REACTION OF 2,7-DIALKYL- AND 1,2,7-TRIALKYLDECAHYDRO-4-QUINOLONES WITH TRIETHYLALUMINUM

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The reaction of triethylaluminum with stereoisomeric 2,7-dimethyl- and 1,2,7-trimethyldecahydro-4-quinolones and their 7-tert-butyl-substituted analogs was studied. The reaction of triethylaluminum with ketones that have an equatorial 2-CH_3 group proceeds in two directions – reduction of the carbonyl group to an alcohol group and alkylation to give tertiary 4-ethyl-substituted alcohols – in benzene, depending on the reagent ratio. The stereochemistry of the reduction of the carbonyl group depends on the temperature. Only an alkylation product is formed in tetrahydrofuran (THF) and diethyl ether. The reaction of triethylaluminum with ketones that have an axial 2-CH_3 group depends on the nature of the solvent. Epimeric secondary alcohols are formed in toluene at various ratios of the reacting substances, whereas tertiary ethyl-substituted alcohols are formed in THF and diethyl ether.

In a study of the stereochemistry of reduction, ethynylation, and Grignard reactions in a series of stereoisomeric 2,7-dimethyl- and 1,2,7-trimethyldecahydro-4-quinolones and their 7-tert-butyl-substituted analogs [1-4] it was noted that there is an anomaly in the behavior of ketones I, V, IX, and XIII, which, according to the PMR data [5], have an equatorially oriented 2-CH_3 group: Each of the reactions mentioned above led only to one of the two possible epimeric alcohols in quantitative yields. The absence of the second epimer of the alcohols created difficulties in the proof of the structures of ketones I, V, IX, and XIII. In this connection, in the present research we continued our study of the stereochemistry of reactions involving nucleophilic addition to the carbonyl group of sterically unhindered and hindered ketones, and, in particular, we studied the reaction of these ketones with triethylaluminum.

It is known [6] that the reaction of 4-tert-butylcyclohexanone with organomagnesium compounds in various solvents leads to the formation of a mixture of tertiary alcohols in which the epimer with an equatorial CH_3 group predominates. A similar result was also obtained in the reactions of this ketone with trimethyl- or triethylaluminum [6, 7] in hydrocarbon solvents and also in diphenyl ether at a reagent ratio of 1 : 1. At and above a reagent ratio of 1 : 2 the stereochemistry of the reaction was reversed to give a mixture of alcohols in which the epimer with an axial CH_3 group predominated. The chief alkylation product in the reaction of sterically hindered 3,3,5-trimethylcyclohexanone with triethylaluminum in benzene and other solvents at any reagent ratios was a tertiary alcohol with an equatorial CH_3 group [7]. Both sterically unhindered and hindered carbocyclic ketones form secondary alcohols as side products in the reaction with $(C_2H_5)_3Al$.

In connection with the available literature data and hoping to obtain the second missing epimer of the ethyl-substituted alcohol, we studied the reaction of unhindered ketones I, V, IX, and XIII with triethylaluminum in various solvents at various reagent ratios (Table 1). The ratio of the reacting substances, the reaction temperature, and the solvent affect the direction and stereochemistry of the reaction of triethylaluminum with sterically unhindered decahydroquinolines. Thus a mixture of epimeric decahydro-4-quinolols, in which torial secondary alcohol II (which we have previously obtained by reduction of the same ketone [1]) predominates, and in which epimer III with an axial hydroxyl group (obtained for the first time) is present in lesser amounts, is formed instead of the expected ethyl-substituted alcohol in the reaction of ketone I with triethylaluminum at reagent ratios from 1 : 1 to 1 : 4 at 40°. Raising the temperature to 70° leads to a reversal of the

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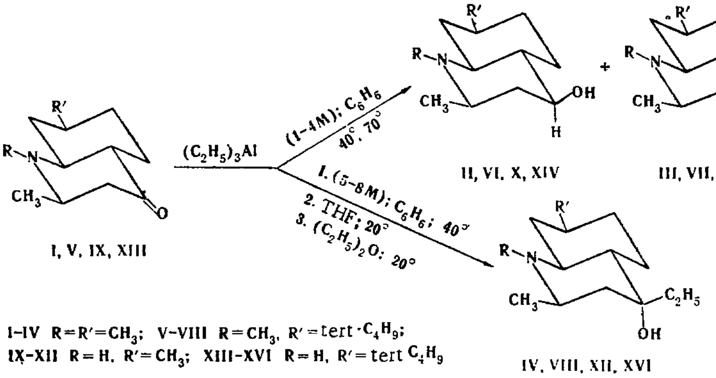
stereochemistry of the reduction reaction: Thermodynamically less stable axial alcohol III predominates in the mixture of reduction products and the fraction of epimeric equatorial alcohol II falls appreciably. A similar result was obtained in a study of the reduction of protected cyclohexanones with lithium aluminum hydride: An increase in the temperature from −60 to +35° led to an increase in the fraction of the conformationally less stable isomer with an axial hydroxyl group [8].



I–IV $R=R'=CH_3$; V–VIII $R=CH_3$, $R'=tert\text{-}C_4H_9$;
IX–XII $R=H$, $R'=CH_3$; XIII–XVI $R=H$, $R'=tert\text{-}C_4H_9$

In a previous study of the stereochemistry of the reduction of ketone I with various reducing agents we were unable to isolate the epimer of secondary alcohol III with an axial hydroxyl group because of its isomerization under these conditions to thermodynamically more favorable equatorial epimer II. The formation of secondary alcohol III in good yield in the reaction of ketone III with $(C_2H_5)_3Al$ is explained by its stability under the conditions of the given reaction; this was also shown by special experiments.

Epimeric secondary alcohols II and III are formed in approximately equal amounts when the ratio of the reacting substances is 1 : 4 (at 70°). The presence of traces of ethyl-substituted tertiary alcohol IV was also detected in the mixture by thin-layer chromatography (TLC). Alcohol IV becomes the principal product as the ratio of the reacting substances is changed further (1 : 5, 1 : 6), regardless of the temperature, and it is the only reaction product at a ratio of 1 : 8.

In contrast to the reaction in benzene, the reaction of ketone I with triethylaluminum in tetrahydrofuran (THF) and diethyl ether, proceeded readily even at room temperature and gave tertiary alcohol IV as the only product; alkylation in THF proceeded considerably more rapidly than in diethyl ether. Secondary alcohols II and III were obtained in small amounts along with tertiary alcohol IV when the reaction was carried out in refluxing THF or diethyl ether (reagent ratio 1 : 2).

Similar results were obtained in the reaction of triethylaluminum with 7-tert-butyl-substituted ketone V and also with demethylated analogs of ketones I and V – ketones IX and XIII. Depending on the reaction conditions, either secondary or tertiary alcohols are formed; the axial epimers of secondary alcohols (VII, XI, and XV) were synthesized for the first time (Table 2), whereas tertiary alcohols IV, VIII, XII, and XVI were found to be identical to the alcohols that we previously obtained in [4]. Thus we were unable to obtain the epimeric tertiary alcohols of alcohols IV, VIII, XII, and XVI by this method.

The reaction with triethylaluminum was also studied in the case of sterically hindered ketones XVII, XXI, XXV, and XXVIII with an axial methyl group in the 2 position. In this case severer conditions than in the case of sterically unhindered ketones were required: The reaction was carried out in toluene at 105° for 10–20 h. The reaction did not occur in benzene.

In contrast to ketones I, V, IX, and XIII, the reagent molar ratio does not affect the reaction of sterically hindered ketones XVII, XXI, XXV, and XXVIII with triethylaluminum. The only reaction pathway in toluene is reduction of the carbonyl group to an alcohol group (Table 3).

In the case of equimolecular amounts of ketone XVII and $(C_2H_5)_3Al$ the reaction gives the axial epimer of secondary alcohol XVIII as the only product with recovery of a considerable amount of the starting ketone. A mixture of two epimeric (with respect to the 4 position) secondary alcohols (XVIII and XIX) with predominance of XVIII is formed in the presence of excess reagent. The reason for the unambiguous reduction in the case of hindered ketones XVII, XXI, XXV, and XVIII is evidently decomposition of triethylaluminum under severe reaction conditions to give diethylaluminum hydride, which is a reducing agent [9].

The reaction of decahydroquinolones XXI, XXV, and XXVIII, which are steric analogs of ketone XVII, with $(C_2H_5)_3Al$ in toluene proceeded absolutely analogously to the reaction of ketone XVII (Table 3). Alkylation leading to the formation of the corresponding alcohols XX and XXIV, which are identical to the 4-ethyl-sub-

TABLE 1. Effect of the Reaction Conditions on the Direction and Stereochemistry of the Reaction of $(C_2H_5)_3Al$ with Sterically Unhindered Decahydro-4-quinolones

Ketone	Ketone : $(C_2H_5)_3Al$ ratio	Solvent	Temp., °C	Reaction time, h	Reaction products (yield, %)		
					secondary alcohol (e-OH)	secondary alcohol (*a*-OH)	tertiary alcohol
I	1 : 1	C_6H_6	40 70	12 6	II (60) II (16)	III (30) III (70)	—
I	1 : 2	C_6H_6	40 70	8 4	II (60) II (20)	III (28) III (76)	—
I	1 : 3	C_6H_6	40 70	4 4	II (54) II (22)	III (44) III (75)	—
I	1 : 4	C_6H_6	40 70	2 4	II (58) II (42)	III (36) III (46)	IV (traces)
I	1 : 5	C_6H_6	40 70	2 4	— —	III (8) III (16)	IV (74) IV (73)
I	1 : 6	C_6H_6	40	2	—	III (15)	IV (75)
I	1 : 8	C_6H_6	40	1	—		IV (82)
I	1 : 1	THF	20	10	—	—	IV (50)
I	1 : 2	THF	60	4	II (7)	III (14)	IV (68)
I	1 : 4	THF	20	8	—	—	IV (82)
I	1 : 1	$(C_2H_5)_2O$	20	12	—	—	IV (50)
I	1 : 2	$(C_2H_5)_2O$	35	8	II (5)	III (12)	IV (60)
I	1 : 4	$(C_2H_5)_2O$	20	18	—	—	IV (80)
V	1 : 1	C_6H_6	40 70	10 6	VI (58) VI (15)	VII (32) VII (70)	— —
V	1 : 2	C_6H_6	40 70	8 4	VI (60) VI (18)	VII (29) VII (76)	— —
V	1 : 3	C_6H_6	40 70	4 4	VI (53) VI (20)	VII (43) VII (76)	—
V	1 : 5	C_6H_6	40	3	—	VII (6)	VIII (75)
V	1 : 6	C_6H_6	40	2	—	VII (14)	VIII (73)
V	1 : 8	C_6H_6	40	1	—	—	VIII (86)
IX	1 : 1	C_6H_6	40 70	8 4	X (62) X (14)	XI (32) XI (68)	— —
IX	1 : 2	C_6H_6	40 70	6 3	X (56) X (19)	XI (34) XI (75)	— —
IX	1 : 3	C_6H_6	40 70	3 4	X (52) X (19)	XI (40) XI (72)	— —
IX	1 : 5	C_6H_6	40	4	—	XI (8)	XII (76)
IX	1 : 6	C_6H_6	40	2	—	XI (16)	XII (76)
IX	1 : 8	C_6H_6	40	1	—	—	XII (84)
XIII	1 : 1	C_6H_6	40 70	6 3	XIV (61) XIV (17)	XV (31) XV (70)	— —
XIII	1 : 2	C_6H_6	40 70	4 4	XIV (57) XIV (16)	XV (35) XV (74)	— —
XIII	1 : 3	C_6H_6	40 70	3 4	XIV (51) XIV (22)	XV (45) XV (72)	— —
XIII	1 : 5	C_6H_6	40	3	—	XV (8)	XVI (74)
XIII	1 : 6	C_6H_6	40	2	—	XV (15)	XVI (76)
XIII	1 : 8	C_6H_6	40	1	—	—	XVI (83)

TABLE 2. 2,7-Dialkyl- and 1,2,7-Trialkyldecahydro-4-quinolols

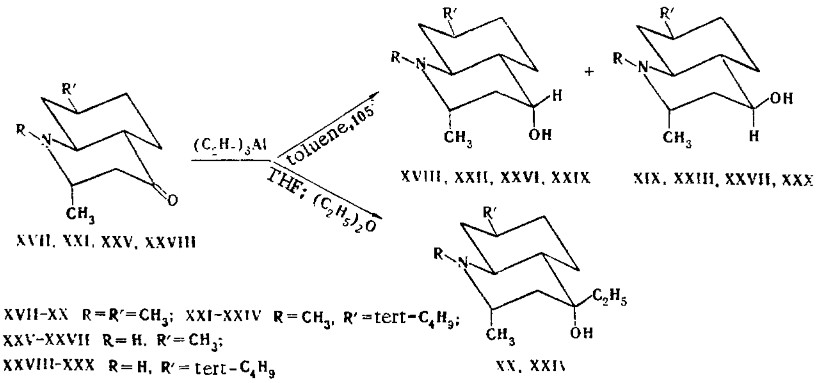
Alcohol	mp, °C	Empirical formula	Found, %			Calc., %		
			C	H	N	C	H	N
III	108—109	$C_{12}H_{23}NO$	73,0	11,5	6,9	73,0	11,4	7,1
VII	104—105	$C_{15}H_{29}NO$	75,2	12,0	5,6	75,2	12,2	5,8
XI	118—119	$C_{11}H_{21}NO$	72,3	11,4	7,8	72,1	11,5	7,6
XV	124—125	$C_{14}H_{27}NO$	74,3	11,8	6,1	74,6	12,1	6,2

TABLE 3. Effect of the Solvent on the Reaction of Sterically Hindered Decahydro-4-quinolones with $(C_2H_5)_3Al$

Ketone	Ketone : $(C_2H_5)_3Al$ ratio	Solvent	Temp., °C	Reaction time, h	Reaction product (yield, %)			
					secondary alcohol (a-OH)	secondary alcohol (e-OH)	tertiary alcohol	starting ketone
XVII	1 : 1	Toluene	105	20	XVIII (20)	—	—	(60)
XVII	1 : 1,5	Toluene	105	18	XVIII (30)	—	—	(52)
XVII	1 : 2	Toluene	105	16	XVIII (40)	XIX (traces)	—	(44)
XVII	1 : 3	Toluene	105	14	XVIII (60)	XIX (10)	—	—
XVII	1 : 4	Toluene	105	12	XVIII (62)	XIX (30)	—	—
XVII	1 : 10	Toluene	105	10	XVIII (75)	XIX (20)	—	—
XVII	1 : 1	THF	60	10	—	—	XX (45)	(40)
XVII	1 : 2	THF	60	5	—	—	XX (83)	—
XVII	1 : 2	$(C_2H_5)_2O$	35	8	—	—	XX (75)	(10)
XVII	1 : 4	$(C_2H_5)_2O$	35	4	—	—	XX (81)	—
XXI	1 : 1	Toluene	105	20	XXII (20)	—	—	(60)
XXI	1 : 1.5	Toluene	105	18	XXII (28)	—	—	(58)
XXI	1 : 2	Toluene	105	16	XXII (38)	XXIII (traces)	—	(46)
XXI	1 : 3	Toluene	105	14	XXII (58)	XXIII (12)	—	—
XXI	1 : 4	Toluene	105	12	XXII (63)	XXIII (28)	—	—
XXI	1 : 10	Toluene	105	8	XXII (76)	XXIII (22)	—	—
XXI	1 : 2	THF	60	5	—	—	XXIV (83)	—
XXV	1 : 1	Toluene	105	17	XXVI (46)	—	—	(44)
XXV	1 : 2	Toluene	105	15	XXVI (56)	—	—	(38)
XXV	1 : 3	Toluene	105	13	XXVI (64)	XVII (12)	—	—
XXVIII	1 : 1	Toluene	105	17	XXIX (45)	—	—	(40)
XXVIII	1 : 2	Toluene	105	15	XXIX (54)	—	—	(36)
XXVIII	1 : 3	Toluene	105	13	XXIX (63)	XXX (14)	—	—

stituted compounds obtained from the same ketones by means of the Grignard reaction [3], is observed when the reaction of $(C_2H_5)_3Al$ with sterically hindered ketones XVII and XXI is carried out in THF and diethyl ether at reacting substance ratios at and above 1 : 1.

Thus the direction of the reaction of triethylaluminum with sterically unhindered ketones I, V, IX, and XIII depends on the relative amounts of reacting substances, the temperature, and the solvent. In contrast to this, in the case of hindered ketones XVII, XXI, XXV, and XXVIII the principal factor that affects the direction of the reaction is the solvent.



The three-dimensional orientation of the hydroxyl group in the secondary and tertiary alcohols was determined by a chemical method [1-4] and by IR spectroscopy.

EXPERIMENTAL

The reaction of triethylaluminum with decahydroquinolones was carried out in an inert gas atmosphere. The course of the reactions was monitored by means of TLC on neutral activity II Al_2O_3 with elution by chloroform–ether–ethanol (3 : 1 : 0.1 for II-VIII and XVIII-XXIII, and 15 : 5 : 2 for X-XVI and XVI-XXX). The results of elementary analysis and the properties of the synthesized secondary and ethyl-substituted alcohols were presented in our previous papers [14].

Reaction of 1,2,7-Trimethyldecahydro-4-quinolone (I) with $(C_2H_5)_3Al$. A) A solution of 0.25 g (1.2 mmole) of ketone I in 15 ml of benzene was added to a benzene solution of 0.14 g (1.2 mmole) of triethylaluminum obtained from an aluminum–magnesium alloy (40 : 60) and ethyl iodide [9], after which the mixture was heated at 40° for 12 h. It was then cooled, treated with water, and acidified with 15% hydrochloric acid. The aqueous solution was saturated with K_2CO_3, and the liberated base was extracted with ether. The extract was dried with $MgSO_4$, and the solvent was removed by distillation. Fractional recrystallization of 0.23 g (91%) of the residue from hexane gave 0.14 g (60%) of 1,2,7-trimethyldecahydro-4-quinolol (II) (mp 142-143° and R_f 0.66) 0.07 g (30%) of epimeric alcohol III (mp 108-109° and R_f 0.54). No melting-point depression was observed for a mixture of alcohol II with the alcohol previously obtained in [1].

The remaining experiments are presented in Table 1.

B) A solution of 0.15 g (0.7 mmole) of ketone I in 20 ml of THF was added to a solution of 0.08 g (0.7 mmole) of $(C_2H_5)_3Al$ in 30 ml of THF, after which the mixture was stirred at room temperature for 10 h. The usual workup and separation of the crude product (0.15 g) on Al_2O_3 (hexane and diethyl ether) yielded 0.05 g (33%) of the starting ketone (R_f 0.98) and 0.075 g (50%) of the alkylation product, which did not depress the melting point of alcohol IV.

C) A 0.15-g (0.7 mmole) sample of ketone I was added to an ether solution of 0.08 g (0.7 mmole) of $(C_2H_5)_3Al$, and the mixture was treated as in method B for 12 h. Workup yielded 0.14 g of crude oily substance; separation of the latter with a column filled with neutral Al_2O_3 under the conditions of method B gave 0.07 g (50%) of alcohol IV and 0.04 g (28%) of the starting ketone.

Reaction of 1,2-Dimethyl-7-tert-butyldecahydro-4-quinolone (V) with $(C_2H_5)_3Al$. A) Reaction of 0.25 g (1 mmole) of ketone V and 0.24 g (2 mmole) of triethylaluminum in benzene at 70° for 4 h gave 0.08 g (18%) of secondary alcohol VI (mp 170-171° and R_f 0.72) and 0.16 g (76%) of its epimer (VII) with respect to the 4 position (mp 104-105° and R_f 0.57). Alcohol VI did not depress the melting point of a sample of the genuine secondary alcohol [2].

B) Reaction of 0.5 g (2 mmole) of ketone V and 1.2 g (10 mmole) of $(C_2H_5)_3Al$ in benzene at 40° for 2 h gave, after purification on neutral Al_2O_3 and subsequent crystallization of the mixture from petroleum ether, 0.35 g (75%) of 1,2-dimethyl-7-tert-butyl-4-ethyldecahydro-4-quinolol (VIII) (mp 111-112° and R_f 0.82) and 0.03 g (6%) of secondary alcohol VII (mp 104-105° and R_f 0.57). Alcohol VIII did not depress the melting point of the product of the reaction of ketone V with C_2H_5MgBr [4].

Reaction of 2,7-Dimethyldecahydro-4-quinolone (IX) with $(C_2H_5)_3Al$. A) Reaction of 0.25 ml (1 mmole) of ketone IX and 0.3 g (2 mmole) of triethylaluminum gave 0.22 g (87%) of a crude substance, crystallization of which gave 0.042 g (19%) of alcohol X (mp 132-133° and R_f 0.70) and 0.165 g (75%) of its epimer with respect to the 4 position (XI) (mp 118-119° and R_f 0.60). A mixed-melting-point determination showed that epimer X is identical to the secondary alcohol previously obtained in [1].

B) Reaction of 0.5 g (2 mmole) of ketone IX and 1.55 g (10 mmole) of $(C_2H_5)_3Al$ in benzene at 40° for 2 h gave 0.48 g of a crude product, purification of which on Al_2O_3 with subsequent fractional crystallization from hexane–acetone (2 : 1) yielded 0.36 g (76%) of 2,7-dimethyl-4-ethyldecahydro-4-quinolol (XII) (mp 114-115° and R_f 0.76), which did not depress the melting point of the alcohol previously obtained in [4], and 0.04 g (9.5%) of secondary alcohol XI.

Reaction of 2-Methyl-7-tert-butyldecahydro-4-quinolone (XIII) with $(C_2H_5)_3Al$. A) The reaction of 0.25 g (1 mmole) of ketone XIII with 0.26 g (2 mmole) of triethylaluminum in benzene at 70° for 4 h gave 0.2 g (79%) of a mixture of secondary alcohols; separation of the mixture by fractional crystallization yielded 0.148 g (74%) of secondary alcohol XV (mp 124-125° and R_f 0.74) and 0.032 g (16%) of epimeric XIV (mp 174-175° and R_f 0.62), which was identical to the product of reduction of ketone XIII [2].

B) The reaction of 1.25 g (10 mmole) of $(C_2H_5)_3Al$ and 0.5 g (2 mmole) of ketone XIII in 25 ml of benzene at 40° for 2 h gave, after purification of the crude product on Al_2O_3 and crystallization [hexane–acetone (3 : 2)], 0.37 g (74%) of 2-methyl-7-tert-butyl-4-ethyldecahydro-4-quinolol (XVI) (mp 128-129° and R_f 0.88), which was identical to the product obtained in [4], and 0.04 g (7.5%) of secondary alcohol XV.

Reaction of 1,2,7-Trimethyldecahydro-4-quinolone (XVII) with $(C_2H_5)_3Al$. A) The reaction of 0.29 g (3 mmole) of $(C_2H_5)_3Al$ and 0.5 g (3 mmole) of ketone XVII in 25 ml of toluene at 105° for 18 h gave 0.46 g of a resinified reaction product; separation of the latter on Al_2O_3 (hexane and diethyl ether) yielded 0.14 g (30%) of secondary alcohol XVIII (mp 155-156° and R_f 0.48) and 0.28 g (60%) of starting ketone XVII (mp 59.5-60° and R_f 0.88). Alcohol XVIII did not depress the melting point of a sample of the genuine secondary alcohol [1].

B) The reaction of 0.25 g (1.2 mmole) of ketone XVII and 1.4 g (12 mmole) of $(C_2H_5)_3Al$ in toluene at 105° for 10 h gave 0.23 g (91%) of a crude mixture, fractional crystallization of which yielded 0.173 g (75%) of secondary alcohol XVIII (mp 155-156° and R_f 0.48) and 0.046 g (20%) of epimeric alcohol XIX (mp 168-169° and R_f 0.76). Alcohols XVIII and XIX did not depress the melting point of mixtures with samples previously synthesized in [1].

C) A total of 0.184 g (83%) of 1,2,7-trimethyl-4-ethyldecahydro-4-quinolol (XX) (mp 113-114°; R_f 0.60), which was identical to the alcohol obtained by reaction of ketone XVII with C_2H_5MgBr [3], was synthesized from 0.2 g (1 mmole) of ketone XVII and 0.22 g (2 mmole) of $(C_2H_5)_3Al$ in THF (60° for 5 h).

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STEREOCHEMISTRY OF THE 1,4-REDUCTION OF CHIRAL N-(α-PHENYLETHYL)-$\Delta^{9,10}$-4-KETOOCTAHYDROQUINOLINE*

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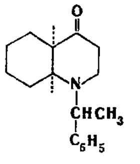
Only trans-N-(α-phenylethyl)-4-ketodecahydroquinoline, which is readily converted to a mixture containing 70% of the thermodynamically more stable cis isomer, is formed in the reduction of chiral N-(α-phenylethyl)-$\Delta^{9,10}$-4-ketooctahydroquinoline with lithium aluminum hydride.

We have previously established [2] that the 1,4-reduction of chiral N-(α-phenylethyl)-$\Delta^{9,10}$-4-ketooctahydroquinoline (I) with lithium aluminum hydride proceeds as an asymmetric synthesis and gives optically active bicyclic 4-piperidones IIa and IIb. The reduction also proceeds to a greater extent to give the corresponding alcohols.



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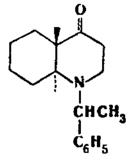

II b

In the present research we have made a detailed analysis of the stereochemical peculiarities of the reduction of enamino ketone I in order to ascertain the primary reaction pathway. The reduction was carried

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