

## Stereospecific Dehalogenation of *vic*-Dibromides by Sodium Naphthalenide<sup>1</sup>

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Received June 23, 1971

The mechanism of the reaction of the naphthalene radical anion with organic halides has been shown to exhibit radical as well as carbanionic character.<sup>2-4</sup> Of synthetic interest is the observation that sodium naphthalenide serves as a convenient and efficient reagent for the dehalogenation of *vic*-dihalides to give olefins.<sup>5</sup> Since two-electron reductants result in stereospecific, while one-electron reductants in stereoselective, dehalogenation of *dl*-stilbene dibromides,<sup>6</sup> it was of synthetic as well as mechanistic interest to examine the stereochemical course of the dehalogenation of *meso*- and *dl*-stilbene dibromides by sodium naphthalenide.

When these dibromides are treated with an excess of sodium naphthalenide in dimethoxyethane (DME) and the reaction mixtures, after quenching with methanol, are submitted to glpc analysis, a complex product mixture is detected, consisting of *cis*- and *trans*-stilbene,  $\alpha$ -bromostilbene, diphenylacetylene, and bibenzyl. These products are formed in variable proportions depending on the reaction conditions, such as concentrations, proportion of the reagents, and reaction time. Clearly, dehydrobromination into  $\alpha$ -bromostilbene and diphenylacetylene competes with the expected debromination to give *cis*- and *trans*-stilbene. However, the formation of bibenzyl suggests immediately that the stilbenes and diphenylacetylene themselves react with the excess sodium naphthalenide leading to this reduction product after methanolysis. Indeed, a control experiment reveals that *cis*-stilbene is rapidly isomerized to *trans*-stilbene, while extended exposure of *trans*-stilbene to sodium naphthalenide produces bibenzyl after methanolysis. Furthermore, it is known that diphenylacetylene is converted to *cis*- and *trans*-stilbene on treatment with alkali metals.<sup>7</sup>

In view of these complications, we abandoned the stilbene system and instead examined the dehalogenation of *erythro*- and *threo*-2,3-dibromo-3-methylpentane (1a and 1b), respectively. The *erythro*-dibromide 1a of 78.6% isomeric purity was prepared from (*Z*)-3-methyl-2-pentene (4a) by the stereospecific addition of bromine. Similarly, the *threo*-dibromide 1b of 87.6% isomeric purity was available from the (*E*)-3-

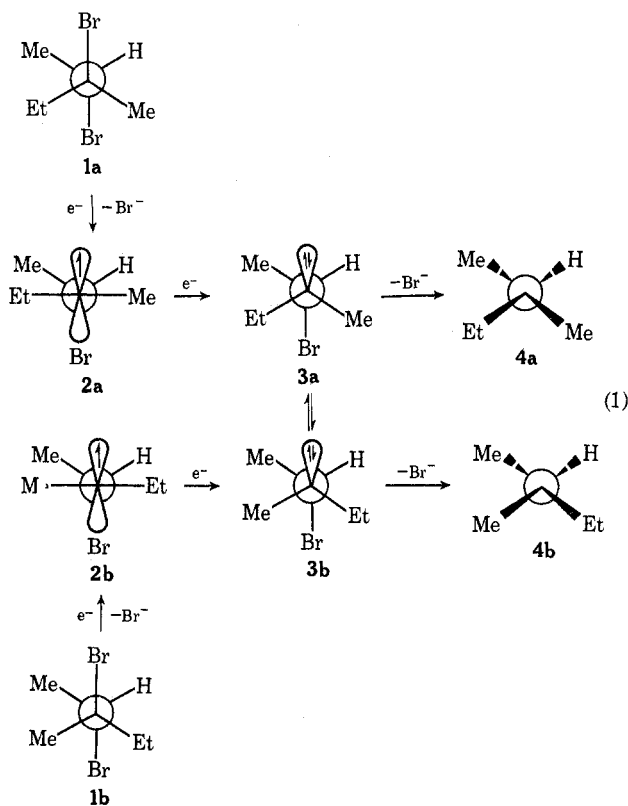
methyl-2-pentene (4b). Control experiments showed that the stoichiometry of the reaction is 2 mol of sodium naphthalenide per mole of dibromide. More important, olefins 4a and 4b do not isomerize with sodium naphthalenide. The results of the dehalogenations are summarized in Table I.

TABLE I  
STEREOCHEMICAL COURSE OF THE REACTION OF  
*erythro*- AND *threo*-2,3-DIBROMO-3-METHYLPENTANE  
WITH SODIUM NAPHTHALENIDE IN DME

Reactant mixture <sup>a</sup>		Product mixture <sup>b</sup>		% <i>trans</i> elimination <sup>c</sup>
<i>erythro</i> - (1a)	<i>threo</i> - (1b)	( <i>Z</i> )- (4a)	( <i>E</i> )- (4b)	
12.2	87.8	15.6	84.3	92.2 ± 0.6
22.2	77.8	23.0	77.0	
78.6	21.4	61.9	38.1	75.6 ± 1.4
79.9	20.1	60.0	40.0	

<sup>a</sup> Determined by glpc using a 12 ft × 0.125 in. stainless steel column packed with 25% Apiezon M on 60-80 mesh Chromosorb P and operated at a column temperature of 125° and a helium flow of 25 ml/min. <sup>b</sup> Determined by glpc using a 24 ft × 0.125 in. stainless steel column packed with 20% Apiezon M on 60-80 mesh Chromosorb P and operated at a column temperature of 40° and a helium flow of 40 ml/min. <sup>c</sup> Calculated according to the equation,  $E = tT + eC$ , where  $E$  is % *E* olefin,  $t$  is % *threo*-dibromide,  $e$  is % *erythro*-dibromide,  $T$  is % *trans* elimination from *threo*-dibromide and  $C$  is % *cis* elimination from *erythro*-dibromide; four sets of experimental values of  $e$ ,  $t$ , and  $E$  are given in the first, second, and fourth columns.

We conclude that the reaction of *vic*-dibromides 1a and 1b with sodium naphthalenide is a two-electron trans elimination, with a stereospecificity of 75.6 ± 1.4% for the *erythro* and 92.2 ± 0.6% for the *threo* isomer. On the basis of our results and previous work<sup>2-4,8</sup> we suggest that the mechanism (eq 1) for



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this reaction involves first the formation of the radicals **2a** and **2b**, respectively, from **1a** and **1b**. Before radicals **2a** and **2b** interconvert to any appreciable extent, they react with the second mole of sodium naphthalenide to produce the respective carbanions **3a** and **3b**. The rate of electron transfer between the naphthalene radical anion and free radicals is virtually diffusion controlled, since the reaction of optically active cyclopropyl bromides affords the respective cyclopropane with net retention.<sup>8</sup> In addition, radicals **2a** and **2b** might be expected to be stabilized by bridged structures involving the neighboring bromine and thus be prevented from interconverting by bond rotation.<sup>9</sup>

Finally, the lower stereospecificity in the case of the *erythro*-dibromide **1a** vs. the *threo* isomer **1b** arises from a methyl-ethyl repulsion in carbanion **3a** vs. a methyl-methyl repulsion in carbanion **3b**. Consequently, for **3a** bond rotation competes more effectively with trans ejection of the bromine than for **3b**.

#### Experimental Section

Sodium naphthalenide was prepared according to the procedure of Scott<sup>10</sup> by dissolving 23 g (1.0 g-atom) of clean sodium metal in 1000 ml of dimethoxyethane (freshly distilled from the benzophenone ketyl radical) containing 134 g (1.0 mol) of naphthalene. The dark green solution was standardized by removing 2.0 ml of the stock solution by means of a calibrated syringe and quenching with 1.0 ml of methanol. The pale yellow solution was titrated with 0.100 *N* hydrochloric acid using methyl red as indicator.

*erythro*-2,3-Dibromo-3-methylpentane (**1a**) was obtained in 34% yield (79.9% isomeric purity by glpc), bp 74° (12 mm),  $n_D^{20}$  1.5126 [lit.<sup>11</sup> 79.5° (16 mm)], using the method of van Risseghem,<sup>11</sup> starting with 5.02 g (0.0597 mol) of (*Z*)-3-methyl-2-pentene [Columbia Organic, bp 67.5° (758 mm),  $n_D^{20}$  1.4021] and 9.6 g (0.060 mol) of bromine.

*threo*-2,3-Dibromo-3-methylpentane (**1b**) was obtained in 36% yield (78.6% isomeric purity by glpc), bp 75° (14 mm),  $n_D^{20}$  1.5121 [lit.<sup>11</sup> 75° (15 mm)], using the method of van Risseghem,<sup>11</sup> starting with 5.02 g (0.0597 mol) of (*E*)-3-methyl-2-pentene [Columbia Organic, bp 70° (758 mm),  $n_D^{20}$  1.4050] and 9.6 g (0.060 mol) of bromine.

**General Method of Dehalogenation.**—A 5-ml vial, capped with a rubber septum and supplied with a spinbar, was charged under a nitrogen atmosphere with 1.0 ml of a 2 *M* solution of the dibromide in DME (freshly distilled from the benzophenone ketyl radical). While stirring magnetically, a stoichiometric (2 mol of naphthalenide per mole of dibromide) amount of the standardized sodium naphthalenide solution was added through the rubber septum by means of a syringe. The colorless reaction mixture was stirred for 60 sec, quenched with 0.5 ml of methanol, and centrifuged to remove the sodium bromide precipitate. The supernatant liquid was submitted to glpc analysis. The results are summarized in Table I.

**Registry No.**—**1a**, 32675-17-5; **1b**, 32675-18-6; sodium naphthalenide, 12521-84-5.

**Acknowledgments.**—Financial aid by the Petroleum Research Fund, the National Science Foundation, and the Sloan Foundation is gratefully appreciated.

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### Marked Differences between the Sodium-Ammonia and Calcium-Ammonia Reduction of Nitriles

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Received July 1, 1971

The reduction of nitriles with the alkali metals has been reported under a variety of conditions.<sup>1-11</sup> Normally the product isolated is the corresponding amine or the hydrocarbon resulting from reductive decyanation, a reductive fission process.<sup>12</sup> Recently, Arapakos, *et al.*, using sodium-ammonia or lithium-ethylamine solutions, found that tertiary nitriles give exclusive reductive decyanation products, whereas primary and secondary nitriles give both the expected amine as well as decyanation products.<sup>10,11</sup> In particular, dodecyl cyanide was reduced to dodecane (35%) and tridecylamine (65%).<sup>11</sup>

While working on another problem it became necessary to learn the fate of various aliphatic nitriles in the presence of calcium-ammonia solutions. For a direct comparison to the results reported for the alkali metal-ammonia or amine reductions,<sup>10,11</sup> dodecyl cyanide was chosen for the initial studies with calcium-ammonia solutions. In the presence of this reducing medium, dodecyl cyanide gave trace amounts of dodecane. Tridecylamine was the major product, accompanied by small amounts of 1-dodecyl-1-amino-tridecane. Because of the marked difference in the amount of reductive decyanation found using calcium-ammonia solutions in comparison to the results reported using sodium-ammonia or lithium-ethylamine solutions,<sup>10,11</sup> other nitriles were reduced by addition of the nitrile to a heterogeneous solution of isooctane, calcium, and ammonia to see if this observation was a general phenomenon.

The results are shown in Table I. For convenience, the more volatile amines were isolated as derivatives from the isooctane solutions after removal of ammonia and represent the minimum amount of amine actually produced. No effort was made to measure the hydrocarbons or HCN produced by reductive fission due to the solvent used, the method of work-up and the *pyrophoric nature* of the calcium residues.

The alkali metal-ammonia or amine reductions of primary, secondary, and tertiary nitriles give increasing quantities of decyanation products (hydrocarbon

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