(33), 128.1 (33), 121.1 (29), 115.1 (32).

(*E,E*)-1-Phenyl-4-(1-cyclopentenyl)-1,3-butadiene (7): mp 36–40 °C; IR ($CHCl_3$) 1596, 1491, 1447, 983 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.17 (m, 5 H), 6.85 (dd, J = 10.6, 15.5 Hz, 1 H), 6.58 (d, J = 15.1 Hz, 1 H), 6.56 (d, J = 15.5 Hz, 1 H), 6.27 (dd, J = 10.6, 15.1 Hz, 1 H), 5.80 (br, 1 H), 2.53–2.42 (br m, 4 H), 1.96 (tt, J = 7.4, 8.1 Hz, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 143.0, 137.7, 132.0, 131.8, 130,2, 129.8, 129.6, 128.7, 127.3, 126.3, 33.2, 31.3, 23.3; mass spectrum, m/e (relative intensity) 196.2 (p, 100), 181.1 (14), 168.1 (65), 167.1 (62), 153.1 (31), 147.2 (12), 141.1 (25), 128.0 (33), 115.1 (24), 105.1 (32), 103.1 (21), 92.1 (42), 91.1 (56). Anal ($C_{15}H_{16}$) C, H.

(*E*)-1-Styrylcyclohexene (10): IR (neat) 1598, 1494, 1447, 958 cm^{-1}; ^1H NMR (90 MHz, DCl_3) δ 7.48–6.96 (m, 5 H), 6.76 (d, J = 15.4 Hz, 1 H), 6.39 (d, J = 15.4 Hz, 1 H), 5.86 (br, 1 H), 2.40–1.92 (br m, 4 H), 1.88–1.50 (br, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 138.2, 136.0, 132.7, 130.8, 128.6, 126.9, 126.2, 124.8, 26.3, 24.7, 22.7; mass spectrum, m/e (relative intensity) 184.0 (p, 43), 169.1 (18), 156.0 (30), 155.1 (41), 142.1 (67), 141.1 (100), 129.0 (41), 128.0 (64), 115.1 (46), 104.0 (20), 91.1 (59).

(*E,E*)-1-Phenyl-4-(1-cyclohexenyl)-1,3-butadiene (11): mp 63–69 °C; IR ($CHCl_3$) 1596, 1490, 1445, 983 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.16 (m, 5 H), 6.84 (dd, J = 8.5, 15.5 Hz, 1 H), 6.53 (d, J = 15.5 Hz, 1 H), 6.36 (d, J = 15.3 Hz, 1 H), 6.29 (dd, J = 8.5, 15.3 Hz, 1 H), 5.83 (br, 1 H), 2.40–1.92 (br m, 4 H), 1.84–1.38 (br m, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 136.8, 136.0, 135.1, 130.0, 129.6, 128.9, 127.5, 126.1, 125.1, 124.5, 25.1, 23.6, 21.5; mass spectrum, m/e (relative intensity) 210.1 (p, 66), 182.2 (13), 168.1 (30), 167.1 (54), 165.1 (14), 154.1 (14), 128.1 (19), 119.1 (24), 115.1 (24) 91.1 (100).

(*E*)-1-Styrylcycloheptene (13): IR (neat) 1598, 1495, 1445, 958 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.50–7.00 (m, 5 H), 6.76 (d, J = 15.8 Hz, 1 H), 6.42 (d, J = 15.8 Hz, 1 H), 6.01 (t, J = 6.9 Hz, 1 H), 2.56–2.00 (br m, 4 H), 1.96–1.38 (br m, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 143.1, 138.3, 135.4, 133.5, 128.6, 126.8, 126.3, 124.8, 32.2, 28.9, 27.5, 26.9, 26.4; mass spectrum, m/e (relative intensity) 198.1 (p, 68), 185.1 (13), 155.1 (77), 142.1 (83), 141.1 (100), 129.0 (41), 128.0 (78), 117.1 (20), 115.1 (61), 105.0 (16), 91.1 (66).

(*E,E*)-1-Phenyl-4-(1-cycloheptenyl)-1,3-butadiene (14): mp 58–63 °C; IR ($CHCl_3$) 1590, 1494, 1447, 985 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.05 (m, 5 H), 6.85 (dd, J = 9.8, 15.4 Hz, 1 H), 6.51 (d, J = 15.4 Hz, 1 H), 6.42 (d, J = 15.1 Hz, 1 H), 6.33 (dd, J = 9.8, 15.1 Hz, 1 H), 5.95 (t, J = 5.9 Hz, 1 H), 2.50–2.12 (br m, 4 H), 1.98–1.40 (br m, 6 H); mass spectrum, m/e (relative intensity) 224.1 (p, 58), 181.1 (24), 169.8 (23), 167.1 (35), 154.1 (15), 141.0 (13), 133.0 (23), 128.0 (21), 115.1 (24), 105.1 (14), 91.1 (100).

(1*E*,3*E*)- and (1*E*,3*Z*)-1,3-diphenyl-1,3-pentadiene (16): 1*E*,3*E*/1*E*,3*Z* = 64/36; IR (neat) 1599, 1492, 1443, 961, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.52–7.08 (m, 10 H), 7.00 (d, J = 15.4 Hz, 1 H), 6.40 (d, J = 15.4 Hz, 1 H), 5.69 (q, J = 7.2 Hz, 1 H) [5.82 (q, J = 7.0 Hz, 1 H) for the 1*E*,3*Z*-isomer], 1.98 (d, J = 7.2 Hz, 3 H) [1.62 (d, J = 7.0 Hz, 3 H) for the 1*E*,3*Z*-isomer]; mass spectrum, m/e (relative intensity) 220.1 (p, 60), 205.2 (100), 203.1 (24), 142.1 (19), 129.0 (20), 115.1 (34), 91.1 (31) for the 1*E*,3*E*-isomer, m/e (relative intensity) 220.1 (p, 70), 205.2 (100), 204.2 (18), 142.0 (13), 129.1 (18), 115.1 (39) for the 1*E*,3*Z*-isomer.

(*E*)- and (*Z*)-1-styryl-3,4-dihydronaphthalene (18): *E*/*Z* = 92/8; IR (neat) 1600, 1496, 1488, 1449, 962 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.54–7.12 (br m, 9 H), 7.07 (d, J = 17.0 Hz, 1 H), 6.78 (d, J = 17.0 Hz, 1 H), 6.31 (t, J = 5.1 Hz, 1 H), 2.73 (t, J = 7.7 Hz, 2 H), 2.36 (dt, J = 5.1, 7.7 Hz, 2 H) for the *E*-isomer, δ 7.48–7.10 (br m, 9 H), 6.65 (d, J = 11.6 Hz, 1 H), 6.32 (d, J = 11.6 Hz, 1 H), 5.96 (t, J = 4.6 Hz, 1 H), 2.81 (t, J = 7.7 Hz, 2 H), 2.28 (dt, J = 4.6, 7.7 Hz, 2 H) for the *Z*-isomer; ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8, 136.8, 136.2, 134.4, 130.0, 128.7, 128.3, 127.7, 127.4, 127.1, 126.7, 126.4, 124.1, 28.3, 23.5 for the *E*-isomer; mass spectrum, m/e (relative intensity) 232.2 (p, 100), 229.2 (11), 217.1 (45), 215.1 (26), 202.1 (24), 189.1 (13), 152.1 (21), 141.1 (40), 128.0 (62), 115.1 (39), 91.1 (31) for the *E*-isomer, m/e (relative intensity) 232.2 (p, 100), 229.2 (8), 217.1 (40), 215.1 (30), 202.1 (25), 153.1 (18), 141.1 (26), 128.1 (38), 115.1 (30) for the *Z*-isomer.

Preparation of (*E*)-1-(1-Octenyl)cyclopentene (8) (entry 5 in Table II). A mixture of PBu_3 (1.0 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and 1 (1.5 mmol) in THF–MeOH (1:1 v/v, 8 mL) was stirred at 65 °C for 24 h. The solvent was removed in vacuo. The oily residue was washed with ether (3 × 10 mL). After removal of ether in vacuo, THF (7 mL) was added. At −40 °C *n*-BuLi (1.0 mmol) was added, the mixture was stirred at 25 °C for 2 h, and a solution of *n*-heptanal (114 mg, 1.0 mmol) in THF (1 mL) was added at −78 °C. The reaction mixture was slowly allowed to warm to 25 °C over 2 h, stirred for 24 h, diluted with ether (50 mL), washed with water (2 × 25 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography of the crude product gave 146 mg (82%) of *8*: *E*/*Z* = 93/7; IR (neat) 959 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.26 (d, J = 15.4 Hz, 1 H), 5.56 (br, 1 H), 5.53 (dt, J = 15.4, 6.7 Hz, 1 H), 2.33 (m, 4 H), 2.23–1.76 (br m, 4 H), 1.55–1.13 (br m, 8 H), 0.88 (t, J = 5.3 Hz, 3 H) for the *E*-isomer; ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 142.8, 131.3, 128.0, 127.0, 32.9, 32.7, 31.9, 31.5, 29.6, 29.0, 23.2, 22.6, 14.1 for the *E*-isomer; mass spectrum, m/e (relative intensity) 178.2 (p, 23), 135.1 (7), 121.1 (15), 107.2 (24), 94.1 (51), 91.2 (31), 79.1 (100) for the *E*-isomer, m/e (relative intensity) 178.2 (p, 22), 135.2 (5), 121.1 (26), 107.2 (24), 94.1 (35), 91.2 (30), 79.1 (100) for the *Z*-isomer.

(1*E*,3*E*)-4,8-Dimethyl-1-phenyl-1,3,7-nonatriene (15):[3c] ^1H NMR (90 MHz, $CDCl_3$) δ 7.52–7.11 (m, 5 H), 7.02 (dd, J = 15.4, 11.0 Hz, 1 H), 6.44 (d, J = 15.4 Hz, 1 H), 6.00 (d, J = 11.0 Hz, 1 H), 5.12 (br, 1 H), 2.13 (m, 4 H), 1.85 (s, 3 H), 1.69 (s, 3 H), 1.62 (s, 3 H).

Acknowledgment. We are indebted to Professor J. Tsuji, Tokyo Institute of Technology, for helpful discussions.

Registry No. **1**, 2562-42-7; **2**, 109432-80-6; **3**, 109432-82-8; (*E*)-**4**, 109432-85-1; (*Z*)-**4**, 109432-86-2; (*E*)-**5**, 109432-87-3; (*E*)-**6**, 109432-88-4; (*E,E*)-**7**, 109432-89-5; (*E*)-**8**, 109432-83-9; (*Z*)-**8**, 109432-84-0; **9**, 5330-61-0; (*E*)-**10**, 68826-53-9; (*E,E*)-**11**, 109432-90-8; (*E*)-**13**, 109432-91-9; (*E,E*)-**14**, 109432-92-0; (*E,E*)-**15**, 53598-04-2; (*Z,E*)-**15**, 53163-68-1; (*E,E*)-**16**, 109432-93-1; (*E,Z*)-**16**, 69366-38-7; **17**, 104489-04-5; **12**, 52315-51-2; (*E*)-**18**, 109432-94-2; (*Z*)-**18**, 109432-95-3; $Pd(PPh_3)_4$, 14221-01-3; PPh_3, 603-35-0; PBu_3, 998-40-3; PhCHO, 100-52-7; $Me(CH_2)_5CHO$, 124-13-0; *p*-ClC_6H_4CHO, 104-88-1; *p*-$MeOC_6H_4CHO$, 123-11-5; (*E*)-PhCH=CHCHO, 14371-10-9; (*Z*)-$NO_2CH_2CH(Ph)$=CHMe, 104488-93-9; (*E*)-$NO_2CH_2CH(Ph)$=CHMe, 104488-92-8; Me_2C=$CH(CH_2)_2C$(Me)=$CHCH_2OAc$, 105-87-3.

Ultrasound in Organic Synthesis. 12.[1] In Situ Generation and Uses of Butyllithium Reagents in Several Synthetic Reactions

J. Einhorn* and J. L. Luche*

Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité, Université Scientifique Technologique et Médicale de Grenoble, Bât.52 Chimie Recherche B.P. 68, 38402 Saint Martin d'Hères Cedex, France

Received March 31, 1987

Butyllithium reagents—primary, secondary, tertiary—are among the most useful organometallics in organic synthesis, as strong bases, as precursors to various lithiated reactive intermediates or other organometallics, and as initiators of several types of reactions including polymerization.[2] Many of these reactions are under stereo- and regiocontrol by complex-induced proximity effects.[3] Due to their reactivity toward etheral solvents, butyllithium reagents are commercially available as hydrocarbon solutions. Standardization is generally necessary before use,

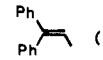
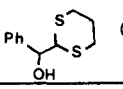
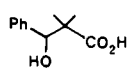
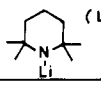
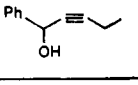
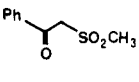
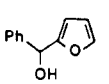
(1) Previous paper in this series: de Souza-Barboza, J. C.; Luche, J. L. Petrier, C. *Tetrahedron Lett.* **1987**, *28*, 2013–2016. See also: Einhorn, C.; Luche J. L. *J. Organomet. Chem.* **1987**, *322*, 177–183.

(2) Wakefield, B. J. *Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, 1974.

(3) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356–363.

0022-3263/87/1952-4124$01.50/0

Table I

Substrate	Conditions	Quencher	product (yield)[a]	Substrate	Conditions	Quencher	product (yield)
$(iPr)_2NH$	nBuCl, Li wire	–	$(iPr)_2NLi$(LDA) (92)	$Ph_3P^+CH_2CH_3\ Br^-$	sBuCl, Liwire	$Ph_2C{=}O$	 (87)
	sBuCl, Li wire	–	– (80)				
	tBuCl, Liwire	–	– (82)		tBuCl, Lisand	PhCHO	 (98)
	nBuBr, Liwire	–	– (40)				
$(iPr)_2NH$ + 	nBuCl, Liwire	PhCHO	 (78)	$nC_6H_{13}C{\equiv}CH$	nBuCl, Lisand	$(CH_2O)_n$[c]	$nC_6H_{13}C{\equiv}C{-}CH_2OH$ (83)
	nBuCl, Liwire	–	 (LiTMP) (90)	$C_2H_5C{\equiv}CH$ $(iPr)_2^+NH$	nBuCl, Lisand	PhCHO	 (61)
$PhOCH_3$	sBuCl, Liwire in THP	CH_3I	 (71)	$CH_3SO_2CH_3$	nBuCl, Lisand	$PhCOOCH_3$	 (77)
 [b]	nBuCl Li sand	PhCHO	 (72)	CH_3SOCH_3	n-, s-, t-BuCl	no reaction	

[a] Isolated yield of purified material. [b] Excess (3-fold) furan was used with respect to the theoretically generated *n*-BuLi. [c] 1 equiv of solid paraformaldehyde.

and frequently the solvent has to be exchanged to ensure optimal rates and yields.

In previous works we established that ultrasonic irradiation is able to stimulate very efficiently the formation of organometallic compounds.[4] Thus it appeared to us that in several synthetic processes it should be possible to replace butyllithium reagents by their inexpensive and safer precursors, i.e., the corresponding butyl halides and lithium metal under sonochemical conditions directly in the desired etheral solvent.

In a first attempt, we observed that the highly useful, nonnucleophilic strong base, lithium diisopropylamide (LDA) can be prepared without effort from diisopropylamine, lithium, and butyl halides by sonication at 15–18 °C of the mixture in dry tetrahydrofuran (THF). As indicated in Table I, much better yields are obtained from chlorides with respect to bromides, and this observation seems to apply to other cases of lithiation. The reagents can be used in stoichiometric amounts, and the reaction is completed as soon as the metal piece has disappeared, i.e., ca. 15 min. The advantages of such a procedure over standard ones appear to be the much greater ease of the preparation, its rapidity, and avoidance of solvent exchange and temperature adjustments. The only byproducts are the corresponding gaseous butanes which are evolved during sonication and lithium chloride which precipitates from the reaction medium. The yield, calculated by standardization,[5] is very high from *n*-butyl chloride as indicated in the table. The same result, within experimental errors, is obtained when the solvent is diethyl ether instead of THF. The efficiency of the method was tested in a 0.5-mol preparation of LDA in THF, which gave an excellent 91% yield.

In some cases it is even possible to generate in situ the lithium diisopropylamide and to use it in a one-step procedure as in the following experiment: LDA is generated as above, in the presence of half an equivalent of isobutyric acid. The formation of the dianion of the acid occurs very efficiently in reasonable times (30 min). Quenching with benzaldehyde gives the expected β-hydroxy acid in 78% isolated yield. It is interesting to note that under these conditions no addition of butyllithium to the carboxylate function was detected (absence of ketonic or alcoholic byproducts).

Other lithium amides can be formed in the same manner as examplified by the preparation of lithium tetramethylpiperidide (LiTMP), another strongly congested base of high utility in synthesis.

In the same way, ultrasonically in situ generated butyllithium is able to deprotonate a phosphonium salt to the Wittig reagent and to effect ortho lithiation of anisole. In contrast to these positive results, which were obtained from various lithium samples, deprotonations of terminal acetylenic hydrocarbons and of 1,3-dithiane to their corresponding anions require the use of higher sodium content (2% Na) lithium sand or pieces. The use of gaseous alkynes (butyne) is also possible but diisopropylamine has to be added to ensure reasonable reaction times (30 min). In these latter cases the complete inertness of lithium with <0.02% Na has not received a satisfactory explanation. It is also noteworthy that all our attempts to generate the anion of DMSO have been unexpectedly negative with any lithium sample, but the reaction occurs with great ease with dimethyl sulfone.

It can be anticipated that the present procedure of in situ generation of butyllithium reagents will find many synthetic applications, owing to its rapidity, efficiency, and simplicity.

Experimental Section

Low sodium content lithium wire (<0.02% Na) was obtained from Aldrich, 2% Na lithium sand from Fluka, and 2% Na lithium piece from Metallgesellschaft. Solvents (THF, THP) were distilled prior to use in the presence of benzophenone–sodium. Sonications were effected in a Sonoclean SHE 2500 cleaning bath thermostated at ca. 15–18 °C by circulation of cold water in a stainless steel coil. Infrared and NMR spectra were recorded on Perkin-Elmer 397 and Brucker WP 80 spectrometers, respectively.

Preparation of LDA. Lithium (0.140 g, 20 mmol) and 0.926 g (10 mmol) of the desired butyl chloride in 10 mL of THF were

(4) Einhorn, J.; Luche, J. L. *Tetrahedron Lett.* **1986**, *27*, 1793–1796, and references cited.

(5) In 1 mL of dry THF, 0.5 mmol of carefully weighted menthol, is dissolved with a small crystal (ca. 0.5 mg) of *o*-phenanthroline. The mixture is cooled to −78 °C; then the solution of LDA is slowly added via a syringe until a red coloration persists. Le Drian, C. Ph.D. Thesis, Grenoble, 1981.

sonicated in the presence of 1.010 g (10 mmol) of diisopropylamine. After disappearance of the metal (usually 15–30 min), and standardization, the solution can be used for deprotonations as usual.

The same experiment effected in the presence of 0.440 g (5 mmol) of 2-methylpropanoic acid gave a thick white precipitate after 5 min, which progressively redissolve to give a slightly turbid solution. Quenching with 0.53 g (5 mmol) of benzaldehyde and stirring for 1 h at 20 °C gave a slightly yellow solution which was hydrolyzed (20 mL of water) and extracted with ether. The alkaline phase was acidified (aqueous 2 N HCl) and extracted with ether, and the organic extract was washed (2 × 20 mL water), dried (Na_2SO_4), and evaporated. The residue was recrystallized (hexane/AcOEt) to give 0.757 g (78% yield) of **2,2-dimethyl-3-hydroxy-3-phenylpropanoic acid**:[6] mp 132–133 °C (lit.[6] mp 133–134 °C); IR 3400, 1700 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, 6 H), 5.07 (s, 1 H), 6.50–7.00 (m, 2 H, exchangeable in D_2O), 7.45 (s, 5 H) ppm.

Large-Scale Preparation of LDA. *n*-Butyl chloride (46.3 g, 0.5 mol) and 50.6 g (0.5 mol) of diisopropylamine in 250 mL of dry THF in a round-bottom flask were placed in the sonicator. Lithium wire (7 g, 1 mol) was added in pieces of ca. 1 g each, progressively to avoid excessive heating. After 2 h of sonication, the metallic pieces were completely consumed and the yellow mixture containing precipitated LiCl was standardized (calculated yield, 91%).

General Procedure for Other Cases. The corresponding butyl chloride (93 mg, 1 mmol), lithium (14 mg, 2 mmol), and 1 mmol of the substrate in 2 mL of THF (THP in the case of the lithiation of anisole) were sonicated until no metal was left. Addition of the quenching agent (1 equiv) and reaction under stirring was followed by workup, after a TLC analysis had shown completion. Purification (chromatography) of the products gave samples that exhibited physical and spectral properties consistent with structures and literature data.

2-Furylphenylcarbinol:[7] liquid; IR 3375, 1500, 1450, 1015 cm^{-1}; NMR ($CDCl_3$) 2.60 (br s, 1 H, exchangeable in D_2O), 5.7–5.85 (m, 1 H), 6.05–6.15 (m, 1 H), 6.25–6.37 (m, 1 H), 7.25–7.50 (m, 6 H) ppm.

2-(1,3-Dithianyl)phenylcarbinol:[8] mp 73–74 °C (lit.[8] mp 71–72 °C); IR 3450, 2900, 1495, 1420, 1280 cm^{-1}; NMR ($CDCl_3$) 1.80–2.20 (m, 2 H), 2.50–3.15 (m, 5 H), 4.15 (d, J = 9 Hz, 1 H), 4.92 (d, J = 9 Hz, 1 H), 7.25–7.50 (m, 5 H) ppm.

Non-2-yn-1-ol:[9] liquid; IR 3325, 2925, 2275, 2225, 1430, 1140, 1010 cm^{-1}; NMR ($CDCl_3$) 0.75–1.10 (m, 3 H), 1.10–1.70 (m, 8 H), 1.80–2.08 (m, 1 H, exchangeable in D_2O), 2.08–2.35 (m, 2 H), 4.15–4.35 (m, 2 H) ppm.

1-Phenylpent-2-yn-1-ol:[10] liquid; IR 3350, 2980, 2280, 2230, 1460, 1010 cm^{-1}; NMR ($CDCl_3$) 1.17 (t, J = 9 Hz, 3 H), 2.15–2.45 (m, 3 H), 5.35–5.55 (m, 1 H), 7.30–7.70 (m, 5 H) ppm.

2-Phenyl-2-oxoethyl methyl sulfone:[11] mp 105–106 °C (lit.[11] mp 106–107 °C); IR 1680, 1310, 1160 cm^{-1}; NMR ($CDCl_3$) 3.15 (s, 3 H), 4.60 (s, 2 H), 7.39–7.70 (m, 3 H), 7.91–8.09 (m, 2 H) ppm.

Acknowledgment. Financial support from the CNRS (UA 332) is gratefully acknowledged. We thank Drs C. Einhorn and A. E. Greene for useful discussions and suggestions.

Registry No. LDA, 4111-54-0; BuLi, 109-72-8; *n*-BuCl, 109-69-3; *sec*-BuCl, 78-86-4; *t*-BuCl, 507-20-0; $(i\text{-Pr})_2NH$, 108-18-9; Li, 7439-93-2; $i\text{-PrCO}_2H$, 79-31-2; PhCHO, 100-52-7; $PhCH(OH)C(CH_3)_2CO_2H$, 23985-59-3; $PhOCH_3$, 100-66-3; CH_3I, 74-88-4; $2\text{-}H_3CC_6H_4OCH_3$, 578-58-5; $Ph_3P^+CH_2CH_3Br^-$, 1530-32-1; $Ph_2C{=}O$, 119-61-9; $Ph_2C{=}CHCH_3$, 778-66-5; $C_6H_{13}C{\equiv}CH$, 629-05-0; $(CH_2O)_n$, 30525-89-4; $PhCH(OH)C{\equiv}CCH_2CH_3$, 51207-10-4; $CH_3SO_2CH_3$, 67-71-0; $C_2H_5C{\equiv}CH$, 107-00-6; $C_6H_{13}C{\equiv}CCH_2OH$, 5921-73-3; $PhCO_2CH_3$, 93-58-3; $PhCOCH_2SO_2CH_3$, 3708-04-1; CH_3SOCH_3, 67-68-5; 2,2,6,6-tetramethylpiperidine, 768-66-1; lithium 2,2,6,6-tetramethylpiperidine, 38227-87-1; furan, 110-00-9; α-phenyl-furanmethanol, 4484-57-5; 1,3-dithiane, 505-23-7; α-phenyl-1,3-dithianemethanol, 5849-19-4.

(6) Hauser, C. R.; Breslow, D. S. *J. Am. Chem. Soc.* **1939**, *61*, 793–798.
(7) Ramanathan, V.; Levine, R. *J. Org. Chem.* **1962**, *27*, 1216–1219.
(8) Corey, E. I.; Seebach, D. *Angew, Chem., Int. Ed. Engl.* **1965**, *4*, 1075–1077.
(9) Hennin, G. F.; Bell, E. P. *J. Am. Chem. Soc.* **1943**, *65*, 1847–1848.
(10) Dupont, G. *C. R. Hebd. Seances Acad. Sci.* **1909**, *148*, 1522–1524.
(11) Becher, H. D.; Russel, G. A. *J. Org. Chem.* **1963**, *28*, 1896–1898.

Selenium-77, Tellurium-125, and Carbon-13 NMR Chemical Shifts and One-Bond ^{77}Se–^{13}C, ^{125}Te–^{13}C, and ^{13}C–^{1}H Coupling Constants of Trialkylselenonium and Telluronium Triflates, Protonated Dialkylselenonium and Telluronium Cations, and Their Corresponding Donor–Acceptor Complexes

Khosrow Laali,* H. Y. Chen, and Robert J. Gerzina

Department of Chemistry, Kent State University, Kent, Ohio 44242

Received March 17, 1987

There is substantial current interest in ^{77}Se and ^{125}Te NMR.[1-8] Pioneering work by McFarlane et al.[9,10] helped establish both selenium and tellurium chemical shifts as useful diagnostic tools. Most of the early measurements of chemical shifts and coupling constants were done by heteronuclear double-resonance technique in the proton NMR spectra. McFarlane et al.[9] were first to show the parallelism in chemical shifts between organoselenium and organotellurium compounds of similar structure, with ^{125}Te being slightly more sensitive (^{125}Te vs. ^{77}Se straight-line plot; slope 1.8).

In analogy with other heavy atoms, ^{77}Se and ^{125}Te chemical shifts are influenced by both paramagnetic (δ^p) and diamagnetic (δ^d) shielding contributions. The δ^d, which involves the inner electrons, is thought to be small and rather insensitive to changes in bonding. Moreover, both ^{77}Se and ^{125}Te chemical shifts are reported to be relatively insensitive to solvent effects.[9,10]

Whereas the literature on ^{77}Se and ^{125}Te chemical shifts of neutral substrates has been growing steadily over the past decade,[1-8] multinuclear NMR studies involving electron-deficient organic selenonium and telluronium cations

(1) Schrobilgen, G. J.; Burns, R. C.; Granger, P. *J. Chem. Soc., Chem. Commun.* **1978**, 957. Lassigne, C. R.; Wells, E. J. *J. Chem. Soc., Chem. Commun.* **1978**, 956.
(2) O'Brien, D. H.; Dereu, N.; Grigsby, R. A.; Irgolic, K. J.; Knapp, F. F., Jr. *Organometallics* **1982**, *1*, 513. O'Brien, D. H.; Dereu, N.; Huang, C. K.; Irgolic, K. J.; Knapp, F. F., Jr. *Ibid.* **1983**, *2*, 305.
(3) Jones, C. H. W.; Sharma, R. D. *J. Organomet. Chem.* **1983**, *255*, 61. Jones, C. H. W.; Sharma, R. D.; Taneja, S. P. *Can. J. Chem.* **1986**, *64*, 980.
(4) Detty, M. R.; Henrichs, P. M.; Whitefield, J. A. *Organometallics* **1986**, *5*, 1544.
(5) Kalabin, G. A.; Kushnarev, D. F.; Kataeva, L. M.; Kashurnikova, L. V.; Vinokurova, R. L. *Zh. Org. Khim.* **1978**, *14*, 2478; *Chem. Abstr.* **1979**, *90*, 102942j. Kalabin, G. A.; Kushnarev, D. F. *Zh. Strukt. Khim.* **1979**, *20*, 617; *Chem. Abstr.* **1980**, *92*, 110126c.
(6) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Anderson, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055.
(7) Sandor, P.; Radics, L. *Org. Magn. Reson.* **1981**, *16*, 148.
(8) Chadha, R. K.; Miller, J. M. *J. Chem. Soc., Dalton Trans.* **1982**, 117.
(9) McFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans* **1972**, 1397. McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1973**, 2416.
(10) For reviews on ^{77}Se and ^{125}Te NMR see: McFarlane, H. C. E.; McFarlane, W. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 2, Chapter 10. Rodger, C.; Scheppard, N.; McFarlane, C.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: New York, 1978; Chapter 12.

0022-3263/87/1952-4126$01.50/0