

## Dehalogenation of Vicinal Dihalides. Exceptional Utility of Dihydroarylides

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DEHALOGENATIONS leading to substituted cyclobutenes, the valence tautomer of cyclo-octatetraene,<sup>1</sup> and "hemi-Dewar naphthalene,"<sup>2</sup> have been effected by treatment of corresponding *vic*-dibromides with disodium dihydrophenanthrenedi-ide. We find that sodium dihydronaphthylide and sodium dihydrobiphenylide are effective in similar cyclobutene-producing reactions, for example, the conversion of (I) illustrated. More important, the dehalogenations proceed in very high yield, even in cases where other reagents, both reductive and nonreductive, lead to much lower yields, often through less convenient procedures or longer reaction times.<sup>3,4</sup> The method is also

highly successful for reactions producing simple, unstrained olefins (Table).

The mechanistic details of reactions of sodium dihydronaphthylide with alkyl halides have been investigated,<sup>5</sup> but similar reactions with dihalides have not. Sodium dihydronaphthylide, however, is finding increasing use as a synthetic reagent,<sup>6</sup> partially because it forms homogeneous solutions in polar ethers. Surface adsorption is therefore not required and subsequent surface reactions, perhaps leading to undesired materials, do not occur. Its reactions are often extremely rapid, even at low temperatures.

Solutions of sodium dihydronaphthylide were prepared

Sodium dihydronaphthylide<sup>a</sup> dehalogenation of vicinal dihalides

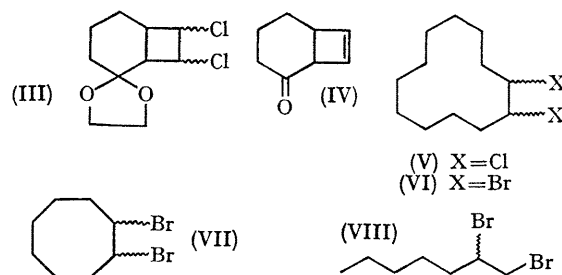
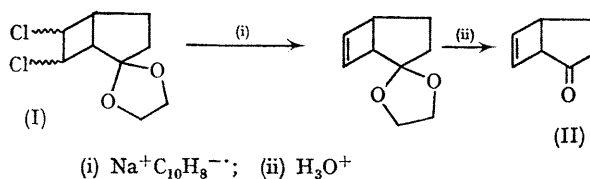
Compound	Product	Isomer	Yield (v.p.c.) <sup>d</sup>	Yield (dist.)
(I) <sup>b</sup>	(II) <sup>c</sup>	<i>cis</i>	96% <sup>c</sup>	78%
(III)	(IV)	<i>cis</i>	81 <sup>c</sup>	68
(V)	cyclododecene	<i>cis-trans</i>	92	
(VI)	cyclododecene	<i>cis-trans</i>	>90	
(VII)	cyclo-octene	<i>cis</i>	>90	
(VIII)	hept-1-ene		>90	

<sup>a</sup> Sodium dihydrobiphenylide [Corco Chemical Corporation, Tyburn Road and Cedar Lane, Fairless Hills, Pennsylvania 19030], gives similar results in those samples tested; <sup>b</sup> a mixture of all four isomers; <sup>c</sup> after hydrolysis of the acetal; <sup>d</sup> yields were determined with a Varian Aerograph 1200 flame-ionization apparatus equipped with a 5 ft., 10% SE-30-Chromosorb W column and a Varian Model 475 digital integrator.

by two methods: (i) for preparation of small amounts of material [up to about 5 mmoles at >0.1M] the method described earlier<sup>5a,d</sup> was found to be convenient, (ii) concentrated solutions were prepared for large-scale reactions [up to 0.2 mole at about 0.4M] by stirring the required amount of clean sodium metal with a solution containing a 2–10 fold excess of naphthalene in dry dimethoxyethane for 24–48 hr. at room temperature. Water, oxygen, and carbon dioxide must, of course, be rigorously excluded. Sodium dihydronaphthylide solutions were not standardized since, in all cases, an excess of reagent was used; the dark green reagent serves as its own indicator in the event that an insufficient amount is used. Solutions more concentrated than 0.1M must be filtered to remove small amounts of sodium metal to avoid serious diminution of yields in some cases. Sodium metal reacts with (I) to give apparently polymeric materials, but not with (II). Sodium dihydrobiphenylide may be prepared in the same way.

The elimination reaction is illustrated by the conversion of (III) into (IV). The dichloroacetal (III) was prepared by the method of House and Cronin.<sup>3</sup> A sodium dihydronaphthylide solution was prepared by stirring naphthalene (25.6 g., 0.4 mole) and clean sodium (2.30 g.) in dry dimethoxyethane (*ca.* 500 ml.) at room temperature for 24 hr. under dry nitrogen. The solution was then filtered through a coarse sintered glass disc into a three-necked flask (1 l.) fitted with a nitrogen source, addition funnel, and stirrer. To the filtrate a solution of dichloroacetal (III) (3.86 g. 0.016 moles in dimethoxyethane (40 ml.) was added during 2 hr. Excess of reagent was destroyed by flushing the flask with oxygen, to leave an orange, cloudy solution. The bulk of the solvent was removed under reduced pressure and the residue, a red oil (75 ml.), was dissolved in ether and stirred for 1 hr. with 3N-HCl (500 ml.). The organic layer

was then separated, washed with sodium hydrogen carbonate, and dried. The ether was removed and the residue was chromatographed twice on silica gel (200 g. each time); the naphthalene was eluted with pentane and the ketone (IV) with ether-pentane. The ketone-containing fractions were combined and distilled, b.p. 71–75°/8.5 mm., to yield (IV) (1.28 g., 68%) identified by i.r., n.m.r., u.v., and mass spectra.



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