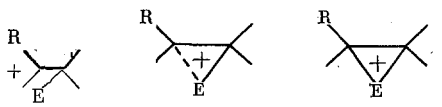
2. U. M. Dzhemilev, R. V. Kunakova, F. V. Sharinova, R. L. Gaisin, and G. A. Tolstikov, Summaries of Lectures at the First All-Union Conference on Organometallic Chemistry [in Russian], Part II, Moscow (1979), p. 323.
3. U. M. Dzhemilev, R. V. Kunakova, R. L. Gaisin, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2702 (1979).
4. R. V. Kunakova, R. L. Gaisin, G. A. Tolstikov, L. M. Zelenova, and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim., 2610 (1980).
5. U. M. Dzhemilev, R. V. Kunakova, R. L. Gaisin, G. A. Tolstikov, R. F. Talipov, and S. I. Lomakina, Zh. Org. Khim., 4, 763 (1981).
6. Houben-Weyl, Methods of Organic Chemistry [in German], Vol. 9, Stuttgart (1955), pp. 804, 290.

STEREOCHEMISTRY OF SULFENYLCHLORINATION OF β-DEUTEROSTYRENES

A. V. Borisov, A. I. Lutsenko, L. V. Chumakov, V. A. Smit, and I. V. Bodrikov

UDC 541.63:542.944+542.945.2:547.538.141

Changes in many fundamental characteristics of electrophilic addition reactions (AD_E-reactions) of alkenes are caused by difference in the degrees of participation of the reagent in the stabilization of the electron-deficient center of the transition state (TS) and (or) the intermediate [1-3]. In terms of a structural scheme, the degree of participation is usually reflected by the ratio of contributions to the addition reaction of the TS (intermediates) of open (I) and cyclic (II), (III) types



(I) (II) (III)

The stereochemical criterion of the passage of the Ad_E reactions through a TS (intermediates) of cyclic (II), (III), and open (I) forms, is considered to be trans-stereospecific and nonstereospecific addition, respectively. Most of the reactions of alkenes with sulfur-containing electriphiles proceed by the first of these paths.

A disturbance of the stereospecificity of the trans-addition of the electrophiles to the alkenes is usually related to the high electron-donor ability of the substituents attached at the reaction center, causing that the reaction proceeds through the TS (intermediates) of an open type.

However, the picture is complicated by the fact that the stereochemical regularities of the addition of the electrophiles to the double bonds was studied mainly on models of nonterminal alkenes [1, 4, 5], and therefore the disturbance of the stereospecificity of the trans-addition can to a great extent be caused by the repulsive interaction of the vicinal groups in the TS (intermediates) of the cyclic type (II), (III). Therefore, strictly speaking, from the configuration of the products of the addition to alkenes with vicinal substituents, we cannot conclude on the contribution of the electronic effects to the stereodirectivity of the Ad_E-reactions of alkenes.

In the present work, we studied the influence of the electronic properties of substituents in the reagents on the stereodirectivity of the addition of arylsulfenyl chlorides to β-deuterostyrenes under conditions excluding the mutual interconversion of the stereoisomers (kinetic control). We also studied the case of conversion of the stereoisomers under the conditions usually used for Ad_E-processes.

To solve our problem, we synthesized stereoisomeric Z- and E-β-deuterostyrenes (IVa-d) and (Va-d) (Table 1) and examined their reactions with sulfenyl chlorides (VIb, c, e, g) in $CDCL_3$ and CD_3COOD (ratio of reagents 1:1)

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. A. A. Zhdanov Gorkii Polytechnical Institute, Gorkii. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2346-2352, October, 1983. Original article submitted January 11, 1983.

 0568-5230/83/3210-2114$07.50

TABLE 1. Parameters of PMR Spectra of β-Deuterostyrenes* in $CDCl_3$ $R^1C_6H_4-\overset{\alpha}{C}H=\overset{\beta}{C}HD$

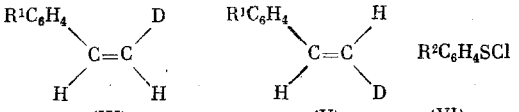
Configuration of alkene	R^1	Chemical shifts, δ, ppm			SSCC $^3J_{\alpha,\beta}$, Hz
		H_α	H_β	R^1	
Z	H	6,64 m	5,17 d		11,0
E	H	6,64 m	5,65 d		17,5
Z	4-Me	6,66 m	5,14 d	2,28 s	11,0
E	4-Me	6,66 m	5,67 d	2,28 s	17,5
Z	4-OMe	6,64 m	5,10 d	3,80 s	11,0
E	4-OMe	6,64 m	5,60 d	3,80 s	18,0
Z	4-NO_2	6,72 m	5,34 d		11,0
E	3-NO_2	6,72 m	5,86 d		17,5

* Signals of aromatic ring protons are also present in the 6.8-8.2 ppm region.

TABLE 2. Parameters of Spectra of Adducts of Styrenes with Sulfenyl Chlorides* in $CDCl_3$

R^1	R^2	Chemical shifts, δ, ppm			
		H_α	H_β	R^1	R^2
$R^1C_6H_4-\overset{\alpha}{C}HCl-\overset{\beta}{C}H_2S-C_6H_4R^2$ (M-adduct)					
H	4-Me	4,82 q	3,39 q, 3,53 q		2,26 s
H	4-NO_2	5,02 q	3,60 q, 3,72 q		
4-Me	4-Me	4,84 q	3,40 q, 3,53 q	2,26 s	2,23 s
4-Me	4-NO_2	4,99 q	3,60 q, 3,72 q	2,31 s	
4-Me	2,4-$(NO_2)_2$	5,09 q	3,68 q, 3,80 q	2,33 s	
3-NO_2	4-Me	4,86 q	3,38 q, 3,58 q		2,23 s
3-NO_2	4-NO_2	5,07 q	3,58 q, 3,80 q		
4-OMe	4-OMe	4,80 q	3,36 q, 3,48 q	3,75 s	3,75 s
4-OMe	4-Me	4,97 q	3,56 q, 3,60 q	3,78 s	2,26 s
4-OMe	4-NO_2	5,00 q	3,62 q, 3,76 q	3,82 s	
$R^1C_6H_4-\overset{\alpha}{C}H(S-C_6H_4R^2)-\overset{\beta}{C}H_2Cl$ (a M-adduct)					
H	4-Me	4,29 t	3,85 d		2,26 s
H	4-NO_2	4,70 t	3,92 d		
3-NO_2	4-NO_2	4,70 t	3,98 d		
3-NO_2	4-Me	4,38 t	3,96 d		2,23 s

* Signals of aromatic ring protons are also present in the 6.7-9.2 ppm region.



(IV) (V) (VI)

$R^1 = R^2 =$ H (a); 4-Me (b); 4-OMe (c); 3-NO_2 (d); 4-NO_2 (e); 2,4-$(NO_2)_2$ (f).

First, it has been shown on deuterated styrenes that the main path of the reaction is always the formation of Markovnikoff adducts. In the PMR spectra of the adducts, the protons of the $CHCl=CH_2S$ fragment form a sharply resolved ABC system (Table 2). We can therefore determine the stereodirectivity of the addition of sulfenyl chlorides (VI) to the deuterated styrenes (IV) and (V) directly from the PMR spectral data (Table 3). The characteristic regions of the spectra of the Markovnikoff (M) and anti-Markovnikoff (aM) adducts obtained in the reaction of styrene, and also its Z- and E-deuterated analogs (IVa) and (Va) with p-toluenesulfenyl chloride (VIb), are shown in Fig. 1. These data show that for the M adducts, obtained from E-β-deuterostyrenes, the values of the vicinal SSCC [spin-spin coupling constants] (^3J) are 8.3-9.3 Hz, while for adducts obtained from the Z-isomers, ^3J are equal to 5.8-6.7 Hz. In accordance with the data in [6] (^3J erythro > ^3J threo), the first series of adducts should be related to the erythro-isomers, and the second to threo. The aM adducts were related in the same way. The ratio of the regioisomers is given in Table 4.

We found that the addition of sulfenyl chlorides (VIb, e) to β-deuterostyrenes (IVa, b, d) and (Va, b, d) in $CDCl_3$ and CD_3COOD at 25°C proceeds strictly trans-stereospecifically irrespective of whether only M or a

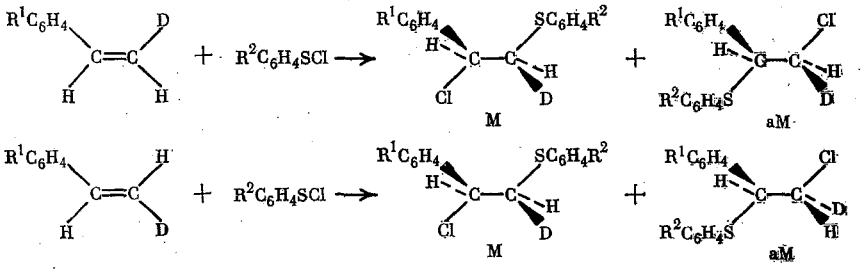
TABLE 3. Parameters of PMR Spectra of Adducts of β-Deutero-styrenes with Sulfenyl Chlorides in $CDCl_3$

Configuration of alkene	R^1	R^2	Configuration of adduct	Chemical shifts, δ, ppm		SSCC $^3J_{\alpha,\beta}$, Hz
				H_α	H_β	
			$R^1C_6H_4-\overset{\alpha}{C}HCl-\overset{\beta}{C}HDS-C_6H_4R^2$ (M-adduct)			
E	4-Me	4-NO_2	erythro-	5,00 d	3,60 d	8,3
Z	4-Me	4-NO_2	threo-	5,00 d	3,72 d	6,4
E	4-Me	4-Me	erythro-	4,84 d	3,47 d	8,6
Z	4-Me	4-Me	threo-	4,84 d	3,56 d	6,4
E	H	4-NO_2	erythro-	5,02 d	3,62 d	8,3
Z	H	4-NO_2	threo-	5,02 d	3,72 d	6,7
E	H	4-Me	erythro-	4,80 d	3,40 d	8,6
Z	H	4-Me	threo-	4,80 d	3,49 d	6,4
E	3-NO_2	4-NO_2	erythro-	5,14 d	3,65 d	8,6
Z	3-NO_2	4-NO_2	threo-	5,14 d	3,74 d	6,0
E	3-NO_2	4-Me	erythro-	4,94 d	3,47 d	9,3
Z	3-NO_2	4-Me	threo-	4,94 d	3,56 d	5,8
E	4-Me	2,4-$(NO_2)_2$	erythro-	5,09 d	3,68 d	8,3
Z	4-Me	2,4-$(NO_2)_2$	threo-	5,09 d	3,78 d	6,8
E	4-OMe	4-NO_2	erythro-	5,00 d	3,60 d	8,6
Z	4-OMe	4-NO_2	threo-	5,00 d	3,72 d	6,4
E	4-OMe	4-Me	erythro-	4,91 d	3,50 d	8,6
Z	4-OMe	4-Me	threo-	4,91 d	3,56 d	6,4
E	4-OMe	4-OMe	erythro-	4,82 d	3,38 d	9,0
Z	4-OMe	4-OMe	threo-	4,82 d	3,47 d	6,4
			$R^1C_6H_4-\overset{\alpha}{C}H-\overset{\beta}{C}HDCl$ (aM-adduct) $\quad S-C_6H_4R^2$			
E	3-NO_2	4-NO_2	erythro-	4,74 d	4,00 d	8,8
Z	3-NO_2	4-NO_2	threo-	4,74 d	3,98 d	5,3
E	3-NO_2	4-Me	erythro-	4,40 d	3,97 d	9,0
Z	3-NO_2	4-Me	threo-	4,40 d	3,96 d	5,5
E	H	4-NO_2	erythro-	4,65 d	3,94 d	9,2
Z	H	4-NO_2	threo-	4,65 d	3,89 d	5,3
E	H	4-Me	erythro-	4,26 d	3,84 d	10,5
Z	H	4-Me	threo-	4,26 d	3,82 d	4,5

TABLE 4. Ratio of Regioisomers in Reactions of $R^1C_6H_4CH=CH_2$ with $R^2C_6H_4SCl$

R^1	R^2	M-adducts, %	aM-adducts, %
3-NO_2	4-NO_2	81	19
3-NO_2	4-Me	82	18
H	4-Me	83	17
H	4-NO_2	94	6
4-Me	4-Me	99	Traces
4-Me	4-NO_2	100	0
4-Me	2,4-$(NO_2)_2$	100	0
4-OMe	4-Me	100	0
4-OMe	4-OMe	100	0
4-OMe	4-NO_2	100	0

mixture of M and aM adducts is formed. The addition of 2,4-dinitrobenzenesulfenyl chloride to Z- and E-β-deutero-p-methylstyrenes (IVb) and (Vb) in CD_3COOD at 25°C is also trans-stereospecific, and the Markovnikoff rule holds.



The stereospecificity of the trans-addition of sulfenyl chlorides to styrenes is retained also in the presence of $LiClO_4$. In the reaction of Z- and E-β-deutero-p-methylstyrenes (IVb) and (Vb) with p-nitrobenzenesulfenyl chloride (VIe) in CD_3COOD with lithium perchlorate additives [(IV), (V):(VI):$LiClO_4$ = 1:1:5], M-adducts are formed with a threo and erythro configuration, respectively, and also an inappreciable amount of products of conjugate addition with the participation of CD_3COOD. In all the above cases, the stereoselectivity of the addition of sulfenyl chlorides is not lower than 98% (according to analysis of reaction mixtures by the PMR method at 250 MHz).

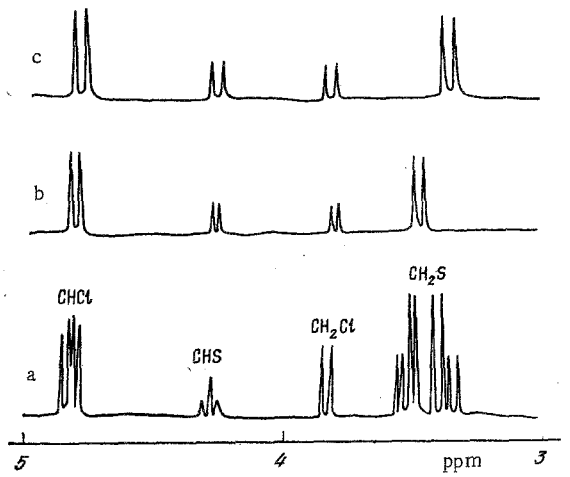


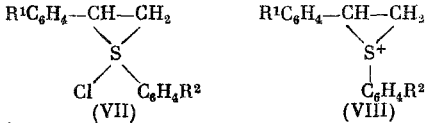
Fig. 1. Characteristic signals in PMR spectra of products of reaction of p-toluenesulfenyl chloride with a) styrene; b) Z-β-deuterostyrene; c) E-β-deuterostyrene.

A seemingly more complex picture is observed for Ad_E-reaction of β-deutero-p-methoxystyrenes (IVc) and (Vc). A priori, it could be expected that particularly in reactions with these styrenes the formation of an open type TS (I) is most probable (because of the additional stabilization of this form by the mesomeric effect of the p-methoxy group). It would appear that the experimental results of the addition of sulfenyl chlorides (VIb, c) at 25°C in $CDCl_3$ or CD_3COOD confirm this assumption, since according to PMR spectra, the formation of one and the same mixture of erythro- and threo-adducts in a 1:1 ratio from (IVc) and (Vc) has been recorded. However, later the following was shown: 1) in the same reactions at −50°C in $CDCl_3$, only trans-addition products were formed for the two alkenes; 2) when samples of individual erythro- and threo-adducts obtained at low temperature were heated to 25°C, a rapid (20 min) interconversion of the stereoisomers takes place with the formation of erythro- and threo-isomers in a 1:1 ratio. From this we can assume that the addition of sulfenyl chlorides (VIb, c) to p-methoxystyrenes at 25°C also proceeds as a trans-process (kinetic control), over which a rapid isomerization of the adducts is superimposed (thermodynamic control).

It is possible that a certain decrease in the degree of trans-stereospecificity takes place on addition of p-nitrobenzenesulfenyl chloride (VIe) to (IVc) and (Vc), since as a result of these reactions at 25°C, mixtures of threo- and erythro-isomers are formed in ratios of 95:5 and 5:95, respectively. However, it is not improbable that in these cases also the disturbance of stereospecificity is the result of the isomerization of adducts, since control experiments have shown that the stereoconversion of the adducts at 25°C does in fact occur, although its rate is considerably lower than in the case of adducts of the same styrenes with (VIb, c) (the erythro: threo = 1:1 ratio is reached only after 24 h).

The results show that variation in the electronic properties of the substituents in styrenes (R^1) and sulfenyl chlorides (R^2) does not lead to a change in the stereodirectivity of the addition. The observed stereospecificity of the trans-addition clearly indicates that in all the cases studied, the reaction of styrenes with sulfenyl chlorides proceeds via the formation of a TS (intermediates) with a cyclic structure of types (II) and (III).

This result qualitatively agrees with the conclusions previously drawn on the basis of a detailed examination of the kinetic regularities of the reactions of $R^1C_6H_4CH=CH_2$ with $R^2C_6H_4SCl$ [7, 8]. In fact, it was found that for all the R^2 and R^1 studied, at the limiting stage of the reaction a bridged-type TS is formed, and in the case of styrenes with electron-donor substituents, the TS is best described by the structure of σ-sulfurane (VII), while for styrenes with electron-withdrawing substituents, by an episulfonium structure (VIII)



It has already been reported that the addition of sulfenyl chlorides to a wide group of linear nonterminal alkenes containing both alkyl and aryl substituents proceeds trans-stereospecifically [1]. For this group of

alkenes, exceptions are Z-isomers of β-methylstyrenes containing alkoxy or phenoxy groups, MeO, i-PrO, PhO, in the p-position, which in the reaction with 2,4-dinitrobenzenesulfenyl chloride give mixtures of products of cis- and trans-addition [4].* It is interesting that on all the models of the E-series, the addition proceeds with more than 95% stereospecificity. It was also shown that the kinetic regularities of the reaction of E- and Z-alkenes are the same, and indicate the formation of a bridged TS at the limiting stage, irrespective of the nature of the substituent in styrene. The authors of this paper believe that the disturbance of the stereospecificity of the addition of Z-styrenes containing donor substituents is due to the formation of an open benzyl cation type intermediate at the product-determining stage of the reaction. It must, however, be stressed that in the case of Z-styrenes, in the cyclic type TS, nonfavorable steric interactions of the substituents (Ar and Me) occur, which in fact may be the main factor for the destabilization of this TS.

The second case of a nonstereospecific addition of sulfenyl chlorides to the double bond is observed in the reaction of Z- and E-isomers of propenyl ethyl ethers with benzenesulfenyl chloride [5]. The authors believe that the disturbance of the stereospecificity in these reactions is due to the considerable stabilization of the open form of the carbocations by α-alkoxy groups. We should note that on these models a smoothly proceeding stereoconversion of the reagents has also been observed, which could appreciably distort the observed stereochemistry of the reaction.

The stereospecificity of the trans-addition that we discovered for the reactions studied of terminal alkenes with sulfonyl chlorides shows that in the absence of unfavorable steric factors, only the electronic effects of the substituents of the reagents do not ensure the possible preferential stability of the open form of TS (intermediates), compared with the cyclic form.

EXPERIMENTAL

The PMR spectra were recorded on the "Bruker WM-250" apparatus (250 MHz) with reference to TMS as internal standard. The styrenes were obtained according to [9, 10], and sulfenyl chlorides according to [11]. The Z-β-deuterostyrenes were synthesized by hydroborination of phenylacetylenes-d_1 [12], obtained by the action of D_2O on phenylacetylenes in the presence of CaO [13], E-β-Deuterostyrenes were obtained according to [12]. The isotopic purity of all the β-deuterostyrenes obtained was not less than 90%.

Addition of Sulfenyl Chlorides to Styrenes. A solution of 5 mmoles of styrene in 30 ml of CH_2Cl_2 was added to a solution of a sulfenyl chloride in 30 ml of CH_2Cl_2. The solvent was distilled at reduced pressure. The overall yield of the addition products according to and against the Markovnikoff rule was quantitative. A satisfactory elemental analysis was obtained for all the products (mixtures of regioisomers). The individual regioisomers were not isolated.

Addition of Sulfenyl Chlorides to β-Deuterostyrenes. The adducts were obtained directly in NMR ampuls. A solution of 0.5 mmole of styrene in 0.3 ml of $CDCl_3$ or CD_3COOD was added dropwise to a solution of 0.55 mmole of a sulfenyl chloride in 0.3 mmole of $CDCl_3$ or CD_3COOD. The reaction mixture was continuously stirred by a current of dry Ar introduced into the ampul through a capillary.

We wish to express our gratitude to V. A. Chertkov for his help in running the low-temperature PMR spectra.

CONCLUSIONS

The addition of arylsulfenyl chlorides to substituted Z- and E-β-deuterostyrenes proceeds trans-stereospecifically, irrespective of the type of substituents in the benzene ring of the two reagents.

LITERATURE CITED

1. G. Schmid and D. Garratt, in: The Chemistry of Double Bonded Functional Groups, S. Patai (ed.), Chap. 9, Wiley, New York (1977), p. 726.
2. V. A. Smit, Zh. Vses. Khim. O-va im. D. I. Mendeleeva, 22, 300 (1977).
3. I. V. Bodrikov and Z. S. Smolyan, Usp. Khim., 35, 853 (1966).
4. G. H. Schmid and V. J. Nowlan, Can. J. Chem., 54, 695 (1976).
5. K. Toyoshima, T. Okuyama, and T. Fueno, J. Org. Chem., 43, 2789 (1978).
6. R. J. Abraham and I. R. Monasterios, J. Chem. Soc., Perkin Trans., 1, 1446 (1973).

* Unfortunately, the authors did not consider the possible isomerization of the Z-β-methylstyrene to E-β-methylstyrene. Therefore, strictly speaking, this paper requires verification.

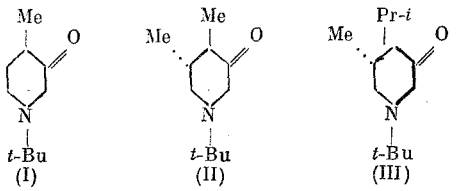
7. W. A. Smit, N. S. Zefirov, and I. Bodrikov, in: Organic Sulfur Chemistry, R. Kh. Freidlina and A. E. Skorova (eds.), Pergamon Press, Oxford–New York (1981), p. 159.
8. I. V. Bodrikov, A. V. Borisov, L. V. Chumakov, N. S. Zefirov, and W. A. Smit, Tetrahedron Lett., 115 (1980).
9. Syntheses of Organic Preparations [Russian translation], Coll. 4, Inostr. Lit., Moscow (1953), p. 540.
10. Syntheses of Organic Preparations [Russian translation], Coll. 5, Inostr. Lit., Moscow (1954), p. 51.
11. Weygand and Hilgetag, Preparative Organic Chemistry, Wiley (1972).
12. H. C. Brown, C. G. Scouten, and R. Liotta, J. Am. Chem. Soc., 101, 96 (1979).
13. J. E. Baldwin and J. A. Kapecki, J. Am. Chem. Soc., 92, 4874 (1970).

INFLUENCE OF AN EQUATORIAL SUBSTITUENT AT C^4 IN 3-KETOPIPERIDINES ON THE STEREOCHEMISTRY OF THE REDUCTION OF THE KETO FUNCTIONAL GROUP

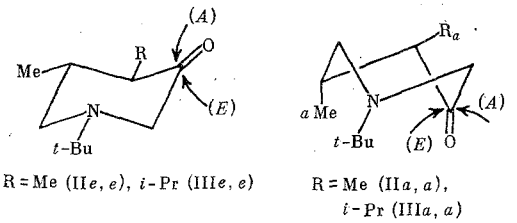
G. T. Katvalyan and É. A. Mistryukov

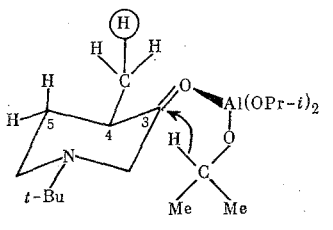
UDC 541.63:542.941.7:547.824

In the investigation of the stereochemistry of the reduction of 3-ketopiperidines it has been shown that the main reaction product is generally the equatorial alcohol, which appears as a result of the attack of the carbonyl function from the axial region [1, 2]. In the case of the appearance of a methyl group on the C^4 atom adjacent to the carbonyl, as in (I), the axial attack of some reagents is hindered, and the axial alcohol may be the predominant reaction product {for example, (I) with $(i\text{-PrO})_3Al$ affords 72% axial alcohol [3]}. However, in view of the conformational lability of ketone (I), it did not seem possible to demarcate the stereochemical details of the reagent and the substrate. In this context, in the present work we studied the reduction of the disubstituted ketones 1-tert-butyl-trans-4,5-dimethyl- (II) and 4-isopropyl-5-methyl-3-piperidone (III), which have equatorial substituents at C^4 and C^5.



Scheme 1





(I) · $Al(OPr\text{-}i)_3$

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2352-2356, October, 1983. Original article submitted November 24, 1982.

0568-5230/83/3210-2119$07.50