectrum is consistent with this prediction.

Imines of this type in which the nitrogen is alkyl rather than aryl substituted are known to be configurationally stable,[8] and therefore the stereochemistry can be established on the basis of the shielding effect of the phenyl group on carbon.[7] The geminal dimethyl protons of TMB in nonaryl substituted imines **6** appear at about 1.2 ppm,

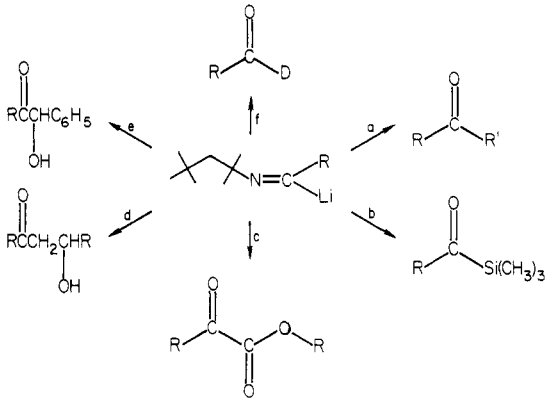


(*Z*)-5 (*E*)-5 6

but in aryl substituted imines like 4 they appear at 0.8–0.9 ppm (see Experimental Section). This upfield shift and the appearance of no other geminal dimethyl proton resonances establishes the configuration of 5 as *Z*. In a similar manner the other aryl imines prepared have also been assigned the *Z* configuration.

Vinyl halides also couple with 1 (Scheme II) although the reaction is not stereospecific. Use of either (*E*)-1-iodo-1-hexene or (*Z*)-1-bromo-1-hexene in THF leads to

Scheme I[a]



[a] (a) CH_3I, CH_3CH_2I; (b) $(CH_3)_3SiCl$; (c) CO_2, $ClCO_2Et$; (d) propylene oxide; (e) C_6H_5CHO; (f) D_2O. Each reaction was followed by acid hydrolysis.

Scheme II

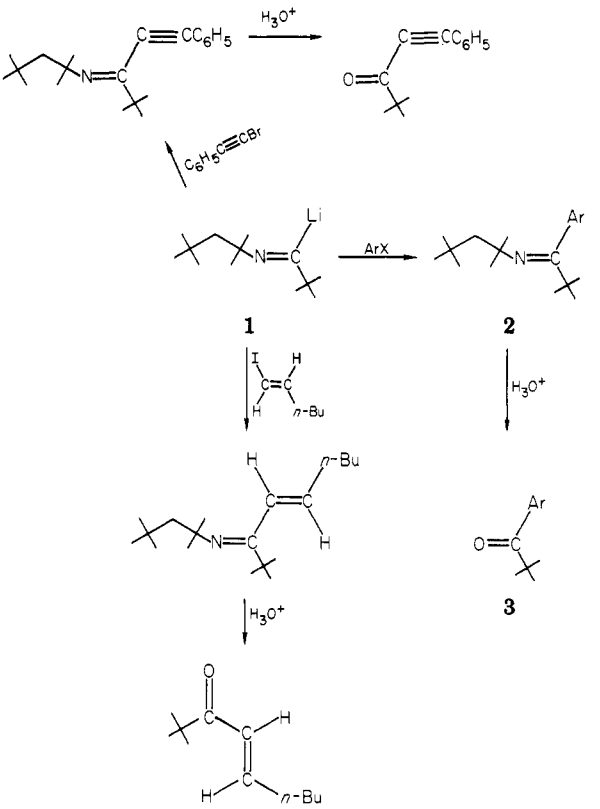


Table I. Reaction of Lithium Aldimines with Aryl Halides

				% yield[a]	
no.	R	Ar	X	2	3
a	*t*-Bu	phenyl	I, Br	95	95
b	*n*-Bu	phenyl	I	*b*	27
c	*t*-Bu	*o*-tolyl	Br	52	52
d	*t*-Bu	*o*-anisyl	Br	64	26
e	*t*-Bu	1-naphthyl	Br	52	50

[a] Percent yield of isolated product, overall yield reported for 3. [b] Imine not isolated.

the formation of the same α,β-unsaturated imine having the *E* configuration. Changing the solvent from THF to hexane resulted in proton abstraction to yield 4 rather than coupling.

Last in this series of coupling reactions is the reaction of 1 with an acetylenic halide, 1-bromo-2-phenylacetylene,

(1) Support of this work by the National Science Foundation is gratefully acknowledged.

(2) Walborsky, H. M.; Niznik, G. E. *J. Org. Chem.* **1972**, *37*, 187.

(3) Niznik, G. E.; Morrison, W. H.; Walborsky, H. M. *J. Org. Chem.* **1974**, *39*, 600.

(4) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231.

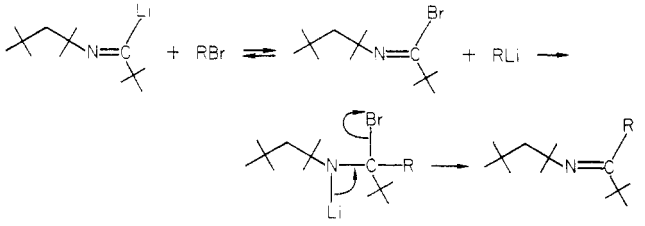
(5) (a) Baldwin, J. E.; Hofle, G.; Lever, O. W., Jr. *J. Chem. Soc., Chem. Commun.* **1975**, 519. (b) For a review of acyl anion equivalents, see: Lever, O. W. *Tetrahedron* **1976**, *32*, 1943.

(6) Coates, G. E.; Wade, M. "Organometallic Compounds, The Main Group Elements"; Methuen: London, 1967; Vol. 1.

(7) Bonnett, G. "The Chemistry of the Carbon–Nitrogen Double Bond"; Patai, S., Ed.; Interscience: New York, 1970; pp 373–383.

(8) Bjorgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B. *J. Chem. Soc., Perkin Trans. 2* **1974**, 757.

Scheme III



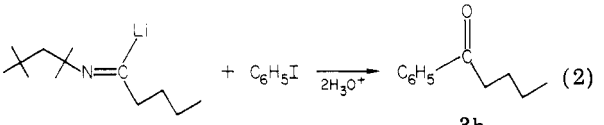
to give an α,β-acetylenic imine in 58% yield. The corresponding ketone can be obtained by oxalic acid hydrolysis in 48% overall yield.

The coupling reaction of **1** with aryl, vinyl, and acetylenic halides would not be expected to occur by a direct S_N2 displacement of the halide. Instead, these coupling reactions can proceed by halogen–metal exchange to form an imidoyl halide and an organolithium reagent followed by an addition of organolithium to the imidoyl halide with subsequent elimination of lithium halide.[9b] (Scheme III). The first step in this sequence, halogen–metal exchange, is a reversible reaction and proceeds to form an organolithium reagent whose stability is at least comparable with that of the lithium aldimine. The relative stability is determined by the hybridization of the charge-bearing carbon;[9a] the greater the percent s character, the more stable is the organolithium. The stability of the sp^2-hybridized organolithium formed from aryl and vinyl halides is roughly equal to that of the lithium aldimine; also, an sp^2-hybridized carbanion and both lithium reagents will exist in equilibrium. The sp organolithium from acetylenic halides is much more stable than the lithium aldimine, and the equilibrium will be almost entirely toward the lithium acetylide. Regardless of the position of the equilibrium, the reaction is driven forward by the irreversible addition of the lithium reagent to the imidoyl halide and subsequent elimination of lithium halide to give the coupled product. Imidoyl chlorides are known to couple with organometallic reagents.[10]

This scheme predicts that an organic halide that would form an organolithium which is significantly less stable than the lithium aldimine will not undergo halogen–metal exchange. Thus, 1-bromo-2,2-diphenyl-1-methylcyclopropane, which would form an sp^2-hybridized[23] cyclopropyllithium,[9a] does not couple.

Halogen–metal exchange is a well-known method of preparing organolithium reagents from organic halides.[11] Coupling of the reagents does not occur to an appreciable extent in diethyl ether or less polar solvents. But the coupling reaction is markedly promoted by THF, producing cleanly cross-coupled products in the reaction of aryl halides with alkyllithiums.[12] Moreover, halogen–metal exchange occurs readily with bromides and iodides but not readily with chlorides.[13] This is consistent with our observation that **1** undergoes reaction with bromo- and iodobenzene but not chlorobenzene. Halogen–metal exchange also accounts for the isomerization observed in the reaction with (*Z*)-vinyl bromide since the (*Z*)-vinyllithium formed would be expected to isomerize to the more thermodynamically stable *E* isomer in THF.[14]

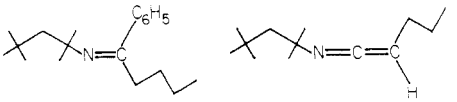
These new coupling reactions are useful only to prepare *tert*-butyl ketones. The reaction of *n*-butyllithium aldimine (**7**) with iodobenzene (eq 2) gives only a 27% yield of 1-phenyl-1-pentanone.



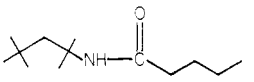
(2)

7 3b

An inseparable mixture of imine products are formed in this reaction. On the basis of spectroscopic evidence, the aryl imine **8** and ketenimine **9** are formed in roughly



8 9



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equal amounts. Column chromatography of this mixture on silica gel yielded the ketone **3b** and the amide **10** by hydrolysis of **8** and **9**. Ketenimine **9** was readily detected in the mixture of the appearance of an intense band at 2050 cm^{-1} in the infrared spectrum, corresponding to the ketenimine stretching frequency, and by the appearance of a multiplet at 3.4 ppm in the ^1H NMR spectrum for the vinyl proton.[15]

The halogen–metal exchange mechanism explains the formation of ketenimine **8**. The first step of halogen–metal exchange gives an imidoyl iodide and phenyllithium. But competing with coupling of these intermediates is elimination of HI from the imidoyl iodide to give benzene and ketenimine **9**. This side reaction makes these new coupling reactions useful only for the preparation of *tert*-butyl ketones.

Experimental Section

Melting points were determined with a Mel-Temp apparatus by using open capillaries. Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer; band positions are reported in wave numbers (cm^{-1}). Ultraviolet spectra were recorded with a Cary 14 spectrophotometer; band positions are reported in nanometers. Nuclear magnetic resonance spectra were obtained on a JEOL C-60-HL Model spectrometer. Microanalyses were performed by Beller Laboratories.

Quantitative GLC analyses were performed on a Hewlett-Packard Model 571A gas chromatograph (thermal-conductivity detector with helium as the carrier gas) with packed columns (15% Lexan on acid-washed 60/80 Chromosorb, P, 10 ft × $^1/_8$ in.). Thin-layer chromatography (TLC) was performed by using glass plates coated with Merck silica gel 60 PF-254 + 366. Column chromatography was carried out by using silica gel 60 F_{254} (70–230 mesh, E. Merck No. 10757).

All bulk solvents were distilled before use. Tetrahydrofuran (THF) and diethyl ether were dried by being refluxed and distilled from sodium benzophenone dianion. Hexane and cyclohexane were dried by being refluxed and distilled from phorphorous pentoxide.

1,1,3,3-Tetramethylbutyl isocyanide (TMBI) was prepared according to the procedure of Niznik and Walborsky.[16] *tert*-

(9) (a) Applequist, D. E.; O'Brien, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 743. (b) Although we do not subscribe to this view, a reviewer has suggested that the coupled product may arise directly from radical pairs generated during the halogen–metal exchange reaction (see: Ward, H. R.; Lawler, R. G.; Cooper, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 746).

(10) Ulrich, H. "The Chemistry of Imidoyl Halides"; Plenum Press: New York, 1968.

(11) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; pp 4–8.

(12) Merrill, R. E.; Negishi, E. *J. Org. Chem.* **1974**, *39*, 3452.

(13) Gilman, H.; Jones, R. G. *Org. React.* **1951**, *6*, 339.

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(15) Riley, J. L.; Krow, G. R. *J. Org. Chem.* **1972**, *37*, 2364.

Butyllithium and *n*-butyllithium, purchased from Aldrich Chemical Co., were titrated before use.[17]

All glassware was flame dried under nitrogen before use. Syringes, needles, and pipets were dried in a 110 °C oven before use.

2-[(2,2-Dimethylpropylidene)amino]-2,4,4-trimethylpentane (4). The *tert*-butyl aldimine **6** (R = H) was prepared in quantitative yield by addition of *tert*-butyllithium to TMBI followed by hydrolysis according to the reported procedure:[4] bp 73–75 °C (10 mm); IR (neat) 1676, 1486, 1370, 1230, 790 cm^{-1}; ^1H NMR (CCl_4) δ 0.91 (s, 9), 1.00 (s, 9), 1.53 (s, 2), 7.33 (s, 1); calcd for $C_{13}H_{27}N$-*t*-Bu *m/e* 140.1439, found *m/e* 140.1445 (deviation 0.6 mmu).

2-[(2,2-Dimethyl-1-phenylpropylidene)amino]-2,4,4-trimethylpentane (2a). To 4.4 mL (3.5 g, 25 mmol) of 1,1,3,3-tetramethylbutyl isocyanide (TMBI) in 50 mL of THF was added at −40 °C, under a nitrogen atmosphere, 20 mL (25 mmol) of a 1.3 M solution of *tert*-butyllithium in pentane. After 30 min, 2.8 mL (15.1 g, 25 mmol) of iodobenzene in 15 mL of THF was added. After another 30 min, 20 mL of water was added, and the mixture was extracted with diethyl ether. The organic layer was separated, washed with saturated sodium chloride, dried (Na_2SO_4 and $MgSO_4$), and evaporated (standard workup) to give 6.4 g (94%) of distilled ketimine: bp 120–125 °C (2.25 mm); IR (neat) 1640 (m), 1600 (w), 1480, 1370, 705 cm^{-1}; ^1H NMR (CCl_4) δ 0.91 (s, 6), 1.0 (s, 9), 1.1 (s, 9), 1.5 (s, 2), 7.2–7.8 (m, 5); UV (*c* 10^{-2} M, ethanol) λ 269 nm (ϵ 430).

Anal. Calcd for $C_{19}H_{31}N$: C, 83.45; H, 11.43; N, 5.12. Found: C, 83.48; H, 11.52; N, 5.06.

Similar results were obtained with bromobenzene and the *tert*-butyllithium aldimines.

2,2-Dimethyl-1-phenyl-1-propanone (3a). Steam distillation of 1.3 g of **3a** from 300 mL of a 2 M oxalic acid solution gave 0.7 g (86% overall) of the ketone: bp 97–100 (16 mm) [lit.[18] bp 97.98 °C (16 mm)]; IR (neat) 1680, 1600 (w), 1200, 720 cm^{-1}; ^1H NMR (CCl_4) δ 1.3 (s, 9), 7.2–7.8 (m, 5).

1-Phenyl-1-pentanone (3b) and *N*-(1,1,3,3-Tetramethylbutyl)-*n*-pentanamide (10). To 3.52 mL (2.78 g, 20 mmol) of TMBI in 50 mL of hexane under a nitrogen atmosphere at room temperature was added 15 mL (22.5 mmol) of a 1.5 M *n*-butyllithium in hexane. After 30 min, the solution was cooled at −70 °C, and 2.24 mL (4.08 g, 20 mmol) of iodobenzene in 15 mL of hexane was added. After 2.5 h, a standard workup gave a clear liquid which was distilled from 2 M oxalic acid to give 1.6 g (27%) of the distilled ketone: bp 92–94 °C (20 mm); IR (neat) 1720 cm^{-1}; 2,4-DNP, mp 164–166 °C (lit.[19] mp 166 °C). If instead of oxalic acid hydrolysis the mixture was chromatographed on a silica gel column with hexane–ether for elution, ketone **3b** and amide **10** [bp 109–112 °C (4 mm) [lit.[23] bp 108–110 °C (4 mm)] IR 3430, 1680 cm^{-1}] were isolated.

2-[[2,2-Dimethyl-1-(2-methylphenyl)propylidene]amine]-2,4,4-trimethylpentane (2c). To a solution of 5 mmol of the *tert*-butyllithium aldimine **1** in 20 mL of THF at −70 °C was added 0.60 mL (0.86 g, 5 mmol) of *o*-bromotoluene. After 1 h of gradual warming of the mixture, a standard workup gave 0.76 g (52%) of the distilled ketimine: bp 90–93 °C (0.05 mm); IR (neat) 1640, 1480, 1470, 1370, 1230, 750, 740 cm^{-1}; ^1H NMR (CCl_4) δ 0.87 (s, 6), 1.00 (s, 9), 1.06 (s, 9), 1.56 (br s, 2), 2.15 (s, 3), 6.74–7.15 (m, 4).

Anal. Calcd for $C_{20}H_{34}N$: C, 83.27; H, 11.88; N, 4.85. Found: C, 83.36; H, 11.68, N, 4.91.

2,2,2′-Trimethylpropiophenone (3c). Steam distillation of 1.5 g of **3c** from 200 mL of a 2 M oxalic acid solution gave 0.9 g (52% overall) of the ketone: bp 100–105 °C (3 mm) [Lit.[20] bp 100 °C (5 mm)]; IR (neat) 1690, 1600 (w), 1200, 720, 700 cm^{-1}; ^1H NMR (CCl_4) δ 1.3 (s, 9), 2.15 (s, 3), 6.74–7.15 (m, 4).

2-[[2,2-Dimethyl-1-(2-methoxyphenyl)propylidene]amino]-2,4,4-trimethylpentane (2d). To a solution of 10 mmol of the *tert*-butyllithium aldimine **1** in 40 mL of THF at −70 °C was added 1.25 mL (1.87 g, 10 mmol) of *o*-bromoanisole. After 1 h of gradual warming of the mixture, a standard workup gave 1.93 g (64%) of the distilled ketimine: bp 99–100 °C (0.10 mm); IR (neat) 1650, 1600, 1580, 1490, 1480, 1470, 1370, 1250, 1230, 1125, 1060, 1040, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.85 (s, 6), 0.97 (s, 9), 1.00 (s, 9), 1.50, 1.53 (2 s, 2), 3.74 (s, 3), 6.56–7.77 (m, 4).

Anal. Calcd for $C_{20}H_{33}NO$: C, 78.89; H, 11.26; N, 4.60. Found: C, 78.95; H, 11.94; N, 4.69.

2,2-Dimethyl-2′-methoxypropiophenone (3d). A solution of 1.9 g of **2d** in 25 mL of THF and 10 mL of 20% sulfuric acid was refluxed for 16 h. The resulting mixture was extracted with diethyl ether; the organic layer was separated and dried ($MgSO_4$). Evaporation and distillation gave 0.5 g (26% overall) of the ketone: bp 138–140 °C (3 mm); IR (neat) 1700, 1600 (w), 1250, 760 cm^{-1}; ^1H NMR (CCl_4) δ 1.1 (s, 9), 3.6 (s, 3), 6.5–7.2 (m, 4).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.09; H, 8.59.

2-[[2,2-Dimethyl-1-(1-naphthyl)propylidene]amino]-2,4,4-trimethylpentane (2e). To a solution of 25 mL of the *tert*-butyllithium aldimine **1** in 50 mL of THF as prepared above at −70 °C was added a solution of 3.5 mL (5.2 g, 25 mmol) of 1-bromonaphthalene in 15 mL of THF. The solution was allowed to slowly warm to room temperature over a few hours. A standard workup provided 4.2 g (52%) of the distilled ketimine: bp 135–137 °C (0.1 mm); IR (neat) 1640, 1600 (w), 1480, 1370, 800, 770 cm^{-1}; ^1H NMR (CCl_4) δ 0.73 (s, 2), 0.79 (s, 2), 0.89 (s, 2), 1.00 (s, 9), 1.10 (s, 9), 6.94–7.83 (m, 7); UV (*c* 4.11×10^{-5} or 1.1×10^{-3} M, ethanol) λ 284 nm (ϵ 5818), λ 225 (68 127).

Anal. Calcd for $C_{23}H_{33}N$: C, 83.39; H, 10.28; N, 4.33. Found: C, 83.18; H, 10.14; N, 4.51.

2,2-Dimethyl-1-(1-naphthyl)-1-propanone (3e). Steam distillation of 2.0 g of **2e** from 2 M oxalic acid gave 1.0 g (77%, 40% overall) of the ketone: mp 75–76 °C (lit.[21] mp 76–77 °C); IR (neat) 1690 cm^{-1}.

(*E*)-2-[(2,2-Dimethylnon-4-en-3-ylidene)amino]-2,4,4-trimethylpentane. To a solution of 25 mmol of the *tert*-butyllithium aldimine **1** in 50 mL of THF at −70 °C was added a solution of 5.2 g (25 mmol) of (*E*)-1-iodo-1-hexene[22] in 25 mL of THF. After 2 h of gradual warming of the mixture, a standard workup gave 3.2 g (46%) of the distilled ketimine: bp 135–140 °C (10 mm); IR (neat) 1660, 1630, 1360, 1240 cm^{-1}; ^1H NMR (CCl_4) δ 0.9 (s, 9), 1.1 (s, 9), 1.2 (s, 6), 1.5 (s, 2), 1.9–2.2 (m, 2), 5.0–5.5 (m, 1), 5.9 (d, J = 17 Hz, 1).

Anal. Calcd for $C_{19}H_{37}N$: C, 81.65; H, 13.34; N, 5.01. Found: C, 81.46; H, 13.47; N, 5.11.

(*E*)-2,2-Dimethylnon-4-en-3-one. Steam distillation of 3.2 g of the above α,β-unsaturated imine from 2 M oxalic acid gave 1.6 g (83%, 38% overall) of the enone: bp 75–78 °C (12 mm); IR (neat) 1690 cm^{-1}; ^1H NMR (CCl_4) δ 0.8–1.5 (m, 16), 2.0–2.2 (m, 2), 6.3 (d, J = 16 Hz, 1), 6.6–7.0 (m, 1).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.65; H, 11.70.

2-[(4,4-Dimethyl-1-phenylpent-1-yn-3-ylidene)amino]-2,4,4-trimethylpentane. To a solution of 25 mmol of *tert*-butyllithium aldimine **1** in 50 mL of THF at −70 °C was added a solution of 4.5 g (25 mmol) of bromophenylacetylene[23] in 20 mL of THF. After 1 h of gradual warming of the mixture, a standard workup gave 4.3 g (58%) of the distilled ketimine: bp 126–131 °C (1 mm); IR (neat) 2200, 1605, 1370, 1080, 750, 680 cm^{-1}; ^1H NMR (CCl_4) δ 0.95 (s, 9), 1.2 (s, 9), 1.4 (s, 6), 1.8 (s, 2), 7.2–7.5 (m, 5).

Anal. Calcd for $C_{21}H_{31}N$: C, 84.79; H, 10.51; N. 4.70. Found: C, 84.83; H, 10.43; N, 4.80.

4,4-Dimethyl-1-phenyl-1-pentyn-3-one. Steam distillation of 4.3 g of the above ynimine from 2 M oxalic acid gave 2.2 g (81%,

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47% overall) of the distilled ynone: bp 115–118 (2 mm); IR (neat) 2200, 1660 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (s, 9), 7.2–7.8 (m, 5); [lit.[22] bp 81–82 (1.5 mm)].

Registry No. 1, 79722-70-6; **2a**, 79722-71-7; **2c**, 79722-72-8; **2d**, 79722-73-9; **2e**, 79722-74-0; **3a**, 938-16-9; **3b**, 1009-14-9; **3c**, 2041-37-4; **3d**, 22526-24-5; **3e**, 25540-73-2; **4**, 79722-75-1; **10**, 49633-73-0; 1,1,3,3-tetramethylbutyl isocyanide, 14542-93-9; *tert*-butyllithium, 594-19-4; iodobenzene, 591-50-4; *o*-bromotoluene, 95-46-5; *o*-bromoanisole, 578-57-4; 1-bromonaphthalene, 90-11-9; (*E*,*E*)-2,2-dimethylnon-4-en-3ylidne)amino]-2,4,4-trimethylpentane, 79722-76-2; (*E*)-1-iodo-1-hexene, 16644-98-7; (*E*)-2,2-dimethylnon-4-en-3-one, 79722-77-3; bromophenylacetylene, 932-87-6; 4,4-dimethyl-1-phenyl-1-pentyn-3-one, 32398-67-7.

Permanganate Ion Oxidations. 14. Kinetics and Mechanism of the Oxidation of Aliphatic Aldehydes in Acid Media[1,2]

Fillmore Freeman,*[3] Doris K. Lin, and Gregory R. Moore[3]

Departments of Chemistry, University of California, Irvine, California 92717, and California State University, Long Beach, California 90840

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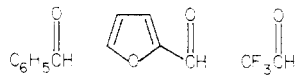
The kinetics and mechanism of the permanganate ion oxidation of 2,2-dimethylpropanal (pivalaldehyde, **4**) and other aliphatic aldehydes over the pH range 2.80–6.86 have been investigated. The oxidation, which shows general-acid catalysis, is first order in [aldehyde] and first order in [MnO_4^-]. The mechanism of the Mn(VII) oxidation of aliphatic aldehydes is compared with that proposed for Cr(VI).

Although the permanganate ion oxidations[4-8] of phenylmethanal (**1**),[9-15] 2-furaldehyde (**2**),[16,17] and trifluoroethanal (**3**)[18-20] have received some study, there are no



1 **2** **3**

systematic mechanistic studies of the oxidation of aliphatic aldehydes.[21-26] This spectrophotometric stopped-flow kinetic study was undertaken in order to determine the mechanisms of the permanganate ion oxidation of aliphatic aldehydes in acid (eq 1)[22,23] and in neutral solution (eq 2).[10,11] It is of importance to determine whether oxidation involves general or specific acid catalysis, the free carbonyl group, and/or the aldehyde hydrate.[7,10,11,16] It is also of interest to compare and contrast the mechanisms for the permanganate ion oxidation of aliphatic aldehydes with those proposed for chromium(VI) mechanisms.[27-33]

$$5RCHO + 2MnO_4^- + 6H^+ \rightarrow 5RCO_2H + 2Mn^{2+} + 3H_2O \quad (1)$$

In order to eliminate the possibility of enolization, we chose the oxidation of 2,2-dimethylpropanal (trimethylacetaldehyde, pivaldehyde, **4**) to 2,2-dimethylpropanoic acid (pivalic acid, **5**) for detailed study.

$$\underset{\mathbf{4}}{3(CH_3)_3CCHO} + 2MnO_4^- \rightarrow \underset{\mathbf{5}}{(CH_3)_3CCO_2H} + \underset{\mathbf{6}}{2(CH_3)_3CCO_2^-} + 2MnO_2 + H_2O \quad (2)$$

Experimental Section

Boiling and melting points are uncorrected and pH determinations were made on a Corning Digital 110 expanded scale pH meter. IR spectra were obtained on a Perkin-Elmer 283 spectrometer, and NMR spectra were obtained on a Varian EM-360 60-MHz spectrometer or a Bruker WH-90 FT NMR spectrometer.

Reagents. All solutions were prepared immediately before use. Deionized water was purified by distillation from potassium

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