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Original Scientific Paper

On the Preparation of Some Tertiary Amines Containing the 2-Furfuryl Group. Isomerization of Allyl-aryl-(2-furfuryl)-amines to *N*-Aryl-4H-5,7a-epoxyisoindolines*

D. Bilović** and V. Hahn***

Department of Organic Chemistry and Biochemistry, Institute »Ruđer Bošković« and Laboratory of Organic Chemistry, Faculty of Technology, University of Zagreb, Zagreb, Croatia, Yugoslavia

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Six new tertiary 2-furfurylamines of the general formula $2\text{-C}_4\text{H}_3\text{O}\cdot\text{CH}_2\text{NRAr}$, where R represents methyl, ethyl or allyl, and Ar phenyl, *p*-tolyl or *p*-methoxyphenyl groups, have been prepared by alkylation of the appropriate secondary aryl-(2-furfuryl)-amines with alkyl or allyl halides.

It was found that the oily allyl-aryl-(2-furfuryl)-amines, on standing at room temperature, spontaneously isomerized to crystalline *N*-aryl-4H-5,7a-epoxyisoindolines, formed by a reversible intramolecular Diels-Alder reaction.

In the course of our recent work on tertiary amines and quaternary ammonium compounds containing the 2-furfuryl group¹, we needed a number of various tertiary alkyl- (and allyl)- aryl-(2-furfuryl)-amines in order to examine their behaviour towards alkyl halides in quaternization experiments². A survey of the literature showed, however, that only a few representatives of this class of tertiary 2-furfurylamines have been previously described.

In 1940 Umnova³ published a convenient method for the preparation of ethyl-(2-furfuryl)-aniline. By alkylation of (2-furfuryl)-aniline with ethyl iodide in the presence of sodium amide in dry ether, the tertiary amine was obtained in good yield. More recently, methyl-(2-furfuryl)-aniline⁴ and the three isomeric methyl-(2-furfuryl)-toluidines⁵ have been prepared in an analogous way.

In the present paper the preparation and some properties of several new alkyl- (and allyl)- aryl-(2-furfuryl)-amines are described.

Ethyl-(2-furfuryl)-*p*-toluidine (I) and ethyl-(2-furfuryl)-*p*-anisidine (III) were prepared by treating (2-furfuryl)-*p*-toluidine and (2-furfuryl)-*p*-anisidine respectively with ethyl bromide and sodium amide, using essentially the same procedure as described by Eliel and Peckham for the preparation of methyl-(2-furfuryl)-aniline⁴. For the preparation of methyl-(2-furfuryl)-*p*-anisidine (II), (2-furfuryl)-*p*-anisidine was allowed to react with a slight surplus of methyl iodide without addition of sodium amide.

* Studies in the Furan Series. XIII. Part XII: B. Glunčić, K. Jakopčić, N. Krvavica, and V. Hahn, *Croat. Chem. Acta* **38** (1966) 119.

** Taken in part from the Thesis of D. Bilović, presented to the University of Zagreb, 1963, in partial fulfilment of the requirements for the degree of Doctor of Chemistry (Ph. D.).

*** To whom inquiries should be sent.

In a similar way, the reactions between (2-furfuryl)-aniline, (2-furfuryl)-*p*-toluidine and (2-furfuryl)-*p*-anisidine, and allyl iodide, have been carried out without sodium amide. The tertiary amines (IV—VI) have been obtained in satisfactory over-all yields as light yellow oils, distilling under reduced pressure without decomposition.

Whereas the newly prepared alkyl-aryl-(2-furfuryl)-amines (I—III) showed similar properties as the hitherto known tertiary amines of the same class³⁻⁵, the allyl-aryl-(2-furfuryl)-amines (IV—VI) manifested a different, rather unexpected, behaviour. On standing at room temperature the oily amines gradually solidified and in a period of time, varying from several days to several months, were completely transformed into crystalline substances. These crystals showed the same basic properties and the same composition as their oily »precursors«.

CHART 1

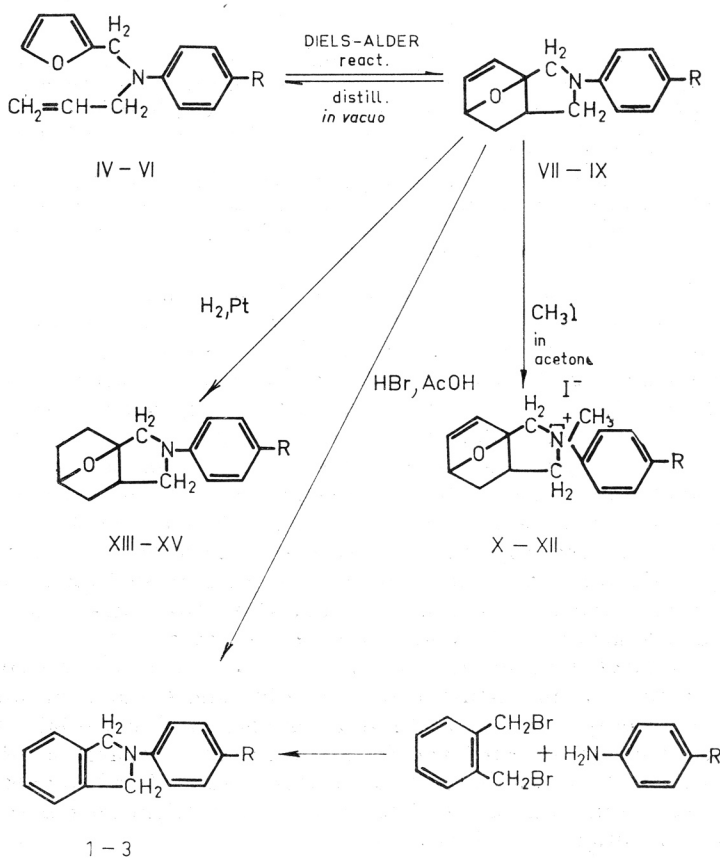
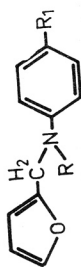


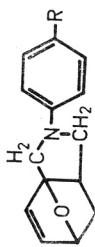
TABLE I
Alkyl-(and allyl)-aryl-(2-furfuryl)-amines and Their Salts



Compd.	R	R ₁	Pro- ce- dure	Yield %	Salt	B. p. °C/mm.	M. p. °C	²⁰ n _D	Formula	Ana- lyses		calc'd. found	
										% C	% H	% C	% H
I	C ₂ H ₅	CH ₃	A	81	—	163—64/15	—	—	C ₁₄ H ₁₇ NO	—	—	—	—
Ia	C ₂ H ₅	CH ₃			Picrate ^a	—	124	—	C ₂₀ H ₂₆ N ₄ O ₈	54.05	4.54	12.61	12.39
II	CH ₃	OCH ₃	B	52	—	173—77/12	53—54 ^b	—	C ₁₃ H ₁₅ NO ₂	71.86	6.96	6.45	6.45
IIa	CH ₃	OCH ₃			Picrate ^b	—	124—25	—	C ₁₉ H ₁₈ N ₄ O ₉	71.88	6.72	12.55	12.55
III	C ₂ H ₅	OCH ₃	A	65	—	180—83/13	—	—	C ₁₄ H ₁₇ NO ₂	—	—	—	12.67
IIIa	C ₂ H ₅	OCH ₃			Picrate ^b	—	121—22	—	C ₂₀ H ₂₆ N ₄ O ₉	52.17	4.38	12.17	12.17
IV	C ₃ H ₅	H	C	51	—	165—68/13	—	1.5757	C ₁₄ H ₁₃ NO	52.29	4.32	12.12	12.12
IVa	C ₃ H ₅	H			Picrate ^b	—	109—10	—	C ₂₀ H ₁₈ N ₄ O ₈	—	—	—	12.67
IVb	C ₃ H ₅	H			Hydriodide ^c	—	88—89	—	C ₁₄ H ₁₆ INO	49.28	4.73	12.92	12.92
V	C ₃ H ₅	CH ₃	C	61	—	178—81/14	—	1.5682	C ₁₅ H ₁₇ NO	49.47	4.83	—	—
Va	C ₃ H ₅	CH ₃			Picrate ^b	—	116—17	—	C ₂₁ H ₂₆ N ₄ O ₈	—	—	—	—
Vb	C ₃ H ₅	CH ₃			Hydriodide ^d	—	101—02	—	C ₁₅ H ₁₈ INO	50.72	5.11	12.28	12.24
VI	C ₃ H ₅	OCH ₃	C	69	—	192—94/13	—	1.5699	C ₁₅ H ₁₇ NO ₂	50.80	5.11	—	—
VIa	C ₃ H ₅	OCH ₃			Picrate ^a	—	98—99	—	C ₂₁ H ₂₆ N ₄ O ₉	53.39	4.27	11.86	11.85

^a From ethanol-water (1:1); ^b From ethanol; ^c From ethyl acetate; ^d From ethanol-ethylacetate (1:1).

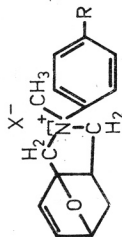
TABLE II
N-Aryl-4*H*-5,7*a*-epoxyisoindolines and Their Salts



Compd.	R	Time ^a	Yield ^b	Salt	M. p. °C	Formula	Analyses		calc'd. found	
							% C	% H	% C	% H
VII	H	30 min. — 12 hrs	100	—	120—21 ^c	C ₁₄ H ₁₅ NO	78.84	7.09	6.57	6.65
VIIIa	H			Hydriodided	138 (dec.)	C ₁₄ H ₁₆ INO	78.60	6.91	—	—
VIIIb	H			Picrate ^c	145 (dec.)	C ₂₀ H ₁₈ N ₄ O ₈	49.28	4.73	12.67	12.85
VIII	CH ₃	2—30 days	100	—	104—05 ^c	C ₁₅ H ₁₇ NO	79.26	7.54	6.16	6.16
VIIIa	CH ₃			Hydriodided	146 (dec.)	C ₁₅ H ₁₈ INO	79.33	7.48	6.29	6.29
VIIIb	CH ₃			Picrate ^c	116—17	C ₂₁ H ₂₀ N ₄ O ₈	50.72	5.11	—	—
IX	OCH ₃	10—60 min.	100	—	136—38 ^c	C ₁₅ H ₁₇ NO ₂	50.78	4.99	12.28	12.32
IXa	OCH ₃			Hydriodided	153 (dec.)	C ₁₅ H ₁₈ INO ₂	74.05	7.04	5.76	5.95
IXb	OCH ₃			Picrate ^c	136—37	C ₂₁ H ₂₀ N ₄ O ₉	48.53	4.89	—	—
							48.70	4.95	11.86	12.03

^a Time needed for beginning of solidification; ^b Yield of crude product; ^c From ethanol; ^d From ethanol-ether.

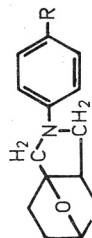
TABLE III
N-Methyl-N-aryl-4H-5,7a-epoxyisoindolinium Iodides and Picrates



Compd.	R	Yield ^a %	Salt	M. p. °C	Formula	Analyses					
						Calcd.			Found		
						% C	% H	% N	% C	% H	% N
X	H	50	Iodide ^b	141—42	C ₁₅ H ₁₈ INO	50.72	5.11	—	50.49	4.96	—
Xa	H	—	Picrate ^c	145	C ₂₁ H ₂₀ N ₄ O ₈	—	—	12.28	—	—	12.41
XI	CH ₃	96	Iodide ^b	145—46	C ₁₆ H ₂₀ INO	52.05	5.46	—	52.10	5.55	—
XIa	CH ₃	—	Picrate ^c	152—53	C ₂₂ H ₂₂ N ₄ O ₈	—	—	11.91	—	—	12.15
XII	OCH ₃	54	Iodide ^b	130—31	C ₁₆ H ₂₀ INO ₂	49.88	5.23	—	50.03	5.21	—
XIIa	OCH ₃	—	Picrate ^c	166—67	C ₂₂ H ₂₂ N ₄ O ₉	—	—	11.52	—	—	11.46

^a Yield of crude product; ^b From ethanol-ether; ^c From ethanol.

TABLE IV
N-Aryl-5,7a-epoxy-perhydroisoindoles



Compd.	R	Yield ^a	M. p. °C	Formula	Analyses					
					Calcd.			Found		
					% C	% H	% N	% C	% H	% N
XIII	H	100	84 ^b	C ₁₄ H ₁₇ NO	78.10	7.96	6.51	78.15	7.82	6.64
XIV	CH ₃	100	102—04 ^b	C ₁₅ H ₁₉ NO	78.56	8.35	6.11	78.40	8.09	6.13
XV	OCH ₃	100	98—99 ^b	C ₁₅ H ₁₉ NO ₂	73.44	7.81	5.71	73.65	7.72	5.96

^a Yield of crude product; ^b From ethanol.

However, on the basis of the different IR-spectra and of the different properties of their salts (picrates, hydriodides), it could be concluded that the oily and the corresponding crystalline substances had not the same structure. It was recognized that isomerization of the oily allyl-aryl-(2-furfuryl)-amines was effectuated by a novel type of intramolecular Diels-Alder reaction, the allyl group being the dienophylic, the furan nucleus the dienic component⁶.

It is to be noted that in the last years several examples of intramolecular Diels-Alder reactions have been described⁷.

The rate of isomerization of the prepared amines (IV—VI) showed marked differences. It was observed that the time needed for solidification of allyl-(2-furfuryl)-*p*-toluidine (V) was sensibly longer than in the case of the other two amines (IV and VI).

The structure of the formed crystalline adducts, as being that of the hitherto undescribed *N*-aryl-4H-5,7*a*-epoxyisoindolines (VII—IX), could be unequivocally established. Hydrogenation of VII—IX over an Adams platinum catalyst at room temperature led always to uptake of only one mole of hydrogen with formation of the corresponding *N*-aryl-5,7*a*-epoxy-perhydroisoindolines (XIII—XV). By heating the epoxy compounds VII—IX with a mixture of 66% hydrobromic acid with glacial acetic acid at 60° for 2 hours⁸, the corresponding *N*-aryl-isoindolines were obtained. They proved to be identical (mixed melting points, IR spectra) with authentic samples prepared from α,α' -dibromo-*o*-xylene, and the appropriate aromatic primary amines, according to previously described procedures^{9,10}. Quaternization of the epoxy-isoindolines (VII—IX) was easily effectuated by heating in acetonic solution with an excess of methyl iodide at 60°. The formed *N*-methyl-*N*-aryl-4H-5,7*a*-epoxyisoindolinium iodides (X—XII), treated with sodium picrate, gave well crystallized picrates.

Isomerization of allyl-aryl-(2-furfuryl)-amines to *N*-aryl-4H-5,7*a*-epoxy-isoindolines proved to be reversible. When the epoxy compounds (VII—IX) were subjected to distillation *in vacuo*, the oily amines (IV—VI) were obtained again, their IR spectra being identical with the spectra of the starting amines and different from the spectra of the epoxy isomers. They showed also in every other respect the same properties as the first obtained amines.

The described isomerization of the amines IV—VI, as well as the transformations of the epoxyisoindolines VII—IX, are outlined in Chart 1. Data concerning the preparations and properties of the compounds described in this paper are given in the experimental part and in Tables I—IV.

EXPERIMENTAL

In most cases only general procedures used in the present work will be described in detail in this section. Data concerning individual compounds are listed in Tables I—IV.

All melting and boiling points are uncorrected.

Materials

The secondary aryl-(2-furfuryl)-amines, needed as starting material, were prepared as described earlier¹¹ and freshly distilled before use. (2-Furfuryl)-aniline boiled at 148—149°/12 mm. (lit.¹¹ b. p. 152—156°/16 mm.), (2-furfuryl)-*p*-toluidine at 156—159°/14 mm. (lit.¹¹ b. p. 157—160°/14 mm.); (2-furfuryl)-*p*-anisidine had b. p. 182—184°/14 mm. and m. p. 46—47° (lit.¹¹ b. p. 190—194°/21 mm., m. p. 47—48°).

Alkyl- (and allyl)- aryl-(2-furfuryl)-amines (I—VI) and their salts (Table I)

A. A reaction mixture of 0.1 mole of aryl-(2-furfuryl)-amine, 0.11 mole of ethyl bromide and 0.15–0.17 mole of sodium amide was prepared and treated as described by Eliel and Peckham⁴ and the isolated tertiary amine distilled *in vacuo*. In this way the amines I and III were obtained as light yellow oils which darkened upon standing.

B. A mixture of 0.1 mole of secondary amine and 0.13 mole of methyl iodide was allowed to stand in a thoroughly stoppered flask for several hours at room temperature and, thereafter, 2 days in a refrigerator (at about 0°). The reaction mixture was treated with water and filtered, the aqueous solution alkalyzed by addition of a 30% NaOH solution and was subsequently extracted with ether. After drying over dry sodium or magnesium sulfate, the solvent was evaporated and the residual oil fractionated under reduced pressure. By this procedure, II was prepared; it could be obtained as a colorless crystalline substance, darkening on longer standing.

C. To the freshly distilled secondary amine (approx. 0.05 mole), allyl iodide (approx. 0.055–0.058 mole) was added dropwise with external cooling and the mixture allowed to stand in a well stoppered flask for several hours at room temperature and then overnight in a refrigerator at about 0°. From the dark semi-solid reaction mixture, the hydriodide of the formed tertiary amine could be separated in some cases. This was filtered off and washed with small portions of ethyl acetate. The crude hydriodide (or, if it could not be isolated, the whole reaction mixture) was dissolved in about 150–400 ml. of water, treated with 30–50 ml. of 40% aqueous NaOH and extracted with ether. The ethereal solution was dried, the solvent evaporated and the residue distilled *in vacuo*. In this way the amines IV–VI were obtained as light yellow oils which, on standing, gradually transformed into the corresponding crystalline *N*-aryl-4H-5,7a-epoxyisoindolines (see below).

The pure hydriodides (IVb and Vb) were obtained as almost colorless crystalline substances by crystallization of the crude hydriodides (see above) from appropriate solvents.

The picrates (Ia–VIa) were prepared from the free bases with picric acid in alcoholic solution, or from the pure hydriodides with sodium picrate in aqueous solution. After crystallization, yellow crystals of the pure salts were obtained.

N-Aryl-4H-5,7a-epoxyisoindolines (VII–IX) and Their Salts (Table II)

The oily allyl-aryl-(2-furfuryl)-amines (IV–VI), obtained after distillation in a pure form, were allowed to stand in stoppered flasks at room temperature. After 10–30 minutes to several days, the time depending on the amine and varying somewhat from experiment to experiment, crystallization began and progressed gradually. After a few days to several months the oil completely solidified into a crystalline mass. The crude product, having no sharp melting point, was recrystallized to give colorless crystals of the pure epoxy compound.

The well crystallized hydriodides (VIIa–IXa) were prepared in the following way: to a solution of 0.25–0.5 g. (1–2.3 mmoles) of the base in 5 ml. of acetone, an excess of 70% hydriodic acid (0.5–0.6 g., *i. e.* 2.7–3.3 mmoles) was added. After standing at room temperature for 60–90 minutes, the acetone was evaporated *in vacuo* without warming and the residue washed with ether. The resulting crude salt was purified by crystallization.

The picrates (VIIb–IXb) were prepared from equivalent amounts of base and picric acid in alcoholic solution and purified by crystallization.

N-Methyl-N-aryl-4H-5,7a-epoxyisoindolinium Iodides (X–XII) and Picrates (Table III)

To a solution of 0.7–1.0 g. (2.9–4.7 mmoles) of the *N*-aryl-4H-5,7a-epoxyisoindoline (VII–IX) in 5 ml. of acetone, a large excess of methyl iodide (2.6–6.6 g., *i. e.* 18–48 mmoles) was added and the mixture heated to 60° for 5–10 hrs. The solution was concentrated *in vacuo* at room temperature to about half its original volume and diluted with ether. On standing, the crude *N*-methyl-*N*-aryl-4H-5,7a-epoxyisoindolinium iodide separated. After several crystallizations, almost colorless crystals of the pure salt were obtained.

The picrates (Xa—XIIa) were prepared by treating the iodides (X—XII) with equivalent amounts of sodium picrate in aqueous solution. After recrystallization crystals of the pure salt were obtained.

N-Aryl-5,7a-epoxyperhydroisoindoles (XIII—XV) (Table IV)

A solution of 0.4—0.5 g. (1.85—2.4 mmoles) of the *N*-aryl-4H-5,7a-epoxyisoindoline (VII—IX) in 45—55 ml. of ethanol was hydrogenated over 30—32 mg. of Adams PtO₂ catalyst* at room temperature and atmospheric pressure as long as uptake of hydrogen could be observed. Ordinarily, one molar equivalent of hydrogen was absorbed after about 10 min. After filtration, the solution was evaporated *in vacuo* to dryness. The crude epoxyperhydroisoindoles (XIII—XV), obtained in quantitative yield, were purified by crystallization. The pure products were colorless, well crystallized substances.

N-Aryl-isoindolines (1—3)

A mixture of 1.0—1.5 g. (4.7—6.6 mmoles) of the *N*-aryl-4H-5,7a-epoxyisoindoline (VII—IX) and 2—5 ml. of 66% hydrobromic acid and 10—15 ml. of glacial acetic acid was heated for 2 hrs. at 60°. The resulting dark solution was concentrated to at least half its original volume and mixed with about 100—150 ml. of water. The crude *N*-arylisindoline was separated by filtration, washed with a few ml. of warm ethanol and crystallized several times from the same solvent.

In this way *N*-phenyl-isoindoline (1), m. p. 171—172° (lit.⁹ m. p. 170—171°, lit.¹⁰ m. p. 172—173°), *N*-(*p*-tolyl)-isoindoline (2), m. p. 193—194° (lit.⁹ m. p. 195°) and *N*-(*p*-methoxyphenyl)-isoindoline (3), m. p. 212—213° (lit.⁹ m. p. 214°) was obtained. The pure products proved to be identical with samples prepared from the reaction of α,α' -dibromo-*o*-xylene with the corresponding aromatic primary amines, as described by Sommers¹⁰. The mixed melting points of the two samples gave no depression and the IR spectra were superimposable.

Distillation of the *N*-aryl-4H-5,7a-epoxyisoindolines (VII—IX) in vacuo

As an illustrative example, the distillation of *N*-phenyl-4H-5,7a-epoxyisoindoline (VII) is described: 8 g. of VII (m. p. 120—121°) was subjected to distillation *in vacuo*. The distillation product (b. p. 168—170°/13 mm.) was a yellow oil (yield 7.2 g.) which showed the same refractive index and IR spectrum as IV [obtained by allylation of (2-furfuryl)-aniline] and gave a picrate, m. p. 109—110°, identical with a sample of IVa (m. p. 109—110°).

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* In our experiments a commercial *puriss.* grade PtO₂ catalyst (Fluka A. G., Buchs, Switzerland) was used.

IZVOD

**O pripravi nekih tercijskih amina koji sadrže 2-furfurilni ostatak.
Izomerizacija alil-aril-(2-furfuril)-amina u *N*-aril-4H-5,7a-epoksiizindoline***D. Bilović i V. Hahn*

Opisuje se priprava etil-(2-furfuril)-*p*-toluidina (I) i etil-(2-furfuril)-*p*-anisidina (III) djelovanjem etilbromida na odgovarajuće sekundarne amine u prisutnosti natrijeva amida^{3,4}. Metil-(2-furfuril)-*p*-anisidin (II) priređen je reakcijom 2-furfuril-*p*-anisidina s metiljodidom bez upotrebe natrijeva amida. Analogno su pripremljeni alil-(2-furfuril)-anilin (V), alil-(2-furfuril)-*p*-toluidin (V) i alil-(2-furfuril)-*p*-anisidin (VI) djelovanjem aliljodida na sekundarne amine, bez natrijeva amida. Svi su amini dobiveni sa zadovoljavajućim iskorišćenjem, a predstavljaju supstancije koje se mogu destilirati pod sniženim tlakom.

Dok su priređeni alkil-aril-(2-furfuril)-amini (I—III) u pogledu svojih svojstava pokazali potpunu analogiju s ranije opisanim tercijskim aminima istoga tipa³⁻⁵, dobiveni alil-aril-(2-furfuril)-amini (IV—VI) ponašali su se posve različito. Naime, stajanjem kod sobne temperature uljeviti amini su se postepeno ukruživali da bi se, nakon nekoliko dana do nekoliko mjeseci, potpuno pretvorili u čvrstu kristalnu masu. Moglo se pokazati da je u stvari došlo do intramolekularne Diels-Alderove reakcije i da su iz uljevitih amina nastali odgovarajući kristalni *N*-aril-4H-5,7a-epoksiizindolini (VII—IX), kojih je konstitucija dokazana na temelju različitih reakcija. Tako je pri katalitičkoj hidrogenaciji kod sobne temperature, uz platinski katalizator po Adamsu, došlo redovito do apsorpcije jednog mola vodika, uz nastajanje *N*-aril-5,7a-epoksi-perhidroizindola (XIII—XV). Djelovanjem metiljodida u acetonskoj otopini dobiveni su odgovarajući *N*-metil-*N*-aril-4H-5,7a-epoksi-izindolinijevi jodidi (X—XII). Osim toga je provedena dehidratacija VII—IX pomoću smjese 66%-tne HBr u ledenoj octenoj kiselini, pri čemu su dobiveni odgovarajući *N*-aril-izindolini koji su već ranije bili opisani u literaturi. Oni su mogli biti identificirani usporedbom s autentičnim uzorcima koji su pripremljeni iz α - α' -dibrom-*o*-ksilena i odgovarajućih primarnih aromatskih amina¹⁰.

Opisana izomerizacija se pokazala reverzibilnim procesom, jer se destilacijom epoksiizindolina (VII—IX) u vakuumu ponovno dobivaju ishodni uljeviti tercijski amini (IV—VI).

INSTITUT »RUĐER BOŠKOVIĆ«
ODJEL ORGANSKE KEMIJE I BIOKEMIJE

I

ZAVOD ZA ORGANSKU KEMIJU
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