## Reduction of Alkyl Esters to Alkanes by Sodium in Hexamethylphosphoric Triamide. A New Method for the Deoxygenation of Alcohols

By HENRI DESHAYES and JEAN-PIERRE PETE\*

(Laboratoire de Photochimie, Equipe de Recherche Associée au C.N.R.S. No. 688, U.E.R. Sciences F. 51062 Reims Cédex, France)

*Summary* Esters of primary, secondary, or tertiary alcohols are reduced by sodium in hexamethylphosphoric triamide containing t-butyl alcohol to provide predominantly the corresponding alkanes and alcohols.

IN our previous reports concerning the reduction of aliphatic esters to alkanes by photolysis in hexamethylphosphoric triamide (HMPA)-water,<sup>1</sup> we suggested that the radical (I) is an intermediate. In principle, such a species might also be



generated by protonation of a radical anion formed during the reduction of an aliphatic ester by a metal. Consistent with the proposition, we now report that treatment of a variety of alkyl esters with sodium in HMPA<sup>2</sup> containing t-

TABLE. Reduction of esters with Na-HMPA-Bu<sup>t</sup>OH.<sup>a</sup>

	Estor B2/(···)OB1b		% Yield	
Expt.	R <sup>1</sup>	<b>N</b>	<sup>R</sup> <sup>i</sup> H	R¹OH
1	Nonvl		56 <sup>e</sup>	d
<b>2</b>	Heptyl		$56^{\rm c}$	30
3	Cyclohexyl		$>40^{ m c}$	34°
4	Bornyl		$> 32^{ m c}$	37°
<b>5</b>	5α-Cholestan-3β-yl		69	20
6	Cholest-5-en-3β-yl		$65^{e}$	28f
7	4,4-Dimethyl-5α-		50	50
	cholestan-3 $\beta$ -yl		50	50
8p	$5\alpha$ -Cholestan- $3\beta$ -vl		30	70
9ь	$5\alpha$ -Cholestan- $3\beta$ -yl		52	<b>48</b>
10b	$5\alpha$ -Cholestan- $3\beta$ -vl		<b>45</b>	50
11 12	$3\alpha$ -Methyl- $5\alpha$ - cholestan- $3\beta$ -yl $3\beta$ -Methyl- $5\alpha$ -		$> 95^{ m g}$	
13 14	cholestan- $3\alpha$ -yl ) $3\alpha$ ,4,4-Trimethyl- $5\alpha$ - cholestan- $3\beta$ -yl $3\beta$ ,4,4-Trimethyl- $5\alpha$ - cholestan- $3\alpha$ -yl	}	>95s	

<sup>a</sup> Reductions were carried out at 25 °C. Typically a solution of the ester (1 g) in ether-Bu<sup>t</sup>OH (1:1; 5 ml) was added to a partial solution of sodium (1 g) in ether (5 ml)-HMPA (10 ml) at such a rate that the solution was never decolorized. When the addition was complete, the filtered solution was poured into ethanol. Usual work up procedures provided the indicated products. Unless otherwise indicated yields refer to pure isolated material. <sup>b</sup>  $\mathbb{R}^2$  = Me throughout except for expts. 8 ( $\mathbb{R}^2$  = H), 9 ( $\mathbb{R}^2$  = hexyl), and 10 ( $\mathbb{R}^2$  = Ph). <sup>c</sup> Determined by g.l.c. <sup>d</sup>Not determined. <sup>e</sup> 5 $\alpha$ -Cholestane. <sup>f</sup> 5 $\alpha$ -Cholestan-3 $\beta$ -ol. <sup>g</sup> The reduction is quantitative and the same hydrocarbon is isolated from the two epimers.

butyl alcohol as a proton source leads to formation of the corresponding alkanes and alcohols. Typical examples are summarized in the Table.



Reductions of tertiary esters give the corresponding alkane quantitatively whereas primary and secondary esters lead to mixtures of the corresponding alkanes and alcohols in good yield. Not only are the readily prepared acetates and benzoates reduced but other esters (expts. 8 and 9) are also reduced under these conditions. However, other functional groups including carbonyl and olefinic groups are competitively reduced. Thus the Na-HMPA-ButOH reagent appears to more general but less selective in the reduction of esters than lithium in ethylamine which is reported to reduce only esters of sterically hindered alcohols.3

In contrast to these results, reaction of esters with Na-HMPA in the absence of Bu<sup>t</sup>OH gives a higher proportion of alcohol.<sup>†</sup> This is consistent with alcohol and alkane formation proceeding from the initially formed radical anion, and alkane formation at least partly requiring the radical (I) as an intermediate. A possible mechanism for the reaction is in the Scheme, although further work is required before the mechanism can be defined exactly.

## (Received, 5th April 1978; Com. 362.)

 $\dagger$  In the absence of Bu<sup>t</sup>OH, 5 $\alpha$ -cholestane (>38%) and 3 $\beta$ -hydroxy-5 $\alpha$ -cholestane (58%) are isolated from 3 $\beta$ -acetoxy-5 $\alpha$ -cholestane, and heptane (33%) and heptan-1-ol (60%) from heptyl acetate.

<sup>1</sup> H. Deshayes, J. P. Pete, and C. Portella, Tetrahedron Letters, 1976, 2019; J. P. Pete, C. Portella, C. Monneret, J. C. Florent, and Q. Khuong Huu Synthesis, 1977, 774.
 <sup>2</sup> H. Normant, Bull. Soc. chim. France, 1968, 791; M. Larchevêque, Ann. Chim. (France), 1970, 129.

<sup>3</sup> R. B. Boar, L. Joukhadar, J. F. McGhie, S. C. Misra, A. G. M. Barrett, D. H. R. Barton, and P. A. Prokopiou, J.C.S. Chem. Comm., 1978, 68.