20°C. The initial concentrations of (I) and (II) corresponded to those that were optimal for use in the reductive ammonolysis process, consisting of 0.07 moles/liter for (I) and 0.1 mole/liter for (II). Ammonolysis was carried out in the presence of 1.3 mmoles of Et_3N under analogous conditions.

We investigated the racemization of chiral (I) by an optical rotatory dispersion method, introducing the solvent into a polarimetric cuvette with a weighed amount of azlactone, adding the RS amine, and mixing the solution in order to follow the change of optical rotation with time (at $\lambda = 380$ nm for (Ia)). For comparison of racemization conditions we also observed a solution without any added amine.

CONCLUSIONS

1. Ammonolysis of 4-benzyl-5-oxazolone by S-(−)α-phenylethylamine in dimethoxyethane and in tert-butyl alcohol leads to the preferential formation of α-phenylamide of the N-acylamino acid with the SS-configuration.

2. We have shown the influence of the substituent in positions 2 and 4 and the influence of the nature of the solvent on the stereoselectivity of the process and on the rates of ammonolysis and racemization.

3. We also show the possibility that ammonolysis can proceed in two directions: by the interaction of the neutral oxazol-5-one molecule with S-α-phenylethylamine and the interaction of the corresponding anion with S-α-phenylethylammonium.

LITERATURE CITED

1. G. V. Chel'tsova, E. I. Karpeiskaya, E. I. Klabunovskii, and E. D. Lubuzh, Izv. Akad. Nauk SSSR, Ser. Khim., 59 (1983).
2. G. V. Chel'tsova, E. I. Karpeiskaya, L. N. Kaigorodova, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 65 (1983).
3. M. Goodman and L. Levin, J. Am. Chem. Soc., 86, 2918 (1964).
4. J. A. Riddick and W. B. Buger, Organic Solvents, Wiley-Interscience, New York (1970), Vol. 2, pp. 155, 213.
5. C. K. Ingold, Structure and Mechanism in Organic Chemistry, 2nd edn., Cornell University Press, Ithaca (1969), p. 1165.
6. I. Z. Siemion and A. Dzugay, Rocz. Chem., 40, 1699 (1966).

ASYMMETRIC SYNTHESIS OF AMINO ACIDS BY MEANS OF CATALYTIC REDUCTION OF AZLACTONES OF SUBSTITUTED ACYLAMINOACRYLIC ACIDS

COMMUNICATION 14. INFLUENCE OF THE NATURE OF THE SOLVENT ON REDUCTIVE AMMONOLYSIS OF Δ^2-OXAZOL-5-ONES

E. S. Levitina, L. F. Godunova, E. I. Karpeiskaya, and E. I. Klabunovskii

UDC 541.12.038.2:541.128:542.91:547.466

In our previous communications we described the reaction of reductive amminolysis of 4-benzylidene- and 4-alkylidene-Δ^2-oxazol-5-ones [1] in 1,2-dimethoxyethane by the action of chiral catalytic systems based on $PdCl_2$ and S-α-phenylethylamine (S-II) [1-5]. Replacement of the dimethoxyethane (DME) by tert-butyl alcohol led to a change in the reaction mechanism in the case of 4-alkylidene-5-oxazolones [4, 5]. The present work is devoted to the study of the influence of the nature of the solvent (DME and t-BuOH) on the kinetics and the stereoselectivity of the reductive ammonolysis reaction (RA) of 4-benzylidene-5-oxazolone.

Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1740-1747, August, 1983. Original article submitted November 15, 1982.

0568-5230/83/3208-1575$07.50

TABLE 1.* Reductive Ammonolysis of 2-Methyl-4-benzylidene-5-oxazolone in DME

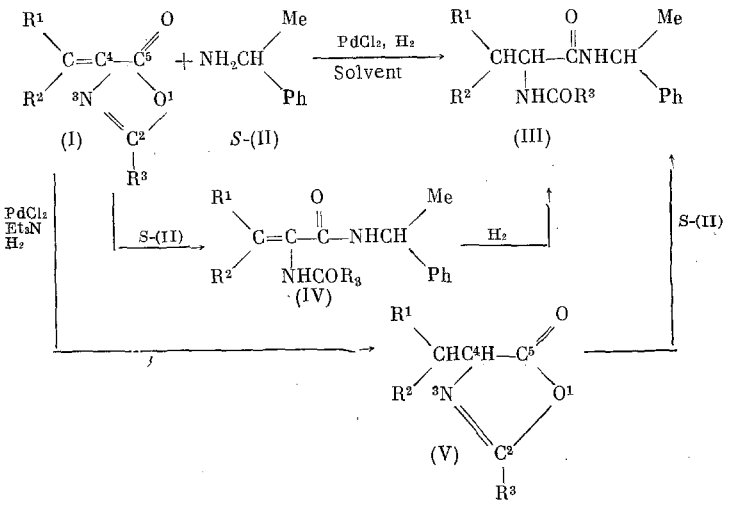
(Ia) moles	S-(II) moles	S-(II)/(Ia)	$PdCl_2$, g	DME, ml	$k_1 \cdot 10^2$, min^{-1}	k_2, liter/mole·min
0,071	0,103	1,5	0,020	15	1,63	0,29
0,071	0,103	1,5	0,025	15	1,91	0,35
0,071	0,103	1,5	0,035	15	1,93	0,31
				Average	1,82±0,17	0,31±0,03
0,107	0,155	1,5	0,020	10	2,32	0,24
0,107	0,155	1,5	0,030	10	3,69	0,34
0,107	0,155	1,5	0,035	10	3,55	0,33
				Average	3,18±0,75	0,30±0,05
0,083	0,20	2,4	0,023	8,4	2,68	0,18
0,054	0,20	3,7	0,035	20	1,77	0,10
0,036	0,20	5,6	0,035	30	2,46	0,14
0,027	0,20	7,5	0,035	40	1,35	0,07

* The coefficients of correlation (r^2) calculated directly for the first and second order equations for each part of the experiment were 0.99-0.98.

DISCUSSION OF RESULTS

Scheme 1 shows the reductive ammonolysis reaction of Δ^2-oxazol-5-ones

Scheme 1



$R^1 = H$, $R^2 = Ph$, $R^3 = Me$ (a); $R^1 = H$, $R^2 = Ph$, $R^3 = Ph$ (b).

We studied the possible steps followed in reductive ammonolysis of (I) (see Scheme 1) leading to the amide (III) as the product, showing that with DME and other aprotic solvents the process proceeds without intermediate formation of unsaturated amides (IV) and saturated oxazolones (V) [1-5]. Carrying out the reaction in alcohols led to the formation, along with the amides, of complex esters of N-acylamino acids in amounts which decrease with decrease in the acidity of the alcohols used [4, 6]. In t-BuOH we obtained amides (III) exclusively [4]. The analysis shown in Scheme 1 of the stepwise mechanism of reductive ammonolysis of 4-isopropylidene-5-oxazolone led to the inference that the saturated oxazolone (V) was an intermediate in the process [4]. The generality of the mechanism of reductive analysis established for a whole series of Δ^2-oxazo-5-ones in aprotic solvents [1-4, 7, 8], makes it possible to assume that in the case of 4-benzylidene-5-oxazolones (Ia, b) replacement of DME by t-BuOH results in an analogous change in the mechanism of the reaction.

With the objective of explaining the influence of the nature of the solvent on the mechanism of the reaction, we investigated the kinetics and stereochemistry of the reductive ammonolysis of (Ia) and (Ib) in DME and t-BuOH. Using the same solvents we studied the hydrogenation of (Ia, b) by the action of the Pd–triethylamine system and the stereoselectivity of the subsequent ammonolysis (PA) by the amine S-II of the saturated oxazolones thus formed (Va, b). We estimated the rates of the reductive ammonolysis (RA) and the protonization ammonolysis (PA) of (Ia, b) by the absorption of hydrogen. The investigation of the kinetics of the ammonolysis reaction (A) and

TABLE 2.* Reductive Ammonolysis of 2-Methyl-4-benzylidene-oxazol-5-one in t-BuOH (Ib) 1 mmole, $PdCl_2$ 0.018 mmoles, t-BuOH 15 ml

S-(II), moles	S-(II)/(Ib)	$k \cdot 10^2$, min^{-1}	k_2, liter/mole·min	EDSS-(III), %
0,10	1,5	1,30±0,03	0,21±0,01	50
0,15	2,0	2,77±0,05	0,24±0,03	48
0,18	2,5	1,04±0,05	0,08±0,01	33
0,20	3,0	1,67±0,02	0,10±0,02	28

* Constants k_1 and k_2 are average values for 2-3 experiments. Coefficients of correlation are 0.98-0.99 for each part of the experiment.

the racemization (R) of saturated oxazolones (Va, b) in DME and t-BuOH are described in [9].

A study of the possible subsequent steps of reductive ammonolysis of (Ia, b) in t-BuOH show that unsaturated amides (IV a, b) cannot be regarded as intermediate products, because hydrogenation of these yields amides of the alternate RS configuration (excess of the diastereomer (ED) 4-5%). The reductive ammonolysis of (Ia, b) with intermediate formation of (Va, b) cannot be excluded in t-BuOH inasmuch as ammonolysis of (Va, b) yields the same SS-(III) configuration as reductive ammonolysis of (Ia, b) [9].

We calculated the kinetic data for reductive ammonolysis of (Ia, b) in DME and t-BuOH by the first-order ($\ln C_0 - \ln C) = k_1 t$) and second-order ($\ln (C + \Delta)/C - \ln (C_0 + \Delta)/C = \Delta k_2 t$) equations where C_0 and C are the initial and present concentrations of (I) and Δ is the change in concentration of S-(II) and (I). As a result we noted that in describing the kinetics of reductive ammonolysis of (Ia) and (Ib) in DME and t-BuOH the graphic method of correlation analysis does not allow us to make an unambiguous choice of one or the other equation. However, variations of the initial concentrations of S(II) and (Ia) for reductive ammonolysis of (Ia) in DME show (Table 1) that the rate constant k_1 calculated on the basis of the first-order equation does not remain constant but changes fairly regularly under the conditions studied. At the same time rate constants k_2 maintained their constancy for concentrations of S-(II) not exceeding 0.15 moles/liter and ratios S-(II)/(Ia) = 1.5. Increasing the original concentration of S-(II) to 0.2 mole/liter and the ratio S-(II)/(Ia) to 2.4 leads to a sharp increase in rate and a change of k_2. Further increases in the S-(II)/(Ia) ratio at constant values of S-(II) in increments of 0.2 mole/liter had no significant effect on k_2. A change in the amount of $PdCl_2$ by a factor of 1.5 has no significant effect on the rate of reductive ammonolysis of (Ia) in DME. The data for reductive ammonolysis of (Ia) in t-BuOH presented a similar picture (Table 2). Changing the initial concentration in steps of 0.1-0.2 moles/liter but with a constant ratio of S-(II)/(Ia) $\leq$ 2.0 does not produce changes in the constants. Increases above 2.5 do result in sharp increases in k_2; k_1 does not remain constant for any concentration intervals which we studied.

The results obtained allow us to assert that the rate of reductive ammonolysis of (Ia) in both solvents is second order: first order with respect to the oxazolone and first order with respect to the amine.

The significant influence of the amount of the amine S-(II) on the stereoselectivity of reductive ammonolysis of (I) has been noted previously [1, 4, 5, 8]. This shows the role played by the amine/substrate ratio for which the optimum value is 1.5. It has been suggested that the reaction takes place by formation of Pd complexes in which the amine and the substrate are present in the form of ligands. Stabilization and regeneration of catalytic activity are partial depending on the course of the reaction of reductive ammonolysis of (I) and are evidently attained at the ratios indicated. Increasing the amount of the amine probably leads to removal of the substrate (I) from the coordination sphere of the catalytic Pd complex and destruction of the equilibrium between it and the reagents. This is expressed in the reduced rate of reaction and makes possible the formation of the byproduct (IV). The latter on hydrogenation yields RS-(III). Therefore a decrease in the stereoselectivity would be observed (see Table 2).

Therefore, the previous suggestion about the influence of the amine on the course of the reductive ammonolysis reaction is quantitatively verified in the present work. The independence of k_2 of the quantity of $PdCl_2$ on changing it by a factor of 1.5 shows that the concentration of the catalytically active portion remains constant within this range.

In Table 3 we show the rate constants for reductive ammonolysis and protonization ammonolysis of (Ia) and (Ib) in DME and t-BuOH, and also the stereoselectivities of these reactions expressed in the form of the

TABLE 3. Reductive Ammonolysis (RA) and Hydrogenation in the Presence of Triethylamine of 4-Benzylidene-5-oxazolones (Ia, b) with Subsequent Ammonolysis (PA) by S-(II) [(I) 1 mmole, S-(II) 1.5 mmoles, $PdCl_2$ 0.018 mmoles, Et_3N 1.5 mmoles, solvent 15 ml]

Reaction	(Ia, b) R^3	Solvent	$k_1 \cdot 10^2$, min^{-1}	k_2, liter/mole·min	ED SS-(III), %
RA	Me	DME	–	0,31±0,05	40
RA	Me	*t*-BuOH	–	0,24±0,04	50
RA	Ph	DME	4,13±0,05	0,79±0,04	9
RA	Ph	*t*-BuOH	2,27±0,60	0,37±0,10	25
PA	Me	DME	2,42±0,05	–	44
PA	Me	*t*-BuOH	1,72±0,05	–	45
PA	Ph	DME	1,20±0,05	–	9
PA	Ph	*t*-BuOH	2,24±0,06	–	25

excess of the SS-(III) diasteromers. The rate constants for reductive ammonolysis of (Ib) were calculated for both the first- and second-order rate equations, but no effort was made to choose between them.

As seen in Table 3 the reaction of reductive ammonolysis of (Ia) and (Ib) in both solvents results in formation of an excess of the SS-diastereomer (III) but the selectivity of reductive ammonolysis of (Ia) is greater than that of (Ib) which testifies to the significant influence of the substituent R^3 (C^2 position in (I)).

The rate of hydrogenation of (Ia) and (Ib) in the presence of Et_3N (PA reaction) in both solvents is described by an equation which is first order for oxazolones. The hydrogenation products (Va) and (Vb) obtained as a result undergo attack by the amine S-(II) with preferential formation of SS-(III) (see Table 3).

The establishment of the kinetic and stereochemical characteristics of the reductive ammonolysis (RA) of 4-isopropylidene and 4-benzylidene-Δ^2-oxazol-5-one and also by comparing these results with those from the ammonolysis and racemization of the corresponding saturated oxazolones in DME and t-BuOH it is possible to elucidate the role of the solvent in the basic process. In Table 4 we show the values of the rate w at the moment of half transformation, calculated from the corresponding constants, and the degree of stereoselectivity in the reactions investigated. In column R of Table 4 we present the rate of racemization w_r of optically active (V) by the racemic amine S,R-(II). It should be noted that the values of the constants used in the calculation of w_r were obtained experimentally in experiments 1-3 and 5. In experiments 4 and 6-8 the rate of racemization was too great which prevented its measurement under the conditions studied. However, taking into consideration the fact that in DME the presence of the $C_6H_5CH_2$ group (position C^4 in (V)) speeds up the process by a factor of 20, phenyl groups (position C^2 in (V)) speed it up by a factor of 100, and that in t-BuOH compared to DME, the rate is increased by a factor of 100 [9], one could estimate with precision the rate of racemization for the whole series of (V) compounds from the sum of the contributions of the substituents and the solvents. By comparison of the w_r values calculated in such a manner and presented in Table 4 in the form of log w_r it is evident that the rate of racemization of optically active (V) strongly depends on the molecular structure and it successively increases with increase in the stability of the carbanions formed from these compounds. A phenyl group in the C^2 position produces an even greater increase in the rate. In t-BuOH we observed a general increase in the rate of racemization which is evidence for the additional stabilization of carbanions [9].

The rate of ammonolysis of saturated oxazol-5-ones is significantly lower than the rate of racemization, which means that the dominant influence on the reaction rate is the substituent in the C^4 position of the oxazolone ring. In both solvents 4-benzyloxazolones open up much faster than the 4-isopropyl derivatives. Along with that is the general increase in rate in t-BuOH compared to DME. In particular the nature of the substituent in the C^4 position influences the stereochemistry of ammonolysis. In DME the 4-isopropyl product (see Table 4, Nos. 1 and 2) leads preferentially to diastereomer (III) with the RS-configuration, the 4-benzyl product to SS-(III) (Nos. 3 and 4). In t-BuOH regardless of the substituent in the C^4 position SS-(III) is formed (Nos. 6-8). The excess of diasteromer SS-(III) in ammonolysis products (V) of the same structure is greater for use of t-BuOH as solvent than for DME. We explained these facts previously [9, 10] by the possibility that the reaction goes in two different directions, either via the reaction of neutral molecules (V) with S-(II), or the reaction of the corresponding carbanions with the substituted ammonium ion, in which a look at the stereochemistry of both directions shows that formation of SS-(III) would be preferred in the first case and RS-(III) in the second. It is evident that in DME the path via the carbanion plays a significant role and leads to a diminished yield of SS-(III) in the products of ammonolysis. In t-BuOH the reaction proceeds mainly through the reaction of neutral molecules of (V), which leads to an increased yield of SS-(III).

TABLE 4. Kinetic and Stereochemical Characteristics of Transformations of Δ^2-Oxazol-5-ones

Number	Solvent	Δ^2-oxazolone			w* (ED, %, configuration of (III))			R† log w_r	log (w_r/w_{RA})
		R^1	R^2	R^3	RA ((I) c *S*-(II))	PA [(I) c Et_3N]	A [(V) c *S*-II]		
1	DME	Me	Me	Me	6,6 (44 *SS*) [3]	–	0,3 (6,2 *R*) [10]	0,48	−0,40
2		Me	Me	Ph	3,6 (5 *SS*) [3]	9,8 (8 *RS*) [3]	1,0 (4,6 *RS*) [10]	2,45	+1,89
3		H	Ph	Me	7,1 (40 *SS*)	8,5 (44 *SS*)	5,5 (13 *SS*) [9]	1,83	+0,98
4		H	Ph	Ph	14,1 (9 *SS*) [2]	4,2 (9 *SS*) [2,3]	2,9 (2,4 *SS*) [9]	3,83	+3,31
5	*t*-BuOH	Me	Me	Me	–	–	5,0 (14 *SS*) [10]	2,43	–
6		Me	Me	Ph	4,5 (25 *SS*) [4]	8,4 (24 *SS*) [3]	2,7 (16 *SS*) [10]	3,20	2,55
7		H	Ph	Me	5,0 (50 *SS*)	6,0 (45 *SS*)	24 (31 *SS*) [9]	3,83	3,13
8		H	Ph	Ph	6,0 (25 *SS*)	7,8 (25 *SS*)	27 (38 *SS*) [9]	5,83	5,01

*w is the reaction rate calculated from the corresponding constant at the moment of half-transformation.
† R is the racemization of optically saturated Δ^2-oxazol-5-ones (V) by the action of RS-(II). A is ammonolysis.

The values of the rates of hydrogenation of (I) in the presence of Et_3N agree closely among themselves, and are essentially independent of the solvent as well as of the structure of the substrate molecule in contrast to the rates of ammonolysis and racemization (see Table 4). These values are also close to the rate of reduction of (I) in the presence of the amine S-(II). This fact is evidence that the RA reaction begins with reduction of the C = C bond in (I).

By comparing the stereoselectivities of the reactions in DME (see Table 4) it may be seen that the RA reaction of (I) in all instances leads to the formation of SS-(III), which emphasizes the generality of the RA mechanism. As a result of the two-step process of (PA) in DME where stereoselectivity is determined by the step involving ammonolysis of (V), the alternate RS-(III) configuration predominates in the case of 4-isopropylidene-5-oxazolone. The ammonolysis of the 4-isopropyl product (V) also leads to RS-(III). We observed analogous formation of these alternate configurations for RA and PA for another 4-alkylidene-5-oxazolone (R^1 = Me; Re^2 = Et) [11]. In these instances when the substituent in the C^4 position (R^1 = H, R^2 = Ph) contains the phenyl group then only the diastereomer with the SS configuration is formed by reductive ammonolysis, protonization ammonolysis or simple ammonolysis.

When t-BuOH is used as the solvent, for RA, PA, and A, SS-(III) forms regardless of the structure of the substrate molecule (see Table 4). In this instance the rates and stereoselectivities in RA and PA of the corresponding substrates essentially do not differ, which indicates that in this solvent the reductive ammonolysis of (I) takes place with the intermediate formation of the saturated oxazol-5-one (V).

Assuming the generality of the RA reaction of (I) in DME, leading in all instances to SS-(III), in contrast to the PA mechanism, which in the case of 4-alkylidene-5-oxazolones yields the alternate RS-(III) configuration, it is possible to exclude the intermediate formation of (V) in the reductive ammonolysis of Δ^2-oxazol-5-ones in DME. In t-BuOH the rates and the stereoselectivities of the comparable (I) compounds do not differ essentially, which is evidence for the identity of the RA and PA mechanisms, and evidently the RA reaction proceeds without intermediate formation of (V).

The comparisons given verify our previous suggestions about the mechanism of the reductive ammonolysis (RA) of 4-alkylidene-5-oxazolones in t-BuOH and DME [4, 5] and make it possible to suggest a more concrete description of the various steps in the catalysis (Scheme 2).

1. The RA reaction begins with the reduction of the C = C bond in (I).

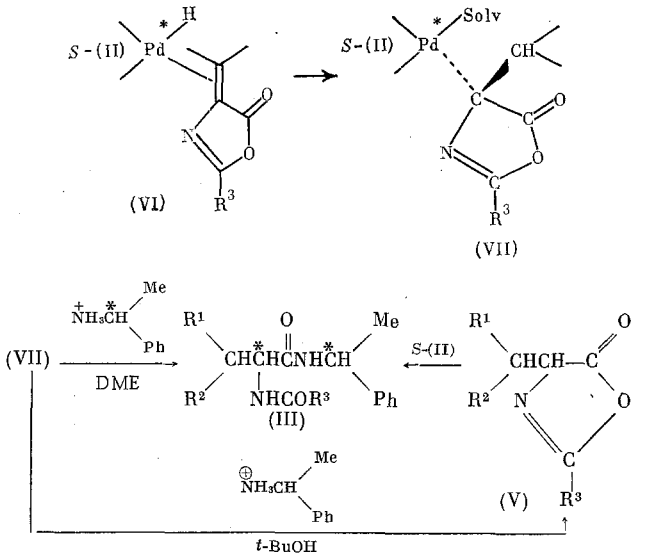
2. Orientation of the prochiral C = C bond preferentially toward one or the other side determines the chirodiastaltic interaction of (I) with the chiral Pd catalyst.

3. In the formation of particle (VI) into which the substrate and the amine S-(II) enter as ligands, hydrogen is transferred to the β-center of the C = C bond giving particle (VII).

4. In particle (VII) the oxazolone fragment, bonded to the Pd by a σ-bond, may be compared in its properties to the corresponding saturated oxazolones (V).

5. Coordination of a proton with the α-center and the opening of the ring leads to the interaction of particle (VII) and S-α-phenylethylamine (see the scheme in [4]). In this the stereoselectivity of reductive ammonolysis (RA) may depend on the stability of the Pd – C bond in (VII). If R^3 = Me the Pd – C bond is sufficiently stable (the tendency of (V) to racemize in DME is comparatively small). The stereoselectivity of RA reaches 44%.

Scheme 2



If R^3 = Ph in (I) the Pd–C bond is significantly weakened (the racemization capability of (V) is greater by a factor of 2) and the possibility of breaking the Pd–C bond increases. This is the reason for the sharp lowering of the stereoselectivity of RA by 9%.

Comparison of the rate of racemization of (V) and the reductive ammonolysis (RA) of (I) in DME (see Table 4) with the stereoselectivity of RA of (I) shows a significant correlation between these quantities. In Table 4 where the dependency of the stereoselectivity of the RA of (I) on the rate ratio w_r/w_{RA} (in the logarithmic form) shows that high stereoselectivity exists for low values of log (w_r/w_{RA}). We observed this with reductive ammonolysis of 2-methyl-5-oxazolone in DME. In the 2-phenyl product, where the ratio is greater by a factor of 2, the stereoselectivity of RA is significantly lower.

Comparison with the values shown with use of t-BuOH as the solvent does not permit an analogous correlation. Regardless of the higher value of log (w_r/w_{RA}), we noted a higher stereoselectivity of the RA of (I) reaching 40-60%. Therefore, in t-BuOH the reaction proceeds by another mechanism but particle (VII) in particular evidently breaks down giving the saturated product (V) by interaction with the substituted ammonium ion which enters into the ammonolysis reaction in quantity. In this instance the chirality of the Pd catalyst does not influence the stereoselectivity of the reductive ammonolysis as the latter is determined by the stereoselectivity of the ammonolysis reaction of (V).

However, by replacing the solvent DME by t-BuOH in the RA reaction, a change in mechanism occurs which is brought out by the fact that the simultaneous reactions of reduction and ammonolysis in DME and t-BuOH occur in separate steps with intermediate formation of saturated oxazolones. The reason for the change in mechanism is the strong solvating effect of t-BuOH attributable to the dissociation of the Pd–C bond of the intermediate particle (VII). Analogous solvent effects would be expected in the instances of reductive ammonolysis of other Δ^2-oxazol-5-ones.

EXPERIMENTAL

^{1}H NMR spectra were determined on a Bruker WM-250 radiospectrometer with HMDS internal standard, pure $PdCl_2$; S-α-phenylethylamine (S-(II)) $[\alpha]_D^{20} = -39°$ (no solvent); 2-phenyl-4-benzylidene-5-oxazolone (Ia) obtained according to [12], mp 165-166°C (from EtOH), 2-methyl-4-benzylideneoxazolone, mp 150°C (from acetone).

We carried out the reductive ammonolysis of (Ia) and (Ib) in t-BuOH and the isolation of products (III) according to [1, 2]. Hydrogenation of (Ia) and (Ib) was carried out in t-BuOH with Et_3N and the subsequent ammonolysis by S-(II) (PA reaction) according to the methods used in [2, 7]. We estimated the reaction rates by the absorption of hydrogen. We calculated the concentration of (I) by the equation $C = C_0(1 + V_t/V)$ where C_0 and C are the initial and present concentrations of (I) in moles/liter; V is the total volume of absorbed hydrogen (in ml), V_t is the amount of H_2 absorbed at any given moment of time (in ml).

The obtained data were evaluated for reductive ammonolysis of (Ia) and (Ib) using the first- and second-order kinetic equations. Data on hydrogenation in the presence of Et_3N show that the process follows a first-order equation. The rate constants were determined by the least squares method.

The isolation and hydrogenation of S-α-phenylethylamides of N-acetyl-(IVa) and N-benzyl cinnamic acids (IVb) in t-BuOH were carried out by the methods of [1, 2].

CONCLUSIONS

1. We show the reductive ammonolysis reaction (RA) of 2-methyl and 2-phenyl-4-benzylidene-5-oxazolones and their hydrogenation in presence of Et_3N with subsequent ammonolysis with S-α-phenylethylamine in t-BuOH.

2. The reductive ammonolysis of Δ^2-oxazol-5-ones proceeds through initial reduction of the C=C bond.

3. We discuss the mechanism of reductive ammonolysis of Δ^2-oxazol-5-ones in DME and t-BuOH. In DME the reaction proceeds as a simultaneous interaction of oxazolone, hydrogen, and amine in the coordination sphere of the Pd complex, and in t-BuOH via the intermediate formation of saturated oxazolones.

4. We show the correlation which we found between the stereoselective reductive ammonolysis of Δ^2-oxazol-5-ones and the relative rates of reductive ammonolysis of (I) and the racemization of the corresponding saturated oxazolones in DME.

LITERATURE CITED

1. E. I. Karpeiskaya, L. F. Godunova, E. S. Neupokoeva, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1104 (1978).
2. E. I. Karpeiskaya, G. V. Chel'tsova, E. I. Klabunovskii, and A. V. Kharchevnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1082 (1980).
3. G. V. Chel'tsova, E. I. Karpeiskaya, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2530 (1981).
4. G. V. Chel'tsova, E. I. Karpeiskaya, L. N. Kaigorodova, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 65 (1983).
5. I. É. Khatskevich, I. K. Kalnin', E. I. Karpeiskaya, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 359 (1983).
6. E. S. Neupokoeva, E. I. Karpeiskaya, L. F. Godunova, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 146 (1979).
7. E. S. Neupokoeva, E. I. Karpeiskaya, L. F. Godunova, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 139 (1979).
8. E. I. Karpeiskaya, E. S. Neupokoeva, L. F. Godunova, I. P. Murina, A. P. Kharchevnikov and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1368 (1978).
9. L. F. Godunova, E. S. Levitina, E. I. Karpeiskaya, E. I. Klabunovskii, and E. D. Lubuzh, Izv. Akad. Nauk SSSR, Ser. Khim., 1733 (1983).
10. G. V. Chel'tsova, E. I. Klabunovskii, E. I. Karpeiskaya, and E. D. Lubuzh, Izv. Akad. Nauk SSSR, Ser. Khim., 59 (1983).
11. I. É. Khatskevich, I. K. Kalnin', E. I. Karpeiskaya, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 366 (1983).
12. E. P. Prokof'ev, E. I. Karpeiskaya, G. V. Chel'tsova, and T. B. Dantsig, Izv. Akad. Nauk SSSR, Ser. Khim., 823 (1980).