(II). This is in agreement with the experimental results available in the literature,[5] where no evidence can be found to consider that β-arylthio radicals are bridged.

Compound I could be formed by further substitution on II, but when II was allowed to react under the conditions of the Fenton reaction, no I was identified in the reaction mixture.

Experimental Section

2-(*p*-Bromophenylthio)furan (II). To a solution of *n*-butyllithium [prepared from *n*-butyl bromide (2.29 g) and lithium (0.297 g) in dry ether] was slowly added at −30° 2-iodofuran[6] (3.68 g) in dry ether. The solution was allowed to reach ambient temperature and stirred for 2 hr. The reaction mixture was then cooled again at −70° and 4,4′-dibromodiphenyl disulfide (8.04 g) in dry ether was added. The reaction mixture was left overnight without further cooling, then hydrolyzed with HCl (10%). From the ethereal layer, after concentration and vacuum distillation, was obtained 2-(4-bromophenylthio)furan (3.1 g), bp 120° (0.5 mmHg). Anal. Calcd for $C_{10}H_7BrOS$:C, 47.07; H, 2.77; S, 12.57; Br, 31.32. Found: C, 47.8; H, 3.0; S, 12.8; Br, 32.0.

Oxidation with H_2O_2 in acetic acid gave the corresponding sulfone, mp 123–124°. Anal. Calcd for $C_{10}H_7BrO_3S$: C, 41.81; H, 2.44; S, 11.15; Br, 27.87. Found: C, 41.7; H, 2.3; S, 11.3; Br, 27.6.

In the same way (from *n*-butyllithium, 3-iodofuran,[7] and 4,4′-dibromodiphenyl disulfide) was prepared 3-(*p*-bromophenylthio)furan, bp 110° (0.5 mmHg) (Anal. Found: C, 47.5; H, 2.81; S, 12.8; Br, 31.12.) and the corresponding sulfone, mp 121–123°.

2,5-Bis(*p*-bromophenylthio)furan. 2,5-Bis(chloromercury)furan[8] (14.7 g) was suspended in dry chloroform (500 ml) and 4-bromosulfenyl chloride[9] (17.8 g) in chloroform (50 ml) was added under vigorous stirring. The mixture was refluxed for 20 min and then washed with water. The dry organic layer was concentrated and the residue was purified by column chromatography on silica gel; 5.0 g of the product, mp 89–90°, was obtained. Anal. Calcd for $C_{16}H_{10}Br_2OS_2$: C, 43.45; H, 2.28; S, 14.5; Br, 36.12. Found: C, 43.5; H, 2.3; S, 14.1; Br, 36.0.

2,3-Bis(*p*-bromophenylthio)furan. A mixture of 3,4-dibromo-2-furoic acid[10] (3 g), copper *p*-bromothiophenate[11] (6.27 g), chinoline (60 ml), and pyridine (5 ml) was stirred at 200–210° for 3 hr. The mixture, originally yellow-orange, turns green, then becomes homogeneous.

To the cooled solution was then added 10% hydrochloric acid (300 ml) and the mixture was extracted with benzene.

Chromatography on silica gel of the concentrated organic layer gave 0.8 g of an oil (Anal. Calcd for $C_{16}H_{10}Br_2OS_2$: C, 43.15; H, 2.28; S, 14.5; Br, 36.08. Found: C, 43.8; H, 2.3; S, 14.5; Br, 36.4.) which was directly oxidized with H_2O_2 in acetic acid to the corresponding disulfone, mp 182–184°. Anal. Calcd for $C_{16}H_{10}Br_2O_5S_2$: C, 37.96; H, 1.99; Br, 31.57. Found: C, 38.0; H, 1.97; Br, 31.7.

Fenton Reaction. To a mixture of furan (70 ml), *p*-bromothiophenol (3.8 g), *tert*-butyl alcohol (40 ml), and water (15 ml) was slowly added an aqueous solution of $FeSO_4 \cdot 7H_2O$ (6.2 g) and concentrated H_2SO_4 (2.2 ml), then, under vigorous stirring, 5.1 ml of 30% H_2O_2 during 1 hr, the temperature of the reaction mixture being 5–10°. The reaction mixture was left overnight at room temperature, then extracted with ether. From the ethereal solution was removed the unreacted thiophenol (3 g) by washing with 10% NaOH.

The residue was chromatographed on silica gel. The following products were separated and identified by analysis and comparison of spectral data (ir, NMR) with those of authentic models: 4,4′-dibromodiphenyl disulfide (0.56 g), 2(*p*-bromophenylthio)furan (0.1 g), and 2,3-bis(*p*-bromophenylthio)furan (0.4 g). The latter product was oxidized to a sulfone, mp 182–184°, identical with that obtained in the previously described independent synthesis. No 2,5-bis(*p*-bromophenylthio)furan or 3-(*p*-bromophenylthio)furan were identified in the reaction products.

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Registry No.—I, 53906-92-6; I disulfone, 53906-93-7; II, 53906-94-8; II sulfone, 53906-95-9; III, 5335-84-2; furan, 110-00-9; *p*-bromophenylthio radical, 31053-90-4; 3-(*p*-bromophenylthio)furan, 53906-96-0; 3-(*p*-bromophenylsulfonyl)furan, 53906-97-1; 2,5-bis(*p*-bromophenylthio)furan, 53906-98-2.

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The Anionic Addition of Dimethylamine to Isoprene

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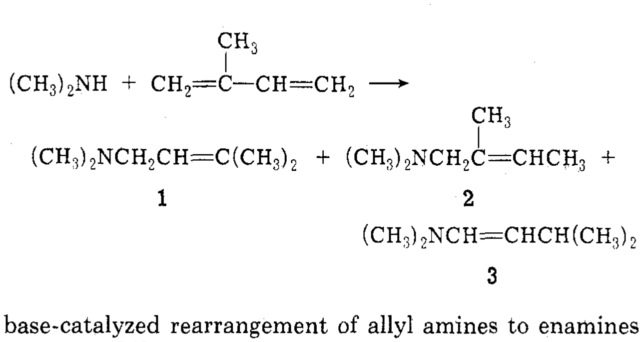
The alkali metal catalyzed anionic addition of amines and ammonia to olefins and conjugated dienes affords an excellent route to alkyl-substituted amine systems.[1–9] Yields as high as 76% have been reported with various amines and olefins using lithium, sodium, or potassium metal or their corresponding hydrides.[6,9] Butyllithium has been employed to form the lithium amide intermediate, which readily adds to both vinyl aromatics and conjugated dienes.[1] The use of sodium metal for the addition of amines to conjugated dienes has been studied extensively. In fact, the sodium-catalyzed addition of dimethylamine to isoprene was originally reported to give 95% *N*,*N*,3-trimethyl-2-butenylamine (**1**) and 3% of an enamine.[4] However, subsequent investigations have shown that the formation of *N*,*N*,2-trimethyl-2-butenylamine (**2**) and 4% of an unidentified material, presumably **3**, also occurred.[10,11] Since the base-catalyzed rearrangement of allyl amines to enamines is known,[12,13] the formation of **3** under these conditions is not unlikely. In fact, the presence of **3** in the reaction mixture has been confirmed by the isolation of the 2,4-dinitrophenylhydrazone of isovaleraldehyde from the acid hydrolysis of the reaction mixture and the sodium-catalyzed rearrangement of **1** to **3** has been studied.[13] This anionic addition presented an interesting problem in the possible control of the ratio of 1,4-addition product to 4,1-addition products, which are formed during the reaction, by changing the alkali metal catalyst used.



$$(CH_3)_2NH + CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow \underset{\mathbf{1}}{(CH_3)_2NCH_2CH{=}C(CH_3)_2} + \underset{\mathbf{2}}{(CH_3)_2NCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_3} + \underset{\mathbf{3}}{(CH_3)_2NCH{=}CHCH(CH_3)_2}$$

The sodium-catalyzed addition of dimethylamine to isoprene was conducted and gave three product peaks when the reaction mixture was analyzed by GLC. The major component, *N*,*N*,3-trimethyl-2-butenylamine (1), had a boiling point of 120° and was obtained in about 70% yield but always contained about 7% of **3** that could not be separated by distillation. The NMR spectrum of 1 had a triplet centered at 5.3 ppm for the lone vinyl proton, a doublet at 2.9 ppm for the methylene between the vinyl group and the nitrogen, a singlet at 2.2 ppm for the amino methyls, and two singlets at 1.8 and 1.7 ppm for the vinylic methyls. The shift in one of these methyl absorptions is due to its being cis to the dimethylamino moiety.

Compound 2 had a boiling point at 76° and was isolated GC pure in 23% yield by spinning band distillation. The NMR spectrum of 2 had a multiplet for the lone vinyl proton centered at 5.4 ppm, a singlet at 2.9 ppm for the methylene protons between the vinyl group and the nitrogen, a singlet at 2.15 ppm for the amino methyls, a singlet at 1.6 ppm for one vinylic methyl, and a doublet at 1.55 ppm for the other vinylic methyl. The latter is partially obscured by the absorption for the other vinylic methyl. Although the nature of the sterochemistry about the double bond cannot be assigned from this data, the cis product is expected because of the nonpolar nature of the reaction media.[1]

In our experiments 3 could not be separated from 1 either by spinning band distillation or by preparative gas chromatography.

Our specific interest in maximizing the yield of 1 led us to investigate the effects of various alkali metal catalysts[9] on the product ratio for this reaction. These results are summarized in Table I.

Table I
Alkali Metal Catalyzed Additions of Dimethylamine to Isoprene

Metal	Addition temp, °C	Addition time, hr	Reaction time, hr[b]	Product percentage[a]			Total yield, %
				1	2	3	
Potassium	22–24	1.5	4	64.4	32.2	3.5	70
Sodium	0	2.5	1	71.8	22.4	4.0	90
Sodium	20–30	3		75.0	21.0	4.0	92[e]
Lithium	0	2	16	76.3	14.7	8.9	70
Lithium	0	6	14	74.2	18.1	7.7	72
Lithium	22–25	2	3	76.6	16.6	6.8	70
Lithium[c]	0	2	14	66.3	20.7	13.1	12
Lithium[d]	23–25	2	3	76.5	13.9	9.6	71

[a] Determined by GLC on a 12 ft × 0.25 in. stainless steel column packed with 15% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W at 60°. [b] Time at room temperature. [c] Lithium dimethylamide prepared from lithium metal and then isoprene added. [d] Tetramethylethylenediamine added to activate the lithium amide. [e] Reference 10.

The yield of 4,1-addition products in this reaction can be thought of as the total of the amounts of 1 and 3, since 3 arises from 1 by anionic rearrangement.[13] Thus, the amount of 4,1-addition increases along the series K < Na < Li under the same reaction conditions, which is in the same order as the increasing tightness of the metal–amide ion pair in nonpolar media. The addition of a small amount of tetramethylethylenediamine to the lithium-catalyzed reaction produced a slight increase in the percentage of 4,1 products from 83.4 to 86.1%. Since detailed kinetic studies of the reaction were not undertaken, mechanistic implications of the data in Table I have not been considered.

Total yields were lower when both potassium and lithium were used as catalysts than when sodium was used. With potassium, the low yield was the result of low conversion, which was shown by a large isoprene peak in GLC analysis, while with lithium, a large amount of a white solid was formed. The infrared spectrum of the white solid was compared to that of an authentic sample of polyisoprene and was found to be identical.

When lithium was used as a catalyst, long room-temperature reaction times resulted in increased amounts of **3.** Longer addition times at lower temperatures seemed to give increased amounts of **2.** These results would be consistent with the need for amine coordination with the metal–amide for enhancement of 4,1-addition. These addition reactions were performed by adding the dimethylamine to a suspension of the metal in isoprene. When lithium dimethylamide was prepared first and the isoprene added to the reaction mixture, only a low total yield of product was obtained that contained large amounts of **2** and **3.**

In conclusion, the ratio of 1,4-addition product to 4,1-addition products from the anionic addition of dimethylamine to isoprene was altered by changing the alkali metal catalyst. A higher yield of 4,1-addition products was realized when lithium metal was used but the total product yield was lower owing to the concurrent formation of polyisoprene. The best total yield of product was obtained using sodium and very low conversions were realized with potassium.

Experimental Section

Gas chromatography was performed on a Perkin-Elmer Model 900 chromatograph using a 12 ft × 0.25 in. stainless steel column packed with 15% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W. The NMR spectra were run on a Jeol JNM-MH-100 100-MHz spectrometer. Distillations were carried out on a Nester-Faust Auto Annular Teflon Spinning Band Distillation column.

Anionic Addition of Dimethylamine to Isoprene. The general procedure that was followed was to weigh 34 g (0.5 mol) of freshly distilled dry isoprene and 0.015 mol of the alkali metal into a three-necked flask equipped with a magnetic stirrer, thermometer, and Dry Ice condenser and add 22.5 g (33.0 ml, 0.5 mol) of dimethylamine (J. T. Baker) slowly by bubbling it through the reaction mixture. The reaction temperature was controlled as desired by the use of an ice–methanol bath. After the addition was complete, the reaction mixture was stirred at room temperature to complete the reaction. The conditions are summarized in Table I. After the reaction was complete, the product ratio was measured by GLC. In one case (sodium catalyst), the product was distilled on a Teflon spinning bond column to obtain **1,** bp 120° (lit.[13] bp 114–118°), and **2,** bp 76°.

Registry No.—1, 17945-72-1; **2,** 40267-41-2; **3,** 18495-55-1; dimethylamine, 124-40-3; isoprene, 78-79-5; potassium, 7440-09-7; sodium, 7440-23-5; lithium, 7439-93-2.

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