New Synthesis of Substituted Isoindolines from Furans *via* Epoxyisoindolines

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The preparation of substituted *N*-arylisoindolines **3** from simple furan derivatives **1** is reported. Oxatricycloadducts **2**, readily accessible by intramolecular Diels-Alder reaction are susceptible to acidic reagents yielding aromatized products **3** by a ring-opening reaction *via* intermediate carbocation.

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The interconversion of heterocycles is often exploited as a useful tool for the preparation of specifically substituted, biologically active or in other respects interesting compounds. Within our interest for the intramolecular Diels-Alder reaction of furans we studied the reaction of tertiary *N*-alkenyl-*N*-aryl-*N*-furfurylamines leading to, sometimes spontaneous, formation of epoxyisoindolines [1]. Although a considerable amount of work has been reported on the syntheses of isoindoles and isoindolines by a variety of methods [2], the straightforward preparation from substituted furans was not evaluated.

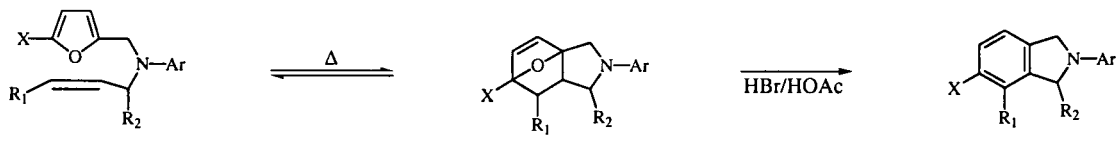
The ring openings of oxa-*n*-cyclo systems are well documented. Among many examples of such reactions the S_N2' ring-opening reaction [3] of substituted oxatricyclo compounds prepared *via* the intramolecular Diels-Alder reaction with a furan diene seems to be a very useful synthetic tool [4] applicable *i. e.* to the enantioselective synthesis of natural products [5]. Another method to open the oxatricyclo adducts obtained by an intramolecular Diels-Alder reaction with furan diene is a simple nucleophilic reaction *via* a carbocation intermediate [6]. The method should be fruitful, especially if the additional driving force is present. As a matter of fact, such a possibility was indicated in an early paper from this laboratory [7a].

The intramolecular Diels-Alder reaction is found to be a method of utmost importance in the syntheses of a variety of bridged and other polycyclic carbo and heterocyclic systems [8]. Due to the predictable, generally high stereo and regioselectivity, such reactions were often effectively included as a key-step in syntheses of many complex natural products. Furan is expected to be a relatively unreactive diene because of its aromaticity, but many examples of furan [4+2] cycloadditions are known. The first observation on the intramolecular [4+2] cycloaddition involving a furan ring incorporated within the complex structure was reported in the early sixties [9]. Shortly afterwards Hahn from this laboratory pointed out that even simple furans *e. g.* allylarylfurfurylamines, underwent an extraordinarily facile intramolecular Diels-Alder reaction [7a]. Since that time, numerous other examples of intramolecular Diels-Alder reactions involving furan nucleus connected by different chains to the dienophylic part of the molecule have been studied [10]. Our studies were oriented so far mostly to the influence of effects caused by substituents either connected to the furan diene [1a] or to the dienophylic, *N*-alkenyl double bond of *N*-alkenyl-*N*-aryl-*N*-(2-furfuryl)amine [1b].

The present paper reports on the synthetically useful route to isoindole derivatives from simple furans. The reaction pathway which includes an intramolecular Diels-Alder reaction of substituted alkenylfurfurylamines **1** and subsequent aromatization of intermediately formed adduct **2** was proposed (Scheme 1).

In the early paper from this laboratory [7a] the aromatization of *N*-phenyl-4*H*-5,7a-epoxyisoindoline (**2**) was

Scheme 1



1 **2** **3**

X = H, CH_3, OCH_3, I, NO_2; R_1 = H, CH_3; R_1, R_2 = -$(CH_2)_3$-; Ar = *p*-$CH_3C_6H_4$.

used to unequivocally confirm the structure of the adduct in a spontaneous intramolecular Diels-Alder reaction of *N*-allyl-*N*-(2-furfuryl)aniline. The proposed reaction pathway seems to be useful as a synthetic tool to isoindole derivatives, providing that the yield in the aromatization step could be improved. The epoxy-bridge in **2** is supceptible to acidic reagents similarly as in many other compounds with an ethereal structure [6]. The dehydration step is known to be quite efficient if the epoxy-bridge connects tertiary carbons and if the aromatic structure in the compound with electron donors both at C-4 (a methyl group) and C-5 (a methoxy group) is enhanced so greatly that the isolation of **2i** after the intramolecular [4+2] cycloaddition of **1i** was prevented. The formation of **2i** was indicated by experiments in nmr tubes, but a spontaneous aromatization of the intermediate epoxyisoindoline was so facile that **3i**, accompanied by traces of an hydroxyenone compound [12], was obtained even without acidic reagents. Similar but not such a drastic influence of the 5-methoxy group was observed in **1c**, enabling isola-

Table 1
N-Arylisoindolines **3** by Aromatization of Epoxyisoindolines **2**

	X	R_1	R_2	Starting Compound	mp(°C)	Analysis Calcd./Found C	H	N
3a [a]	H	H	H	**2a**	196-197 [b]			
3b	CH_3	H	H	**2b**	216-217	86.05	7.67	6.27
						86.09	7.77	6.29
3c [c]	OCH_3	H	H	**2c**	161-163	80.30	7.16	5.85
						80.37	7.24	5.78
3d [d]	OH	H	H	**2c**	159-160	79.96	6.72	6.22
						79.93	6.43	6.18
3g	H	CH_3	H	**2g**	89-91	86.05	7.67	6.27
						86.06	7.69	6.25
3h	CH_3	CH_3	H	**2h**	105-107	86.03	8.07	5.90
						86.11	8.08	5.97
3i [e]	OCH_3	CH_3	H	**1i**	150-152	80.60	7.56	5.53
						80.63	7.56	5.54
3j	I	CH_3	H	**2j**	108-110	55.03	4.62	4.01
						55.08	4.60	4.12
3k [f]	H	$-(CH_2)_3-$		**2k**	87-88 [g]			

[a] Prepared earlier [7a]. [b] Lit. mp. 195° [11]. [c] Aromatization was effectuated without an acidic reagent either in the course of chromatographic purification of crude **2c** or by allowing **2c** to stand in dry ether over neutral aluminium oxide. [d] The only isolable product of the reaction with hydrogen bromide in acetic acid. The same 5-hydroxy-compound **3d** was obtained with ethanolic hydrogen chloride or by heating the ethereal solution of **2c** in the presence of silicon dioxide. [e] The result of spontaneous aromatization during the attempted preparation of **2i** from **1i**. [f] Prepared earlier [1c]. [g] Lit. mp 87-88° [1c].

the product could be established. In our examples among several applied reagents (sulphuric acid, polyphosphoric acid, ethanolic hydrogen chloride or bromide), the most useful was a mixture of 48% hydrobromic acid and glacial acetic acid (1:2). Other reagents were either ineffective or caused profound resinification, especially at higher temperatures and/or prolonged heating.

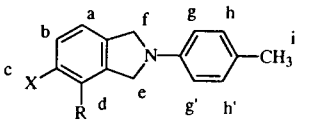
As expected, the influence of substituents at the carbon connected with the epoxy-bridge was significant (Table 1) and is very much in agreement with a carbocation mechanism of the reaction.

It should be noted that the presence of an electron donor group, *i. e.* a methyl group, situated in the vicinity of the bridge at C-4 (compounds **2g-2j)** is favorable, so even with electron acceptors at C-5 the aromatization was successful. A characteristic example is the 5-iodo-derivative **2j,** with a methyl group at C-4, which was successfully aromatized (yield: 69%) unlike the similar compound **2e** without a substituent at C-4 when no reaction using different acidic reagents was observed. Even more, reactivity of tion of **2c** after an intramolecular [4+2] cycloaddition, but aromatization has taken place during purification by column chromatography on neutral alumina with ether/petroleum ethers 5:2. Therefore, most of the crude product was isoindoline **3c.**

EXPERIMENTAL

Melting points were determined on an Original Kofler Mikroheitztisch apparatus (Reichardt, Wien) and were not corrected. Infrared spectra were taken in potassium bromide pellets with a Perkin-Elmer Model 297 instrument (vs = very strong, s = strong, m = medium, w = weak, vw = very weak). Proton nmr spectra were taken on a Varian GEMINI 300 spectrometer with tetramethylsilane as the internal standard. ^{13}Carbon nmr spectra were taken on a Varian GEMINI instrument at 75 MHz using the APT technique. Mass spectra were recorded on an Extrel FTMS 2001 DD spectrometer by direct insertion probe. Compounds **2a-2k** were prepared according to reported procedures.

Table 2
^{1}H NMR Spectra [a] of *N-p*-Tolylisoindolines **3a-3d** and 4-Methyl-substituted Derivatives **3g-3j**

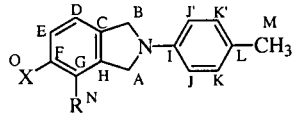


Compound	H [a]	H [b]	H [c]	H [d]	H [e]	H [f]	H [g,g']	H [h,h']	H[i]
3a X = H R = H	7.38-7.30 (m, 4H)				4.64 (s, 4H)		6.63 (d, 2H) J = 8.5	7.15 (d, 2H) J = 8.5	2.31 (s, 3H)
3b X = CH_3 R = H	7.27 (d,1H) J = 7.4	7.16 (d, 1H) J = 7.4	2.45 (s, 3H) [b]	7.16 (s, 1H)	4.62 (s, 4H)		6.65 (d, 2H) J = 8.5	7.18 (d, 2H) J = 8.5	2.36 (s, 3H) [b]
3c X = OCH_3 R = H	7.17 (d, 1H) J = 8.2	6.78 (bd, 1H) J = 8.2	3.81 (s, 3H)	6.81 (s, 1H)	4.55 (bs, 2H) [c]	4.58 (s, 2H) [c]	6.53 (d, 2H) J = 8.3	7.03 (d, 2H) J = 8.3	2.27 (s, 3H)
3d X = OH R = H	7.16 (d, 1H) J = 8.3	6.76 (bd, 1H) J = 8.3	5.10 (s, 1H) [d]	6.79 (bs, 1H)	4.55 (bs, 4H)		6.58 (d, 2H) J = 8.4	7.10 (d, 2H) J = 8.4	2.28 (s, 3H)
3g X = H R = CH_3	7.15-7.06 (m, 3H)			2.32 (s, 3H)	4.55 (bs, 2H) [e]	4.57 (bs, 2H) [e]	6.60 (d, 2H) J = 8.5	7.11 (d, 2H) [f] J = 8.5	2.28 (s, 3H)
3h X = CH_3 R = CH_3	7.03 (bs, 2H)		2.26 (s, 3H) [g], [h]	2.19 (s, 3H) [h]	4.53 (s, 4H)		6.57 (d, 2H) J = 8.5	7.08 (d, 2H) J = 8.5	2.26 (s, 3H) [g]
3i X = OCH_3 R = CH_3	7.13 (d, 1H) J = 7.2	6.81 (d, 1H) J = 7.2	3.86 (s, 3H)	2.21 (s, 3H)	4.55 (s, 2H) [i]	4.59 (s, 2H) [i]	6.62 (d, 2H) J = 8.5	7.13 (d, 2H) J = 8.5	2.30 (s, 3H)
3j X = I R = CH_3	6.86 (d, 1H) J = 7.6	7.73 (d, 1H) J = 7.6		2.40 (s, 3H)	4.56 (bs, 4H)		6.58 (d, 2H) J = 8.5	7.11 (d, 2H) J = 8.5	2.28 (s, 3H)

[a] In deuteriochloroform. Chemical shifts (δ) are given in ppm relative to tetramethylsilane. Coupling constants (J) are given in Hz. [b] Not necessarily respectively. [c] Not necessarily respectively. [d] Deuterium oxide exchangeable; [e] Not necessarily respectively. [f] Part of the multiplet with aromatic **a**, **b** and **c** protons. [g] H^c and H^i coalesce as the 6H signal. [h] Not necessarily respectively. [i] Not necessarily respectively.

Table 3

^{13}C NMR Spectra [a] of *N*-(*p*-Tolyl)isoindolines **3a-3d** and 4-Methyl-substituted Derivatives **3g-3j**



	3a [b] X = H R = H	**3b** X = CH_3 R = H	**3c** X = OCH_3 R = H	**3d** X = OH R = H	**3g** X = H R = CH_3	**3h** X = CH_3 R = CH_3	**3i** X = OCH_3 R = CH_3	**3j** [c] X = I J = CH_3
C^A	53.8 (t)	53.6 (t)	53.9 (t)	53.9 (t)	54.2 (t)	54.2 (t)	53.6 (t)	54.2 (t)
C^B	53.8 (t)	53.5 (t)	53.1 (t)	53.3 (t)	53.1 (t)	53.4 (t)	53.2 (t)	54.2 (t)
C^C	138.2 (s)	135.1 (s)	129.8 (s)	130.2 (s)	137.2 (s)	130.8 (s)	125.5 (s)	135.8 (s)
C^D	122.6 (d)	122.2 (d)	123.1 (d)	123.4 (d)	119.8 (d)	119.5 (d)	119.9 (d)	121.7 (d)
C^E	127.1 (d)	127.8 (d)	113.2 (d)	114.4 (d)	127.3 (d)	128.8 (d)	109.3 (d)	138.0 (d)
C^F	127.1 (d)	136.7 (s)	159.3 (s)	155.1 (s)	127.8 (d)	135.4 (s)	156.9 (s)	99.4 (s)
C^G	122.6 (d)	123.1 (d)	107.7 (d)	109.5 (d)	132.4 (s)	135.0 (s)	121.0 (s)	141.8 (s)
C^H	138.2 (s)	138.3 (s)	139.6 (s)	139.8 (s)	137.9 (s)	137.4 (s)	138.8 (s)	138.3 (s)
C^I	145.2 (s)	145.2 (s)	145.3 (s)	145.2 (s)	145.2 (s)	145.3 (s)	145.3 (s)	144.8 (s)
$C^{J, J'}$	111.6 (d)	111.5 (d)	111.4 (d)	111.5 (d)	111.5 (d)	111.5 (d)	111.4 (d)	111.5 (d)
$C^{K, K'}$	129.9 (d)	122.4 (d)	129.6 (d)	129.9 (d)	129.5 (d)	129.8 (d)	129.8 (d)	129.9 (d)
C^L	125.2 (s)	125.0 (s)	125.1 (s)	125.3 (s)	125.0 (s)	125.0 (s)	125.0 (s)	125.5 (s)
C^M	20.1 (q)	20.1 (q)	20.0 (q)	20.3 (q)	20.3 (q)	20.3 (q)	20.1 (q)	20.3 (q)
C^N						19.4 (q)	12.0 (q)	24.4 (q)
C^O		21.4 (q)	53.3 (q)			15.6 (q)	55.7 (q)	

[a] In deuteriochloroform. Chemical shifts given in ppm (δ) relative to internal tetramethylsilane. Multiplicity of signals: s = singlet, d = doublet, t = triplet, q = quartet. [b] Signals for carbons C^A and C^B, C^C and C^H, C^D and C^G, C^E and C^F respectively, coalesce. [c] Signals for carbons C^A and C^B coalesce.

Aromatization of Epoxyisoindolines (Table 1).

General Procedure.

To the solution of an appropriate epoxyisoindoline **2** (5 mmoles) in 10 ml of glacial acetic acid 5 ml of 48% hydrobromic acid was added and the mixture was heated for 5 hours at 60-70°. The reaction mixture was poured into water (100 ml). After careful neutralization (*p*H 7) with sodium hydroxide (5% solution) the product was dissolved in ether (3 x 20 ml). The ethereal extract was dried over anhydrous magnesium sulfate and the solvent evaporated to yield a tarry crude product. Further processing of the crude products is indicated in the following paragraphs.

2-(4-Methylphenyl)-2,3-dihydro-1*H*-isoindole (**3a**).

This compound was obtained in 19% yield from the dark resinous crude **3a** by repeated column chromatography on silica gel using petroleum ether/chloroform 10:1 and petroleum ether/ether 10:1 as eluents. The colorless crystals had ms: m/z (relative intensity) 209 (100, M^+), 210 (60), 194 (4), 179 (2), 166 (5), 119 (2), 118 (7), 106 (4), 105 (4), 92 (6), 91 (9), 79 (4), 67 (11), 65 (4), 41 (4); ir: ν 2980 (s), 2860 (s), 1620 (m), 1520 (s), 1470 (s), 1380 (s), 1240 (s), 1160 (s), 1100 (w), 800 (s), 740 (s) cm^{-1}.

2-(4-Methylphenyl)-5-methyl-2,3-dihydro-1*H*-isoindole (**3b**).

This compound was obtained from **2a** (1.2 g, 5 mmoles) as above in a yield of 72% as light yellow crystals; ms: m/z (relative intensity) 223 (100, M^+), 222 (40), 208 (5), 132 (7), 91 (9); ir: ν 2960 (s), 2880 (s), 1620 (m), 1570 (w), 1520 (s), 1470 (m), 1380 (s), 1180 (m), 800 (s), 700 (s) cm^1.

The preparation of 2-(4-Methylphenyl)-5-methoxy-2,3-dihydro-1*H*-isoindole (**3c**).

From Tertiary Amine **1c**.

Freshly prepared tertiary amine **1c** (1.29 g, 5 mmoles) was allowed to isomerize by standing at 25° by the reported procedure [1b]. The column chromatography of crude reaction product on neutral aluminium oxide with petroleum ether/ether 10:1 as eluent yielded 835 mg (70%) of aromatized compound **3c** and 250 mg (19%) of the expected epoxyisoindoline **2c**, accompanied by less than 10% of starting tertiary amine **1c**.

From Epoxy Derivative **2c**.

To the solution of 1.29 g (5 mmoles) of **2c** in 10 ml of anhydrous ether, 2 g of neutral aluminium oxide (Grade I) was added. The reaction mixture was kept at room temperature under dry nitrogen for 3 days. The aluminium oxide was filtered. After evaporation of the solvent under reduced pressure 870 mg (73%) of isoindoline **3c**, mp 159-164° was obtained. An analytically pure sample was obtained by column chromatography on silica gel using petroleum ether/ether 5:1 as colorless crystals melting at mp 161-163°; ms: m/z (relative intensity) 239 (93, M^+), 238 (100), 209 (15), 208 (22), 194 (9), 180 (4), 165 (5), 118 (3), 95 (3), 91 (7); ir: ν 2950 (m), 2880 (m), 1640 (s), 1570 (vs), 1495 (s), 1480 (s), 1400 (s), 1320 (w), 1280 (m), 1170 (m), 1110 (w), 1050 (m), 945 (m), 870 (m), 830 (vs), 820 (vs) cm^{-1}.

2-(4-Methylphenyl)-5-hydroxy-2,3-dihydro-1*H*-isoindole (**3d**).

This compound was prepared as described in the general procedure starting with 1.29 g (5 mmoles) of **2c**, but concomitant hydrolysis of the 5-methoxy group occurred, preventing

isolation of **3c**. The crude product was purified by column chromatography (neutral alumina, Grade I) using petroleum ether/ether 10:1 to yield 1.0 g (90%) of colorless crystalline **3d**; ms: m/z (relative intensity) 225 (17, M^+), 224 (100), 210 (8), 194 (5), 149 (4), 118 (5), 91 (9); ir (Nujol): 3480 (s, ν_{OH}), 2960 (s), 2840 (s), 1620 (s), 1520 (s), 1470 (m), 1460 (m), 1380 (s), 1170 (m), 1100 (s), 800 (s), 740 (m) cm^{-1}.

2-(4-Methylphenyl)-4-methyl-2,3-dihydro-1*H*-isoindole (**3g**).

This compound was prepared from 1.2 g (5 mmoles) of **2g** as described for preparation of **3a** as colorless crystals (0.88 g, 72%); ms: m/z (relative intensity) 223 (60, M^+), 222 (100), 209 (6), 208 (14), 91 (10); ir: ν 2910 (s), 2840 (s), 1620 (m), 1520 (s), 1470 (s), 1370 (s), 1160 (m), 1070 (w), 800 (s), 770 (s), 700 (m) cm^{-1}.

2-(4-Methylphenyl)-4,5-dimethyl-2,3-dihydro-1*H*-isoindole (**3h**).

This compound was prepared by substantially the same procedure from 1.28 g (5 mmoles) of **2h**, except that heating of the reaction mixture was 3 hours at 60-70°. The colorless crystalline **3h** was obtained in 84% yield; ms: m/z (relative intensity) 237 (70, M^+), 236 (100), 221 (13), 91 (5), 65 (8); ir: ν 2940 (s), 2849 (s), 1620 (m), 1520 (s), 1465 (s), 1380 (s), 1170 (m), 1070 (m), 810 (s), 800 (s) cm^{-1}.

2-(4-Methylphenyl)-4-methyl-5-methoxy-2,3-dihydro-1*H*-isoindole (**3i**).

Freshly prepared tertiary amine **1i** (1.36 g, 5 mmoles) was heated 3 days at 70° in dry benzene to isomerize by the reported procedure [1e]. Column chromatography of the crude reaction product on neutral aluminium oxide with petroleum ether/ether 10:1 as the eluent yielded 1.1 g (87%) of aromatized compound **3i**. An analytically pure sample was obtained by rechromatography; ms: m/z (relative intensity) 253 (40, M^+), 252 (100), 238 (10), 149 (8), 118 (5), 91 (3); ir: ν 2960 (s), 2840 (s), 1620 (s), 1520 (s), 1470 (s), 1380 (s), 1170 (m), 800 (s), 740 (m) cm^{-1}.

2-(4-Methylphenyl)-4-methyl-5-iodo-2,3-dihydro-1*H*-isoindole (**3j**).

This compound was prepared from 1.84 g (5 mmoles) epoxyisoindoline **2j** by substantially the same procedure as described for **3a**, except that reaction mixture was heated at 60-70° for 7 hours. Purification by repeated column chromatography on silica gel with petroleum ether/chloroform 5:2 and petroleum ether/ether 10:1 gave light yellow crystals of pure **3j** (1.2 g, 66%); ms: m/z (relative intensity) 363 (14, M^+), 349 (100), 348 (81), 222 (24), 220 (33), 103 (48), 91 (62), 87 (43), 65 (40), 57 (45), 49 (19), 43 (38); ir: ν 2920 (s), 2850 (s), 1620 (m), 1520 (s), 1460 (s), 1360 (m), 1170 (m), 1060 (m), 700 (m) cm^{-1}.

2-(4-Methylphenyl)-6,7,8,8a-tetrahydro-1*H*-benzo[*c,d*]isoindole (**3k**).

This compound was prepared by the reported procedure [1c]; ms: m/z (relative intensity) 249 (45, M^+), 250 (22), 222 (18), 221 (100), 220 (20), 180 (3), 179 (3), 128 (5), 91 (5); ir: ν 2980 (s), 2860 (s), 1470 (s), 1390 (m), 1370 (s), 1240 (m), 1220 (m), 800 (s), 740 (s) cm^{-1}.

Attempted Preparations of 2-(4-Methylphenyl)-5-iodo-2,3-dihydro-1*H*-isoindole (**3e**), 2-(4-Methylphenyl)-5-nitro-2,3-dihydro-1*H*-isoindole (**3f**) and 2-(4-Methylphenyl)-4-methyl-5-nitro-2,3-dihydro-1*H*-isoindole (**3i**).

Similarly to the general procedure, a solution of the corresponding epoxyisoindoline **2e** [1b], **2f** [1b], **2i** [1e] was heated at 70-90° in a mixture of glacial acetic acid and hydrobromic acid but aromatized products were not detected even after prolonged heating (24 hours). Experiments with reagents like dry ethanolic hydrogen chloride, sulfuric or polyphosphoric acid were also unsuccessful.

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[12] To be reported elsewhere.