4.0 equiv of SO_3 in nitromethane at 0 °C and its dipotassium salt isolated after the addition of excess of water, neutralization with aqueous KOH, and freeze drying. Samples of **3**, **10**, and the potassium salts of **5**, **6**, and **12** were obtained commercially from Merck and Fluka. The ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer.

Sulfonation Procedures and Analysis. Procedure A. To a heterogeneous mixture of 2.0 or 5.0 equiv of SO_3 in 0.70 mL of ($^{2}H_8$)dioxane was added, while stirring under nitrogen, at 15 °C a solution of 0.25 mmol of the substrate in 0.70 mL of ($^{2}H_8$)dioxane and the temperature of the mixture subsequently adjusted. With the substrates **1**, **3**, and **15** the reaction mixtures were homogeneous, whereas with **2** and **10** they proved to be heterogeneous.

Procedure B. To a heterogeneous mixture of 0.7, 1.0, or 1.2 equiv of SO_3 in 0.20 mL of ($^{2}H_8$)dioxane was added at 15 °C 0.40 mL of ($^{2}H_2$)methylene chloride and the temperature lowered to −70 °C. To this solution was then added at −70 °C a solution of 0.25 mmol of the substrate in 0.60 mL of ($^{2}H_2$)methylene chloride precooled at −70 °C.

Of the homogeneous reaction mixtures, obtained by the procedures A and B, the progress of the reaction was monitored by ^{1}H NMR by recording spectra after appropriate time intervals. For the low-temperature experiments the temperature of the reaction mixture was raised by 10 °C a time and then kept constant for a chosen period of time. Ultimately, all the reaction mixtures were worked up by pouring them into 2–3 mL of water and adding dilute aqueous KOH till the pH was between 7.5 and 8.5. The solvents of the resulting solution were removed by freeze-drying and their NMR spectra, using ($^{2}H_2$)water and/or ($^{2}H_6$)Me_2SO as solvent, recorded.

Analysis. The components of the reaction mixtures resulting from **1** and **3** have been assigned on the basis of both the ^{1}H and ^{13}C NMR signals of authentic samples of **3**, **5**, **6**, and **8** in ($^{2}H_2$)water and ($^{2}H_6$)Me_2SO at the same alkalinity as the worked up reaction mixture samples. The ^{13}C NMR chemical shifts of **5**, **6**, and **8** are listed in Table III (supplementary material).

The components of the reaction mixtures of **2** and **10** were assigned (i) on the basis of a comparison of the ^{1}H NMR signals with those of an authentic sample of **13** by application of the sulfo and amino substituent shifts, the relative intensities, and the multiplicities of the various signals.

The presence of each of the following assigned components **3**, **5**, **6**, **8**, **10**, and **13** in the various worked up reaction mixtures was further established unequivocally by showing that addition of an equimolar amount of an authentic sample of the sulfonate in question to the soltuion to be analyzed did not lead to an enhancement of the number of ^{1}H NMR signals.

The procedures for the sulfonation in nitromethane and the subsequent workup and isolation of the potassium sulfonates were dscribed before.[13]

Acknowledgment. The authors wish to thank Prof. E. Vogel for stimulating this study by generously supplying samples of the three [10]annulenes, Prof. D. Cremer and Dr. P. de Wit for valuable discussions, and Mmes. Van der Laan-Ctvrteckova and C. A. M. Mittendorf-van Rijn and C. Kruk for recording the NMR spectra.

Registry No. **1**, 4759-11-9; **2**, 4753-55-3; **3**, 90-15-3; **4**, 3197-94-2; **5**, 567-18-0; **6**, 84-87-7; **7**, 102234-08-2; **8**, 1857-16-5; **9**, 102234-09-3; **10**, 134-32-7; **11**, 24344-19-2; **12**, 81-06-1; **13**, 84-86-6; **14**, 14245-99-9; **15**, 36628-80-5; SO_3, 7446-11-9; 11-oxo-2-sulfo-1,6-methano[10]-annulene, 102234-10-6; 2,7-disulfo-11-oxo-1,6-methano[10]-annulene, 102234-11-7.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectral data of **1–3**, **10**, and **15** and their sulfo products in various solvents [($^{2}H_8$)dioxane, ($^{2}H_8$)dioxane/($^{2}H_2$)methylene chloride (5:1, v/v), ($^{2}H_6$)Me_2SO, and ($^{2}H_2$)water] and a reaction scheme (6 pages). Ordering information is given on any current masthead page.

Dianions from 2,3-Dimethyl-2-butene. Metalation–Elimination in an Acyclic System

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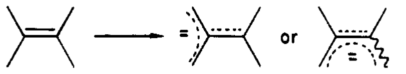
The metalation of 2,3-dimethyl-2-butene results in the preferential formation of cross-conjugated dianions which agrees with predictions from the resonance energy per atom (REPA) calculation on unsubstituted dianions. In addition, metalation with potassium *tert*-butoxide/*n*-butyllithium results in elimination to the mono- and dianions of 2,3-dimethylbutadiene, the first elimination with this metalating system reported in an acyclic system. An examination of acyclic and cyclic dianions with the potential for elimination shows that for acyclic and small (≤6) ring hydrocarbons, elimination occurs to form mono- or dianions with REPA values ≥0.060β. For seven- or eight-membered rings, REPA values are not reliable in predicting elimination.

We have been involved in an examination of factors affecting the stability of delocalized dianions.[1-3] We have determined that cross-conjugated dianions are thermodynamically more stable than linearly conjugated dianions. This enhanced stability has been attributed to Y-aromaticity.[4,5] In systems in which multiple delocalized dianions are possible, the use of REPA[6,7] values has effectively predicted the relative stabilities and therefore concentrations of the various dianionic species present.[2,3]

Scheme I



3 **4** **5**

When 2-methyl-2-butene is dimetalated by using either *n*-butyllithium/tetramethylethylenediamine (TMEDA) or

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Table I. Distribution of Alkylated and Silylated Products

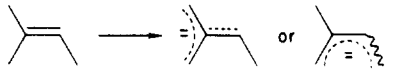
		products from monoanions			products from dianions				butadienes	
base/alkene	days	**11**	**12**	total	**7**	**10**[a]	**6, 8, 9**	total	**20**	**22**
		Reaction with *n*-Butyl Bromide								
KO-*t*-Bu/*n*-BuLi										
1:1	2	16	17	33	11	26	5	42	11	14
2:1	0.04	21	19	40	22	8	13	43	9	8
2:1	1	12	24	36	13	18	5	36	10	18
2:1	2	11	12	23	17	10	11	38	13	25
2:1	4	4	10	14	15	26	7	48	12	26
3:1	1	4	20	24	12	15	7	34	21	21
3:1	3	6	11	17	7	24	4	35	12	35
4:1	1	7	15	22	20	14	10	44	18	17
4:1	3	4	9	13	13	23	6	42	12	35
TMEDA/*n*-BuLi										
2:1	5	24	54	78	7		15	22		
2:1	9		61	61	10		28	38		

Reaction with Chlorotrimethylsilane

		products from monoanions			products from dianions			butadiene
base/alkene	days	**14**	**15**	total	**17**	**18**	total	**22**
KO-*t*-Bu/*n*-BuLi								
2:1	1	30	14	44	30	13	43	13
2:1	2	27	11	38	37	4	41	20
2:1	3	26	11	37	33	5	38	26
4:1	2	19	13	32	24	13	37	31

[a] See discussion in text.

potassium *tert*-butoxide/*n*-butyllithium, the major product is the cross-conjugated dianion **1** (REPA = 0.069β) rather than the linearly conjugated dianion **2** (REPA = -0.040β).[1]



1 **2**

Because the REPA values, which had proven to be so useful in predicting relative stabilities of dianions, were calculated for unsubstituted systems,[6] we were interested in examining dianion formation in a more highly substituted system, 2,3-dimethyl-2-butene (**3**).

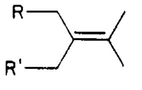
Metalation of **3** with either *n*-butyllithium/TMEDA[8-10] or *n*-butyllithium/potassium *tert*-butoxide[11] resulted in formation of dianionic products by abstraction of two allylic protons, as shown in Scheme I. The anionic mixtures were characterized by quenching with *n*-butyl bromide or chlorotrimethylsilane followed by gas chromatographic separation of the alkylated products (see below) and ^{1}H NMR spectroscopic analysis. As anticipated, the yield of dianions was affected by the length of time the starting material was in contact with the metalating system and by the nature and amount of the metalating system, as shown in Table I. In general, longer reaction times and greater concentrations of base gave higher yields of dianion at the expense of monoanion. Metalation with potassium *tert*-butoxide/*n*-butyllithium resulted in a higher yield of dianion than did metalation with *n*-butyllithium/TMEDA.

The dianions in the reaction mixture were quenched with *n*-butyl bromide to give four dialkylated butenes, **6**–**9**.

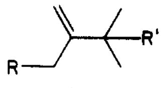
Table II. Butene Dianion Formation (*n*-Butyl Bromide Quench)

base/alkene	days	4/(4 + 5) = 7 + 10/(7 + 10 + 6, 8, 9), %
KO-*t*-Bu/*n*-BuLi		
1:1	2	88
2:1	0.04	70
2:1	1	86
2:1	2	74
2:1	4	85
3:1	1	79
3:1	3	89
4:1	1	77
4:1	3	86
TMEDA/*n*-BuLi		
2:1	5	32
2:1	9	26

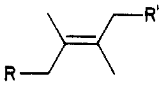
In addition, one of the monoalkylated products, **10**, could only have been formed from a dianion by a combination of protonation/alkylation with the proton source being adventitious water, either from the atmosphere through the septum capping the tubes of dianion or from moisture inadvertently introduced during the quench. The yields of dianion reported therefore are deduced from an inclusion of **10** in the total of dialkylated products. Products **7** and **10** unquestionably form from the cross-conjugated



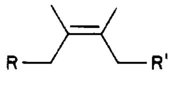
6, R = R' = *n*-Bu
12, R = *n*-Bu, R' = H
14, R = SiMe$_3$, R' = H
17, R = R' = SiMe$_3$



7, R = R' = *n*-Bu
10, R = *n*-Bu, R' = H
11, R = H, R' = *n*-Bu
13, R = H, R' = SiMe$_3$
15, R = SiMe$_3$, R' = H
16, R = R' = SiMe$_3$
20, R = R' = SiMe$_3$



8, R = R' = *n*-Bu
18, R = R' = SiMe$_3$



9, R = R' = *n*-Bu
19, R = R' = SiMe$_3$

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Table III. Butene Dianion Formation (Chlorotrimethylsilane Quench)

base/alkene	days	4 = (15 + 17/15 + 17 + 18)	5 = (18/15 + 17 + 18)
2:1	1	77	23
2:1	2	92	8
2:1	3	90	10
4:1	2	73	27

dianion. Unfortunately 60-MHz ^{1}H NMR spectroscopy does not allow differentiation between **6**, also formed from cross-conjugated dianion and **8**/**9**, from linearly conjugated dianion. While we are currently exploring other methods of differentiating between these isomers, we can estimate the minimum fraction of cross-conjugated dianion in the total butene dianion milieu by summing the yields of **7** and **10**. Table II indicates that in these potassium *tert*-butoxide/*n*-butyllithium reaction mixtures the percentage of cross-conjugated dianion is between 70% and 89% of the total dianion. As mentioned initially, the cross-conjugated dianion with REPA = 0.069β would be predicted to be more stable than the linearly conjugated dianion (REPA = 0.040β) product.

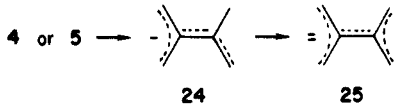
The products from the use of chlorotrimethylsilane as quenching agent are reported in the last four entries of Table I. As compared to the dialkylated butenes, the chemical shifts of the three isomeric 2-butenes (**17**–**19**) are sufficiently different to allow confirmation of the cross-conjugated product **6**. The *E* and *Z* isomers have been reported previously[12,13] to have proton chemical shifts of 1.53 and 1.6 ppm, respectively, for the methyl protons and 1.48 and 1.43 ppm, respectively, for the methylene protons. The 2-butene product we observe formed in the largest concentration we identify as **17** on the basis of its methyl (1.54 ppm) and methylene (1.39 ppm) proton chemical shifts. Because of a similarity of retention times it was not possible to isolate the other 2-butene product uncontaminated by **17** but the ^{1}H NMR spectrum of the mixture allowed the minor isomer to be identified as **18**. Once again, reasoning that **15** (analogous to **10**) can most logically be formed by protonation and then alkylation of **4**, the minimum yield of **4** as a percentage of alkenyl dianion formation (15 + 17/15 + 17 + 18) can be evaluated. An examination of Table III shows that the cross-conjugated dianion forms at the expense of trans (*E*) linearly conjugated dianion yielding an equilibrium mixture containing approximately 90% cross-conjugated dianion **4**. This is in reasonable agreement with the results seen in the *n*-butyl bromide quench (Table II).

In summary, when the metalating system is potassium *tert*-butoxide/*n*-butyllithium, the cross-conjugated dianion is formed in higher yield than linearly conjugated dianions, reflecting its greater stability as predicted through REPA calculations. Thus we have demonstrated (a) the preference for cross-conjugative stabilization of delocalized dianions even in highly alkylated systems and (b) the continued success of REPA calculations[6,7] in predicting the relative stability of delocalized dianions.

Table IV. Reaction Mixtures without Monoanion Products

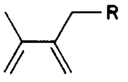
base/alkene	days	dianion products, %	monoalkylated butadienes, %	dialkylated butadienes, %
From Quench with *n*-Butyl Bromide				
1:1	2	63	15	21
2:1	0.04	72	15	13
2:1	1	56	16	28
2:1	2	50	17	33
2:1	4	56	14	30
3:1	1	45	28	28
3:1	3	43	15	43
4:1	1	56	23	22
4:1	3	47	13	39
From Quench with Chlorotrimethylsilane				
2:2	1	76		24
2:1	2	67		33
2:1	3	66		34
4:1	2	54		46

Scheme II

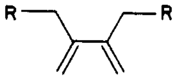


The minimum amount of cross-conjugated dianion as a fraction of the total dianion product is much lower when the reaction mixture is *n*-butyllithium/TMEDA. We present no explanation for the smaller percentage of **7** in the dianion mixture when the metalating system was *n*-butyllithium/TMEDA as compared to the potassium *tert*-butoxide metalating system except to note that a similar trend was observed in the metalation of 2-methyl-2-butene.[1]

Of greater interest to us was the observation of butadiene products **20**–**23** in the reaction mixture formed by metalation with potassium *tert*-butoxide. As shown in Table IV, increasing ratios of metalating system to starting alkene or longer periods of contact result in higher yields of the butadiene products at the expense of products from dianions **4**/**5**. Presumably the hydride elimination necessary to form **22** and **23** (after quenching with RX) is from the dianion of **3** as shown in Scheme II rather than the monoanion because the yield of butadiene products increases with the increase in the amount of metalating complex.



20, R = *n*-Bu
21, R = SiMe$_3$



22, R = *n*-Bu
23, R = SiMe$_3$

There has been a recent flurry of interest in metalation/elimination reactions catalyzed by potassium *tert*-butoxide/*n*-butyllithium,[14-17] but the formation of **24** and **25** represent, to the best of our knowledge, the first metalation/elimination by potassium *tert*-butoxide/*n*-butyllithium in an acyclic system.[18] At this point, two questions presented themselves to us: (a) since potassium *tert*-butoxide/*n*-butyllithium has been fairly extensively used as a metalating system since 1970,[11] why has metalation/elimination not been observed with other acyclic dianions, and (b) why, even with cyclic precursors, does metalation/elimination only occur in certain precursors and can

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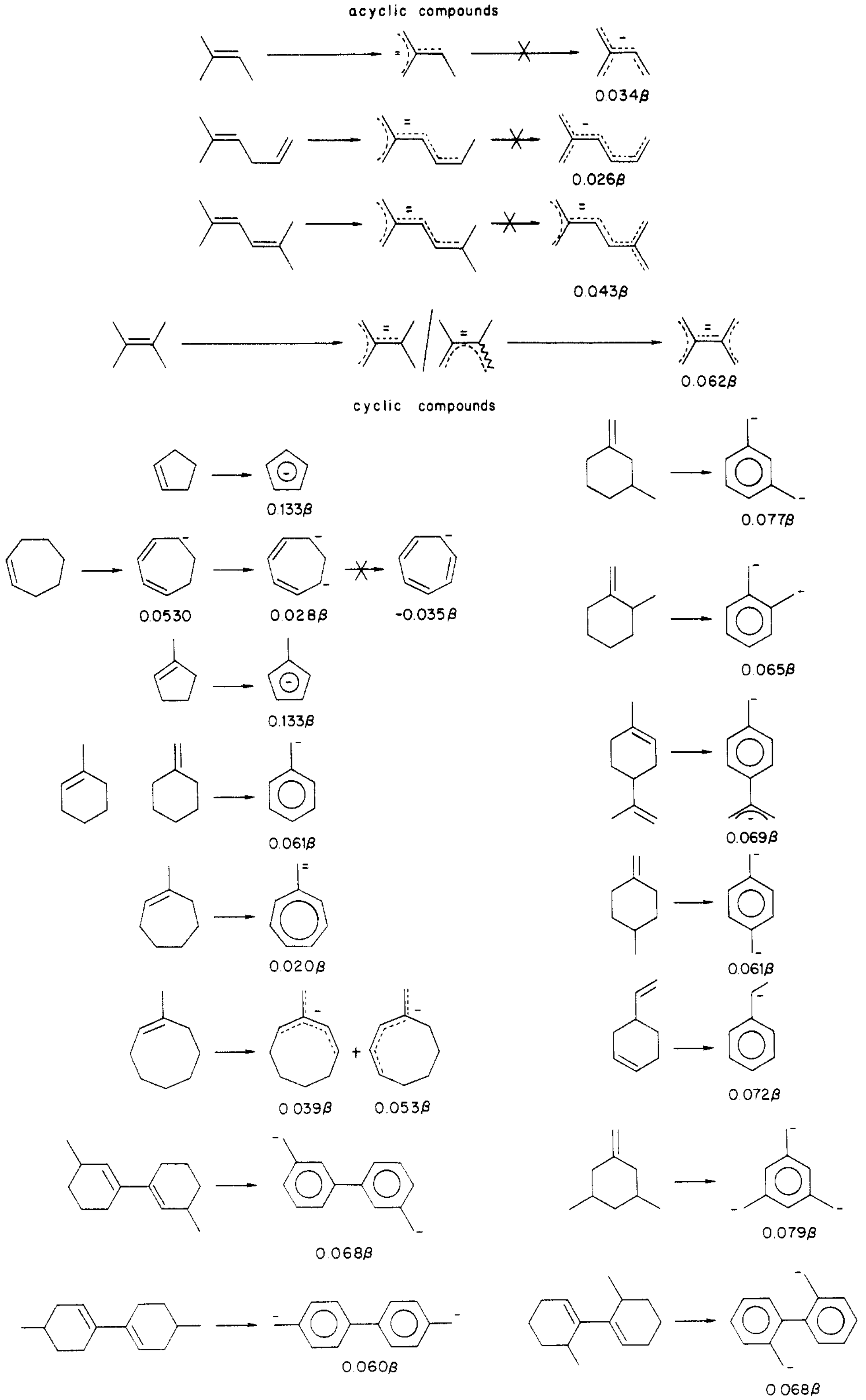
Scheme III



metalation/elimination be accurately predicted for various precursors?

An examination of dianion preparation in acyclic systems by metalation with potassium *tert*-butoxide/*n*-butyllithium[1-3] reveals that only three acyclic systems in addition to 2,3-dimethyl-2-butene have the potential for hydride elimination to yield anions or dianions. These are shown in Scheme III, along with the representative cyclic dianions whose structural features allow them the potential for metalation/elimination. In addition, the REPA values for the final anionic product(s) are shown. From both acyclic and cyclic precursors, with three exceptions, metalation/elimination forms anions whose REPA values are larger than 0.060β. The three exceptions all contain seven or eight-membered rings. Cycloheptene under metalation/elimination conditions gives the cycloheptadienyl dianion (REPA = 0.028β), methylenecycloheptene gives heptafulvene (REPA = 0.020β), and 1-methylcyclooctene gives products from linearly and cross-conjugated pentadiene dianions (REPA = 0.034β and 0.053β, respectively). We suggest that the REPA values, based on Hückel molecular orbital calculations, which do not account for angle

Table V. Infrared and ^{1}H NMR[a] Spectral Data for Compounds 6–20

compd	IR, cm^{-1}	^{1}H NMR chem shifts, δ[b]
6, 8, 9[19]		2.1 (t, J = 10 Hz, 4 H), 1.62 (s, 3 H), 1.61 (s, 3 H), 1.35 (m, 12 H), 0.98 (t, J = 6 Hz, 6 H)
7		4.62 (m, 2 H), 1.93 (m, 2 H), 1.26 (m, 12 H), 1.00 (s, 6 H), 0.98 (t, 6 H)
10		4.62 (d, J = 4 Hz, 2 H), 2.18 (m, J = 8 Hz, 1 H), 1.98 (m, 2 H), 1.53 (m, 6 H), 1.04 (d, J = 8 Hz, 6 H), 0.96 (t, J = 7 Hz, 3 H)
11		4.60 (m, 2 H), 1.61 (s, 3 H), 1.42 (m, 6 H), 1.00 (t superimposed on s, 9 H)
12		2.00 (t, 2 H), 1.60 (s, 9 H), 1.30 (m, 6 H), 0.90 (t, 3 H)
14		1.60 (s, 6 H), 1.52 (s, 3 H), 1.44 (s, 2 H), 0.00 (s, 9 H)
15		4.31 (m, 2 H), 1.95 (septet, J = 7 Hz, 1 H), 1.40 (s, 2 H), 0.96 (d, J = 7 Hz, 6 H), 0.00 (s, 9 H)
17		1.54 (s, 6 H), 1.39 (s, 4 H), 0.00 (s, 18 H)
18[12]		1.53 (s, 6 H), 1.48 (s, 4 H), 0.00 (s, 18 H)
20	1600	4.95 (m, 4 H), 2.00 (t, 2 H), 1.60 (s, 3 H), 1.30 (m, 6 H), 0.90 (t, 3 H)
22[20]	1600	4.88 (m, 4 H), 2.17 (t, 4 H), 1.32 (m, 12 H), 0.90 (t, 6 H)
23[21]	1615	4.71 (m, 2 H), 4.58 (m, 2 H), 1.62 (s, 4 H), 0.00 (s, 18 H)

[a] All spectra run in $CDCl_3$. [b] Units relative to Me_4Si.

strain and which assume a planar conformation, are less reliable in predicting relative stabilities for anion systems containing large (greater than seven atoms) rings. As further evidence for this lack of reliability we note that the cyclooctatetraene dianion (REPA = 0.073β) is not formed by metalation/elimination from cyclooctene,[14] an observation which Schleyer suggests is due to ring strain, preventing coplanarity, or to an unexplained predilection for odd-numbered rings to eliminate better than their even-membered counterparts. It should be mentioned that REPA values have been examined with respect to their predictive value. Hückel theory, upon which REPA values are based, is inherently suspect for doubly charged ions where electrostatic interactions play a major role. The success of REPA values in predicting elimination may be due to a combination of factors rather than an assessment of stability as evaluated solely by Hückel theory.

Conclusion

The outcome of metalation/elimination reactions by potassium *tert*-butoxide/*n*-butyllithium has been examined for a variety of cyclic and acyclic alkenes. For alkenes containing rings of six or fewer carbons and for acyclic alkenes, the formation of the final anionic product can be predicted by its REPA value with a REPA value of 0.060β occurring as the minimum value observed. For alkenes larger than cyclohexene, the REPA values do not allow a reliable prediction of the final anionic product. Finally, the only acyclic alkene to give elimination with potassium *tert*-butoxide/*n*-butyllithium, 2,3-dimethyl-2-butene is reported.

Experimental Section

Apparatus and Materials. NMR spectra were recorded in $CDCl_3$ or CCl_4 on a Varian T-60 nuclear magnetic resonance spectrometer using Me_4Si (when appropriate) as an internal standard. Gas chromatographic separations were performed on a Perkin-Elmer Sigma 3-B gas chromatograph. Pentane was obtained from Aldrich Chemical Co. and washed with sulfuric acid and dried by distillation from phosphorus pentoxide. TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) from Aldrich Chemical Co. was distilled from the sodium/benzophenone ketyl. *n*-Butyllithium (2.4 M in hexane) was procured from Alfa Products. All other reagents were obtained from Aldrich Chemical Co. and used without further purification.

General Procedure for Metalation. (A) With Lochman's Base. Potassium *tert*-butoxide (3.2 g, 28.4 mmol) in pentane and *n*-butyllithium (12.0 mL, 28.4 mmol) were combined in a septum-capped test tube under argon to form a beige complex. To the metalating system at 0 °C was added 2,3-dimethyl-2-butene (1.69 mL, 14.2 mmol). The metalated butene was quenched with *n*-butyl bromide (3.30 mL, 31.2 mmol) or chlorotrimethylsilane (4.0 mL, 32.0 mmol), the solution was neutralized with aqueous ammonium chloride, the layer were separated and dried, and the organic layer was flash distilled [180 °C (0.3 torr)]. The products were separated by temperature-programmed GC (110–168 °C, 2.7-m, 6% OV-17 column).

(B) With *n*-Butyllithium/TMEDA. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) (4.4 mL, 28.4 mmol) and *n*-butyllithium (12.0 mL, 28.4 mmol) were combined in a septum-capped test tube under argon. To the metalating system was added 2,3-dimethyl-2-butene (1.69 mL, 14.2 mmol). *n*-Butyl bromide (3.30 mL, 31.2 mmol) was added to the solution at 0 °C to quench the anions. The products were isolated as described above.

Spectral data for all compounds reported is summarized in Table V.

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Registry No. 6, 102261-94-9; **7**, 102261-95-0; **8**, 102261-96-1; **9**, 102261-97-2; **10**, 102261-98-3; **11**, 29772-43-8; **12**, 19781-18-1; **14**, 54008-73-0; **15**, 102261-99-4; **17**, 102262-00-0; **18**, 16054-38-9; **20**, 102262-01-1; **21**, 83180-80-7; **22**, 84652-75-5; **23**, 82167-48-4; 2,3-dimethyl-2-butene, 563-79-1; *n*-butyl bromide, 109-65-9; chlorotrimethylsilane, 75-77-4.