Table I, Thermal Decomposition of N-Alkylidenesulfinamides

Sulfinimine	% yield	Mp, °C	Solvent <sup>a</sup>	Temp, °C	Time, hr	Products <sup>b</sup> (% yield)
1b	92	78–79	Benzene	80	36	<b>6b</b> (44), <b>7b</b> (44), <b>c 4</b> (82)
			Ethyl acrylate	<b>9</b> 0	15	8a (60), <sup>11</sup> 7b (10), 4 (71)
1c	93	95-96	Benzene	80	36	6c (35), 7c (24), <sup>d</sup> 4 (75)
			Ethyl acrylate	90	15	8b (77), <sup>11</sup> 4 (77)
1d	95	84-15	Benzene	80	15	6d (51), 7d (20) <sup>e</sup>
			Methyl propynoate	100	15	9 (71)
1e	85	96–98	Benzene	80	24	6e (31), 7e (29), 4 (85)
			Ethyl acrylate	90	14	8c (56), 7e (10)
			Methyl propynoate	90	14	9 (72)
a) falar rati	a of other la or	late and meethed	ronuncete to sulfinimines ?	5,1 and 15,1 mag	nontivolu /	Determined by a combination of

<sup>a</sup>Molar ratio of ethyl acrylate and methyl propynoate to sulfinimines, 25:1 and 15:1, respectively. <sup>b</sup> Determined by a combination of gas chromatography and column chromatography. S. Oae, R. Nomara, Y. Yoshikawa, and W. Tabaki, Bull. Chem. Soc. Jap., 42, 2903 (1969). <sup>d</sup> G. Bulmer and F. Mann, J. Chem. Soc., 684 (1945). <sup>e</sup> G. Leandri and A. Tundo, Ann. Chim. (Paris), 44, 255 (1954); Chem. Abstr., 49, 15782h (1955).

*N*-Alkylidenesulfinamides **1b**–e were crystalline solids whereas 1a was an oil for which a satisfactory analysis could not be obtained. The infrared spectra of 1a-e showed strong S-O stretching at 1080 cm<sup>-1</sup>. The diastereotopic methyl groups in 1a consist of a broad doublet at ambient temperature which reversibly coalesced to a singlet at 55°. The calculated<sup>5</sup> free energy ( $\Delta G^{\pm}$ ) for stereomutation was 17.0 kcal/mol and is 3 kcal/mol lower than that observed for the corresponding N-alkylidenesulfenamide.<sup>6</sup>

Whereas 1b was obtained as a single diastereomer its precursor was a 56/44 mixture of E and Z diastereomers.<sup>3</sup> The preference for a single diastereomer for 1b, presumably E, may reflect an enhanced stability as a result of an attractive interaction between the sulfinyl oxygen and the proton on the imino carbon (vide infra).

N-Alkylidenesulfenamides have proven to be relatively stable compounds with most of their reactions occurring at the S-N rather than the C-N bond.<sup>1</sup> By contrast the sulfinyl group in 1a-e greatly activates the C-N double bond. Compound 1a was the most reactive and was rapidly hydrolyzed in moist air to benzenesulfinamide.

Both 1a and 1d rapidly react with methanol to give adducts 2a-b in 90 and 50% yields, respectively. Adduct 2b was formed as a 70/30 mixture (by nmr) of two diastereoisomers.<sup>7</sup> N-Benzylidenesulfinamides, 1b, c, and e, were more stable and failed to react with water or alcohols under comparable conditions.

N-Alkylidenesulfinamides prepared from aldehydes undergo a Cope-type elimination to yield arylsulfenic acids (3). Sulfenic acids have been implicated in a wide variety of organsulfur reactions<sup>8</sup> but have been little studied owing to their inherent instability. When heated in benzene for 15-36 hr, 1b-c decompose to give disulfide (6), thiolsulfonate (7), and nitrile (4) as major products<sup>9</sup> (Scheme I). These results are summarized in Table I.

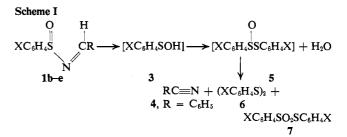
(5) The free energy for stereomutation was calculated from the equation  $K_c = \Delta v_0 \pi/2^{1/2}$  and the Eyring equation ( $\Delta v_0 = 13.5$  Hz). (6) F. A. Davis, W. A. R. Slegeir, and J. M. Kaminski, J. Chem. Soc.,

Chem. Commun., 634 (1972).

(7) The major isomer crystallized as yellow plates mp 96-97° and

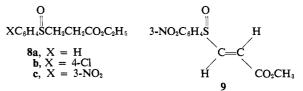
(i) The high radius crystalleed system plates in plates i ibid., 91, 3634 (1969); (f) R. D. G. Copper, ibid., 92, 5010 (1970); (g) T. S. Chou, J. R. Burgtorf, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, ibid., 96, 1609 (1974)

(9) A number of minor products were detected whose structures are under investigation.



The isolation of 4, 6, and 7 in the thermal decomposition of 1b-e is consistent with the formation of an arylsulfenic acid, 3, which gives the thiolsulfinate, 5, and water<sup>10</sup> (Scheme I). Arylthiosulfinates are unstable and disproportionate to give disulfide and thiolsulfonate.11 Alkylsulfenic acids prepared by the decomposition of thiolsulfinate esters<sup>8b</sup> and tert-butyl sulfoxide<sup>80</sup> gave alkyl thiolsulfinate esters.

The formation of the sulfenic acid was confirmed by trapping experiments with ethyl acrylate or methyl propynoate to give 8 and 912 (Table I).



N-Alkylidenesulfinamides are a potentially useful intermediate for organic synthesis and are a mild, high yield<sup>13</sup> source of arylsulfenic acids.

(10) Water as detected in the decomposition of 1b-e.

(11) P. Koch, E. Ciuffarin, and A. Fava, J. Amer. Chem. Soc., 92, 5971 (1971); D. Barnard, J. Chem. Soc., 4675 (1957).

(12) Adducts 8a and c were oils that decomposed on heating; 8b was a solid, mp 78-79°. Compounds 8a and b were prepared independently by condensing the corresponding thiol with ethyl acrylate followed by oxidation with m-chloroperbenzoic acid. Adduct 9 crystallized from ether as white needles, mp 91-92; J = 15 Hz.

(13) As indicated by the yield of benzonitrile isolated (Table I).

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## Crotyllithium by Direct Metalation. Relative Stabilities of Z- and E-Crotyl Anions<sup>1</sup>

## Sir:

In 1965 Bank, Schriesheim, and Rowe rationalized the rapid base-catalyzed isomerization of 1-butene to Z-2-

(1) Presented in part at the First Fall Organic Conference, American Chemical Society, N. Falmouth, Mass., Sept 30, 1973.

butene on the basis that Z-crotyl anion (I) is more stable than E-crotyl anion (II).<sup>2</sup> Although considerable spectral evidence has been accumulated that Z is more stable than E in related anions,<sup>3</sup> the only study in which a relative stability assignment was made for crotyl anion itself led to the conclusion that the E form (II) predominated.<sup>4</sup> We wish to report that crotyllithium, previously prepared by a laborious route,<sup>5</sup> is readily available by metalating 1-butene or Z- or E-2-butene, that at 35° in tetramethylethylenediamine (TMEDA) it is ionic, with the Z form (I) predominating over the E

$$J = 10.2 \text{ Hz} \qquad \begin{array}{c} & \delta & 6.0 \\ J = 10.2 \text{ Hz} \qquad H \qquad J = 10.2 \text{ Hz} \\ H \qquad \alpha \qquad \beta \qquad \gamma \qquad H \qquad \delta 2.9 \\ \delta & 1.2 \qquad \Theta \qquad \delta \\ H \qquad CH_3 \qquad \delta \qquad 1.4 \qquad \Theta \qquad CH_3 \\ I \qquad I \qquad I \end{array}$$

form (II) by  $\sim 85:15$ , and that on alkylation with *n*-butyl bromide, it gives a 6:1 ratio of Z- to E-2-octene.

Crotyllithium is readily prepared by slowly adding TMEDA (5 ml) at  $-10^{\circ}$  to a solution of 1-butene or Zor E-2-butene (0.02 mol), *tert*-butyllithium (0.02 mol), and hexane (10 ml).<sup>6</sup> After 0.5 hr at room temperature (or 24 hr if *n*-butyllithium is used instead), the reaction is essentially complete. If desired, the bulk of the hexane can be removed by vacuum.

The most obvious pmr spectral feature of crotyllithium prepared in this way is the 1:3:3:1 quartet (J =10.2 Hz) for the  $\beta$ -proton at  $\delta$  6.0, also observed in earlier preparations in diethyl<sup>5</sup> and dimethyl ether.<sup>4,5</sup> The other peaks for crotyllithium, visible though partially obscured by TMEDA or residual hexane, were shown by spin decoupling experiments to be consistent with the assignments on formula I and give essentially the same parameters observed in ether solvents.<sup>4,5</sup> Indication that these parameters are due to an ionic species comes from the upfield location of the  $\gamma$  proton ( $\delta$  3.0; ionic 3-neopentylallyllithium (NAL),  $\delta$  3.3;<sup>3f</sup> covalent Z-NAL<sup>3f</sup> and crotylmagnesium bromide,  $\delta$  4.5<sup>7</sup>), downfield location of the  $\alpha$ -proton ( $\delta$  1.2; ionic NAL,  $\delta$ 1.2<sup>3f</sup>; covalent Z-NAL<sup>3f</sup> and crotylmagnesium bromide,<sup>7</sup>  $\delta$  0.8), and especially from the nonequivalence of the  $\alpha$ -protons at  $-90^{\circ}$  when rotation about the  $C_{\alpha}-C_{\beta}$ 

(2) S. Bank, A. Schriesheim, and C. A. Rowe, J. Amer. Chem. Soc.,
87, 3244 (1965); S. Bank, *ibid.*, 87, 3245 (1965).
(3) (a) 1-Methyl-3-phenylallylpotassium, 83 % Z, H. Kloosterziel and

(3) (a) 1-Methyl-3-phenylallylpotassium, 83% Z, H. Kloosterziel and J. A. A. van Drunen, Recl. Trav. Chim. Pays-Bas, 87, 1025 (1968); (b) 1-methylpentadienylpotassium,  $\sim 100\%$  Z, G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *ibid.*, 88, 1377 (1969); H. Kloosterziel and J. A. A. van Drunen, *ibid.*, 89, 270 (1970); (c) 1-methylpentadienyllithium, 45% Z, D. E. Potter, Ph.D. Thesis, University of Arizona, 1969; (d) 1-methylpentadienyllithium, 96% Z, W. T. Ford and M Newcomb, J. Amer. Chem. Soc., 96, 309 (1974); (e) 1-methylpentatienyllithium, 80% Z, H. Kloosterziel and J. A. A. van Drunen, Recl. Trav. Chim. Pays-Bas, 88, 1471 (1969); (f) 1-neopentylallyllithium, 57% Z, W. H. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, J. Organometal. Chem., 51, 13 (1973), and earlier papers in this series. (4) E. R. Dolinskaya, I. Ya. Poddubnyi, and I. Yu. Tsereteli, Dokl.

(4) D. R. Doniskaya, I. Fa. Foldbory, and I. Fu. Tserfell, Dox.
 *Akad. Nauk SSSR*, 191, 862 (1970).
 (5) D. Seyferth and T. F. Jula, J. Organometal. Chem., 8, P13 (1967).

(5) D. Seyferth and T. F. Jula, J. Organometal. Chem., 8, P13 (1967). (6) Metalations with this reagent have yielded allylithium and 2alkylallyllithiums, e.g., R. J. Crawford, W. F. Erman, and C. D. Broaddus, J. Amer. Chem. Soc., 94, 4298 (1972); S. Akiyama and J. Hooz, Tetrahedron Lett., 4115 (1973). Metalation derivatization of  $\alpha$ -olefins involving 1-alkylallyllithium intermediates has been employed by C. D. Broaddus, Abstracts of the 159th American Chemical Society Meeting, Houston, Texas, Feb 22–27, 1970, Division of Petroleum Chemistry, No. 91, and W. L. Mock, private communication, but the lithiated intermediates were not studied.

(7) D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner J. Amer. Chem. Soc., 95, 7075 (1973), and references therein.

bond has been frozen out.<sup>4,8</sup> The Z nature of the predominant isomer is shown by the relatively small magnitude of  $J_{\beta\gamma}$  (10.2 Hz; cf. 8.7–10.2 Hz in related ionic Z anions and 13.4–14.3 Hz in related ionic E anions<sup>3</sup>). The amount of E isomer is difficult to estimate accurately from the  $\beta$ -proton absorption due to partial overlap, but in dimethyl ether the  $\alpha$  and  $\delta$  absorptions of the minor isomer are well resolved and show ~15% of the minor isomer to be present.<sup>4</sup>

Alkylation results correlate well with these pmr findings. When a solution of crotyllithium in TMEDAhexane prepared as described above was added at  $-78^{\circ}$ to excess *n*-butyl bromide, the resulting C<sub>8</sub> alkene mixture was 46% Z-2-octene, 8% E-2-octene, and 46% 3methyl-1-heptene.<sup>9</sup>

These findings contrast with the report that in dimethyl ether the equilibrium mixture contains mostly *E*crotyllithium (II),<sup>4</sup> with stereochemical assignments based on an interpretation of small chemical shift differences. These chemical shift arguments are evidently unreliable, since they give the answer opposite to that derived from the generally employed<sup>3a-f</sup> method of coupling constant differences used above.

The 85% value of Z-crotyllithium (I) at equilibrium is higher than that found for NAL ( $57\%^{3f}$ ), presumably because in the latter the attractive interaction in the Z isomer<sup>10</sup> is partially offset by a larger steric interaction. It is close to most of the values found for 3-substituted 1-methylallyl anions<sup>3a-e</sup> and is sufficiently high that it can indeed serve as the major cause for the rapid basecatalyzed isomerization of 1-butene to Z-2-butene.<sup>2</sup>

Acknowledgment. We thank the National Science Foundation for financial support (Grants GU-1534 and GP-21115).

(8) Analogous appearance of such terminal protons at low temperature has been used to indicate the ionic nature of pentadienyllithium (R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967)), allyllithium (P. West, J. I. Purmort, and S. V. McKinley, *J. Amer. Chem. Soc.*, **90**, 797 (1968)), and polybutadienyllithium (M. Morton, R. D. Sanderson, and R. Sakata, *J. Polymer Sci.*, *Part B*, **9**, 61 (1971)).

(9) Analyzed by gc and pmr comparisons with authentic material from Chemical Samples Co.

(10) Of the many rationalizations of this effect, the most convincing involves increased 1,4-electronic attraction in the Z-isomer: R. Hoff-mann and R. A. Olofson, J. Amer. Chem. Soc., 88, 943 (1966); I. Elphimoff-Felkin and J. Huet, C. R. Acad. Sci., Ser. C, 268, 2210 (1969); J. R. Grunwell and J. F. Sebastian, Tetrahedron, 27, 4387 (1971); N. D. Epiotis, D. Bjorquist, L. Bjorquist, and S. Sarkanen, J. Amer. Chem. Soc., 95, 7558 (1973).

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## Stereochemical Control of Valence. II. The Behavior of the {MNO}<sup>n</sup> Group in Ligand Fields<sup>1</sup>

Sir:

It is well-known that M-N-O angles ranging from 120 to 180° occur in mononitrosyl complexes.<sup>2</sup> Both valence-bond concepts<sup>3</sup> and molecular orbital con-

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(3) (a) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson,

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