Summary

1. The 5-(*p*-halobenzylamino)-9-diethylaminobenzo[a]phenoxazine chlorides and corresponding 5-allylamino compound have been prepared. The intermediates, N-(*p*-halobenzyl)-α-naphthylamines and N-(allyl)-α-naphthylamine, have been prepared.

2. The attempted preparation of N-(*p*-iodobenzyl)-α-naphthylamine by treatment of N-(*p*-aminobenzyl)-α-naphthylamine with nitrous acid and iodide was unsuccessful.

3. The reaction of 5-bromo-1-naphthylamine with 2-nitroso-5-diethylaminophenol does not yield a benzophenoxazine dye.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Reduction of Terminal Epoxides[1]

BY MELVIN S. NEWMAN, GERALD UNDERWOOD AND MARY RENOLL

Although the reduction of the epoxide function has been studied,[2] little systematic work has been done on the production of primary alcohols from terminal epoxides. The formation of *n*-propyl, *n*-butyl[3,4] and β-phenylethyl alcohols by catalytic reduction of the corresponding epoxide by hydrogen has been mentioned in the patent literature.

In this paper we report the successful reduction of 1,2-epoxydecane and of styrene oxide to the corresponding primary alcohols by catalytic methods. Reductions involving sodium amalgam and lithium aluminum hydride[5] gave mainly secondary alcohols and hence were not studied in detail.

TABLE I

REDUCTION OF 1,2-EPOXYDECANE AND STYRENE OXIDE

	Reaction conditions	T, °C.	Pr (p. s. i.)	n^{20}D[a]	Epoxide	Analyses,[b] % Sec. alc.	Pri. alc.
		1,2-Epoxydecane					
1	Raney nickel[c]	20	37	1.4292	+[d]		
2	Raney nickel[c] (large amount)[e]	20	15	1.4355			+[d]
3	Platinic oxide (Adams)	20	37	1.4289	+[d]		
4	Raney nickel[c]	150	900	1.4362	5	10	83[g]
5	Raney nickel[f]	150	900	1.4360	<5	<10	90
6	Raney nickel[c] + 0.01 g. NaOH	150	900	1.4353	5	10	85
7	Raney nickel[c] + 0.1 g. NaOH	150	900	1.4347	5	85	7.5[g]
8	Raney nickel[f] + 0.1 g. NaOH	150	900	1.4343	<5	95	<5
9	Raney nickel[c] + 0.1 g. H_3PO_4[h]	150	900	1.4359	<5	50	50[g]
10	Raney nickel[f] + 0.1 g. H_3PO_4[h]	150	1100[i]	1.4354	<5	50	50
11	Raney nickel[f]	25	1000	1.4298	+[d]		
12	Ni-on-kieselguhr (UOP)	200	1450	1.4358	5	10	85
13	Sodium amalgam				60	35	5
14	Lithium aluminum hydride				10	90	
Standards	1,2-Epoxydecane			1.4289			
	2-Decanol			1.4340			
	1-Decanol			1.4373			
		Styrene Oxide					
15	Raney nickel[c] and [f]	25	700	1.5309	0	0	100[g]
16	Raney nickel[c] and [f] + 0.1 g. NaOH	25	700	1.5317	0	0	100[g]
17	Raney nickel[c] + 0.1 g. H_3PO_4	25	700	1.5299	41[j]	0	75[h]
18	Raney nickel[f] + 0.1 g. H_3PO_4	25	700	1.5295	40	0	60[h]
19	Raney nickel[c]	150	700	1.4770[k]			

[a] The indices of refraction are those of the crude distillate obtained directly from the hydrogenation experiments. [b] The analytical results reported were carried out by Dr. J. J. Shipman of the B. F. Goodrich Co. using an infrared spectrophotometer. Calibration curves for pure 1-decanol, 2-decanol and 1,2-epoxydecane were obtained and synthetic

Our results are summarized in Table I. Of particular interest is the effect of small amounts of acidic or basic substances on the course of the reduction of 1,2-epoxydecane but *not* of styrene oxide. In the absence of such additives reduction

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[1] The work herein reported was carried out during 1946 and 1947 on research project 162 of the Ohio State University Research Foundation and was sponsored by the B. F. Goodrich Company of Akron, Ohio.

[2] Grignard, "Trâité de chime organique," Vol. VI, Masson et Cie, Paris, 1940, p. 286.

[3] Usines de Melle and H. M. E. Guinot, British Patent 496,264 (1938).

[4] I. G., German Patent 573,535 (1933).

[5] Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947); Finholt, Bond and Schlesinger, *ibid.*, **69**, 1199 (1947).

mixtures analyzed by comparison with the standard curves at suitable wave lengths. The values cited are approximate only. We have checked several results qualitatively by formation of the phenyl urethans. Our qualitative results checked the infrared results about as well as could be expected. [c] Raney nickel prepared as described in "Organic Syntheses," Vol. XXI, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 15. [d] Presence of this component judged qualitatively either by n^{20}D and b. p. or by formation of phenyl urethan. [e] Attempted hydrogenolysis by adsorbed hydrogen as in desulfurization reactions. [f] Raney nickel prepared as by Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946). [g] Average of two identical runs, per cent. calculated from infrared analysis; see *b*. [h] Reductions with added phosphoric acid much more sluggish. [i] Higher pressure to attempt speedier reduction, however, still sluggish. [j] Some compound other than styrene oxide was also present. [k] At the higher temperature the ring reduced yielding cyclohexane derivatives.

gave mainly primary alcohol but in the presence of as little as 0.1 g. of acid or base in over 100 cc. of solution primary alcohol formation was markedly decreased.

Experimental

1-Decene was converted to 1,2-epoxydecane, b. p. 82-83.5° at 10 mm., by reaction with peracetic acid.[6] 1-Decanol, b. p. 111.5-113.5° at 11 mm., and 2-decanol, b. p. 104.5-106.0° at 13 mm., were prepared by treating *n*-octylmagnesium bromide with ethylene oxide and acetaldehyde. The corresponding phenylurethans melted at 58.5-59.5 and 37-38°.

A commercial sample of styrene oxide (Dow) was rectified to yield pure styrene oxide, b. p. 81.5° at 15 mm., n^{20}D 1.5350. Pure rectified α-phenylethyl alcohol, n^{20}D 1.5272, formed a phenylurethan which melted at 93-94° and pure rectified β-phenylethyl alcohol, n^{20}D 1.5325, formed a phenylurethan which melted at 78-79°.

General Procedure for Catalytic Reduction.—A mixture of 10 g. of 1,2-epoxydecane, 2.5 g. of wet catalyst (wet with absolute alcohol but containing 1 g. dry weight of catalyst), and 115 cc. of absolute alcohol was reduced in standard high pressure equipment. After reduction the catalyst was removed by filtration and washed well with solvent. The solvent was stripped and the residue was vacuum distilled without attempting fractionation. The entire distillate which usually amounted to 8.5 g. was weighed and its index of refraction determined. Part of the sample was then sealed in a glass ampoule and sent to the Goodrich Company for infrared analysis. In several cases the reaction mixture was treated with excess phenyl isocyanate and the melting point of the mixed phenylurethans taken. For runs which analysis indicated to consist of mainly primary alcohol there was no difficulty in isolating fairly good yields of the phenylurethan of the primary alcohol. The same was true for the phenylurethan of the secondary alcohol in mixtures rich in this compound. From reaction mixtures which analysis indicated a mixture of about equal parts, no pure urethan was isolated.

In the catalytic reductions involving styrene oxide conditions were the same as above except that only 100 cc. of alcohol was used.

Chemical Reduction of 1,2-Epoxydecane.—To a solution of 10 g. of epoxide in 100 cc. of water and 200 cc. of ethyl alcohol was added 500 g. of 3% sodium amalgam. After standing at room temperature for sixteen hours with occasional shaking and neutralization of excess alkali with carbon dioxide the product was isolated as above. The reduction, incomplete under these conditions, yielded mainly 2-decanol.

When 1,2-epoxydecane was treated with an equivalent amount of lithium aluminum hydride[5] in dry ether the product consisted exclusively of 2-decanol except for some unreacted epoxide.

Summary

On catalytic hydrogenation over Raney nickel 1,2-epoxydecane yields mainly 1-decanol. In the presence of small amounts of sodium hydroxide, however, mainly 2-decanol results. With sodium amalgam and lithium aluminum hydride 2-decanol is the main product.

Styrene oxide yields β-phenylethyl alcohol exclusively on catalytic reduction over Raney nickel either with or without added sodium hydroxide. The addition of phosphoric acid retards the reduction markedly and causes complications but primary alcohol is still the main product.

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[6] Swern, Billen and Scanlan, THIS JOURNAL, **68**, 1504 (1946).

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The Polymorphism of Saturated 1,3-Diglycerides

BY F. J. BAUR, F. L. JACKSON, D. G. KOLP AND E. S. LUTTON

Introduction

Malkin, Shurbagy and Meara[1] have described the polymorphism of both even and uneven monacid saturated 1,3-diglycerides of the series dicaprin through distearin. They have reported two sets of long spacings which give two straight lines if spacings are plotted against chain length. For the lower members, including dilaurin (LL) and dimyristin (MM), the greater long spacings were reported to be associated with short spacings of a type specified as "a"; the lesser long spacings were associated with short spacings of type "b." In the case of dipalmitin (PP) and distearin (SS) only the lesser long spacings were observed and these were associated, oddly, with "a" instead of "b" short spacings.

In the present paper are reported results of a reexamination of the even diglycerides, dilaurin through distearin, in the course of which two long spacing values were found uniformly for each compound, and the lesser and greater long spacings were respectively associated with "a" and with "b" type short spacings.

Experimental

The dipalmitin used in this study was prepared according to the directed rearrangement procedure described by Eckey and Formo.[2] Cottonseed oil stearin containing approximately 35% of saturated fatty acids was rearranged

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[1] Malkin, Shurbagy and and Meara, *J. Chem. Soc.*, 1409 (1937).

[2] Eckey and Formo, *J. Am. Oil Chem. Soc.*, **26**, 207 (1949).