Studies in the Furan Series. 23. Preparation of some New 5-Substituted furfurylallylarylamines. Influence of Substituents on the Intramolecular Diels-Alder (IMDA) Reaction

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Several new *N*-allyl-*N*-(5-substituted)-2-furfuryl-*p*-toluidines **IIIa-e** with Cl, Br, I, NO_2 or CH_3O groups in position 5 of the furan nucleus were prepared by allylation of the corresponding secondary furfurylarylamines. Both, electron withdrawing and releasing substituents enhanced the yield of intramolecular [4+2] cycloaddition.

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In recent years the intramolecular Diels-Alder (IMDA) reactions became a very useful synthetic tool and has been used to synthesize a variety of bridged polycyclic systems. Because of their stereo and regioselectivity they were effectively included in the syntheses of complex natural products [1].

A benefit from entropy factors due to the spatial proximity of diene and dienophile in the same molecule is most important in many examples studied, but the reactivity of diene and dienophile which can be significantly influenced by electrical effects of substituents should not be neglected.

It is well known that electron rich dienes and electron deficient dienophiles react easily with good yields of the [4+2] cycloadducts. On the other hand electron deficient dienes react preferentially with electron rich dienophiles by Diels-Alder reaction with "inverse electron demand" [2].

Furan is expected to be a relatively unreactive diene because of its aromaticity, but many examples of furan [4+2] cycloadditions (especially with activated dienophiles) are known. In the early sixties Hahn [3a] reported from this laboratory a spontaneous IMDA reaction of tertiary allylaryl-2-furfurylamines, which was probably the earliest report of a thermal IMDA reaction with a simple furan derivative. Since that time numerous other cases of cyclizations involving a furan nucleus connected by different chains to the dienophilic part of the molecule have been studied [4].

Though many useful conclusions about structural and electronic demands have been established, the substitution effect in IMDA reactions with furans have not been studied systematically. From several reports one may draw a conclusion that electron acceptors at the dienophile part promote, while electron donors diminish or prevents cycloaddition of this type [4b,5,6]. On the other hand the IMDA reactions with electron acceptors at furan dienes were achieved only if additional intramolecular interaction *i.e.* hydrogen bonding or an internal chelate complex were present, promoting the reaction by bringing both diene and dienophile to come into the proper position suitable for a [4+2] cycloaddition [5].

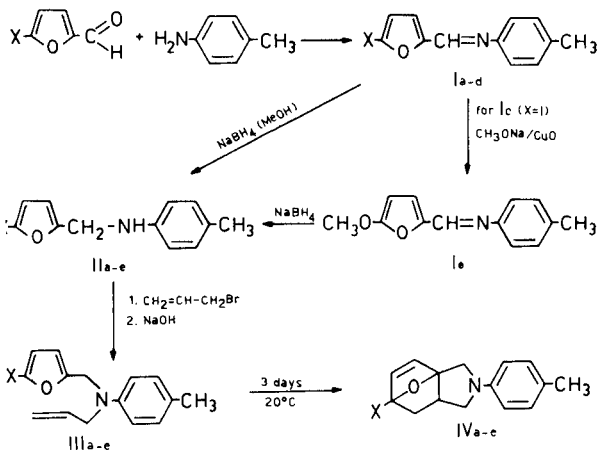
If an intramolecular [4+2] cycloaddition with a furan diene as an electrodonor [4b] is regarded as a "normal" Diels-Alder reaction, one should expect that electron donors at the diene part of the molecule should promote the addition [7]. Surprisingly, in our earlier studies dealing with the influence of substituents with regard to the rate of the IMDA reaction of *N*-allyl-*N*-(2-furfuryl)arylamines [8] it has been found that the 5-methyl group, *i.e.*, the electron donor at the diene decreased the reaction rate [8a]. We rationalized this effect by an unfavourable steric demand of the 5-methyl group in the transition state, but electronic effects should not be neglected.

The relative unimportance of electronic effects was claimed at least in the case of furfuryl allyl sulphides [9] but most conclusions leading to this claim were taken from the fact that substituents (including a methyl group) in the 3-position (next to the connecting chain) sterically promote the reaction by eclipsing "*ortho*" interaction with the side chain methylene group. This effect can not wholly explain the substitution effect in the 4- and especially at the 5-positions. Some benefit from a positive methyl group in all three positions with a "normal" Diels-Alder reaction may be supposed. Probably a complex combination of effects may arise. In our case [8] for 5-substitution, an opposing steric effect of an overshadowing methyl group led to a relative decrease in the cycloaddition rate as the net effect.

Continuing our studies on the influence of substituents in the IMDA reaction of tertiary allyl furfurylamines, in present paper we wish to report the preparation and internal cycloaddition of several new allyl-(5-substituted)furfuryl-*p*-toluidines with nitro, halogeno or methoxy groups as substituents (Scheme I) with an intention to test the importance of electronic effects in the 5-substituted furan

nucleus as a diene in intramolecular reactions.

Scheme I



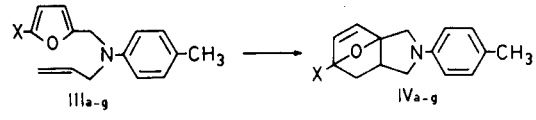
Based on the yields of the IMDA reaction of neat reactants, we found a promotion of cycloaddition when either strong electron donors or electron acceptors were present in position 5 of the furan diene (Table I). The influence of a 5-methoxy group could be explained by its strong positive effect [9a], but such an explanation does not hold in the case of halogens and especially of a nitro group. Only a few papers related to dienes substituted with a nitro group have been noted [5], claiming cycloaddition only when dienophiles substituted with electron donating groups *i.e.* the Diels-Alder reaction with "inverse electron demand" [2] or conformational enhancement were present [9b]. Unlike such results we found that a nitro group of 5-nitrofurfurylallylarylamine **IIId** enhances the yield and accelerates the IMDA reaction (Table I)

Because it is difficult to draw firm conclusions on the basis of examples thus far studied, such observations are intriguing enough to warrant further study in order to provide a possible explanation of a "neutral" type [7c] Diels-Alder reaction. This will be a subject for our further study.

The tertiary amines **IIIa-e** (Table I) were prepared starting from the corresponding 5-substituted 2-furaldehyde and *p*-toluidine as shown in Scheme I [9c]. Mostly new secondary amines **IIa-e** were obtained by the reduction of the corresponding azomethynes **Ia-e** with sodium borohydride at room temperature. The allylation of **IIa-d** was performed with allyl bromide according to reported procedures [8,10] and for **IIe** in the presence of sodium hydride in dimethylformamide. Chromatographically pure samples [10a] of tertiary amines **IIIa-e** and unsubstituted **IIIf** [3b] or 5-methyl-substituted **IIIg** [8] analogues spontaneously started to isomerize and were left for 3 days at 25°. The epoxyisoindolines **IVa-g** (Table I) which were separated from unchanged **IIIa-g** by silica or neutral alumina column chromatography were obtained in the yields indicated. The yields obtained in the rigorously identical conditions could be easily compared. All studied substituents regardless of different electronic effects (Cl,

Table I

Tertiary Amines and Isomeric Epoxyisoindolines

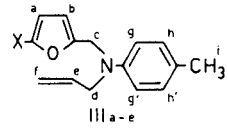


No.	X	Yield [a] %	Eluent [d]	No.	X	Yield %	Eluent [e]	Mp °C	Formula	*Anal.* Calcd. Found C %	H %	N %
IIIa	Cl	78 [b,d]	A	**IVa**	Cl	48 [b]	C	150-151	$C_{15}H_{16}ClNO$	68.82 68.97	6.17 6.42	5.35 5.44
IIIb	Br	72 [b,d]	A	**IVb**	Br	54 [b]	D	148-149	$C_{15}H_{16}BrNO$	58.83 58.95	5.27 5.06	4.43 4.52
IIIc	I	76 [b,d]	A	**IVc**	I	34 [b]	E	160-161	$C_{15}H_{16}INO$	51.00 51.06	4.57 4.43	3.97 3.96
IIId	NO_2	60 [b,d]	A	**IVd**	NO_2	73 [c]	F	164 [f]	$C_{15}H_{16}N_2O_3$	66.16 66.44	5.92 6.09	
IIIe	OCH_3	82 [c,d]	B	**IVe**	OCH_3	37 [c]	G	117-118 [f]	$C_{16}H_{19}NO_2$	74.67 74.57	7.44 7.47	5.45 5.18
IIIf	CH_3	72 [8]	A	**IVf**	CH_3	5	H	107-108 [8]				
IIIg	H	81 [3b]	A	**IVg**	H	7	D	104-105 [3b]				

[a] All tertiary amines were obtained as light yellow oils. [b] Column chromatography on silica. [c] Column chromatography on alumina. [d] Dec on heating. [e] A = petroleum ether/ether (10:1); C = 1. benzene/petroleum ether (1:1), 2. chloroform; D = benzene/petroleum ether (1:1); E = 1. petroleum ether/chloroform (3:1), 2. chloroform; F = 1. petroleum ether/ether (1:1), 2. chloroform/petroleum ether (5:1); G = 1. petroleum ether/ether (10:1), 2. petroleum ether/ether (1:1), H = petroleum ether/benzene/ether (10:7:1). [f] Explodes on heating above 180°.

Table II

^{1}H NMR Spectra [a] of Tertiary Amines



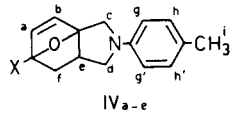
IIIa-e

No.	X	a and b	c	d	e	f	g,g' and h,h'	i
IIIa	Cl	5.88 6.04 2H, AB_q, J = 3.2	4.28 (2H, s)	3.86 (2H) d, J = 4.7	5.84-5.59 1H, m	5.22-5.04 2H, m	6.63 (2H) 6.97 (2H) $J_{A_2X_2}$ = 8.4	2.20 (3H, s)
IIIb	Br	6.11 6.16 2H, AB_q, J = 3.2	4.36 (2H, s)	3.91 (2H) d, J = 4.7	6.05-5.64 1H, m	5.28-5.03 2H, m	6.67 (2H) 7.01 (2H) $J_{A_2X_2}$ = 8.2	2.22 (3H, s)
IIIc	I	6.40 6.03 2H, AB_q, J = 3.2	4.41 (2H, s)	3.91 (2H) d, J = 5.0	5.93-5.64 1H, m	5.28-5.04 2H, m	6.65 (2H) 7.01 (2H) $J_{A_2X_2}$ = 8.5	2.22 (3H, s)
IIId	NO_2	7.22 6.35 2H, AB_q, J = 3.5	4.51 (2H, s)	4.01 (2H) d, J = 5.0	6.10-5.59 1H, m	5.29-5.04 2H, m	6.66 (2H) 7.03 (2H) $J_{A_2X_2}$ = 8.2	2.24 (3H, s)
IIIe	CH_3O [b]	5.16 5.99 2H, AB_q, J = 3.2	4.27 (2H, s)	3.91 (2H d, J = 5.0	5.94-5.64 1H, m	5.26-5.04 2H, m	6.70 (2H) 7.00 (2H) $J_{A_2X_2}$ = 8.5	2.22 (3H, s)

[a] In deuteriochloroform. Chemical Shifts given in ppm (δ) relative to internal TMS. Coupling constants (J) given in Hz. [b] 3.76 (3H, s) for 5-CH_3O group.

Table III

^{1}H NMR Spectra [a] of Epoxyisoindolines



IVa-e

No.	X	a and b	c	d [b]	e	f	g,g' and h,h'	i
IVa	Cl	6.39 6.56 2H, AB_q, J = 5.8	3.91 3.57 2H, AB_q, J = 11.7	3.83 3.03 2H, AB_q, J = 11.1	2.61-2.32 (1H, m)	2.10 (2H) d, J = 5.6	6.48 (2H) 7.03 (2H) $J_{A_2X_2}$ = 8.5	2.25 (3H, s)
IVb	Br	6.45 (2H, s)	3.91 3.58 2H, AB_q, J = 11.7	3.81 3.03 2H, AB_q, J = 11.2	2.47-2.34 (1H, m)	2.17 (2H) d, J = 5.2	6.47 (2H) 7.03 (2H) $J_{A_2X_2}$ = 8.5	2.24 (3H, s)
IVc	I	6.52 6.33 2H, AB_q, J = 5.6	3.94 3.73 2H, AB_q, J = 11.7	3.82 3.04 2H, AB_q, J = 11.4	2.63-2.05 (2H, m)		6.48 (2H) 7.03 (2H) $J_{A_2X_2}$ = 8.5	2.25 (3H, s)
IVd	NO_2	6.73 (2H, s)	3.98 3.71 2H, AB_q, J = 12.2	3.92 3.08 2H, AB_q, J = 11.8	2.63-2.36 (1H, m)	2.29 (2H, s)	6.49 (2H) 7.04 (2H) $J_{A_2X_2}$ = 8.5	2.25 (3H, s)
IVe	CH_3O [c]	6.58 6.41 2H, AB_q, J = 5.9	3.85 3.56 2H, AB_q, J = 11.4	3.71 3.04 2H, AB_q, J = 9.2	2.49-2.19 (1H, m)	1.89-1.71 (2H, m)	6.49 (2H) 7.03 (2H) $J_{A_2X_2}$ =8.5	2.25 (3H, s)

[a] In deuteriochloroform. Chemical Shifts given in ppm (δ) relative to internal TMS. Coupling constants (J) in Hz. [b] Two proton AB quartets appeared as triplets (J = 3.0-3.8). [c] 3.55 (3H, s) for 5-CH_3O group.

Br, I, OCH_3 and NO_2) increase the yield (35-75%) in comparison to unsubstituted analogues (yield 7%), while a 5-methyl substituent decreased the yield to less than 5%. The structures of the epoxyisoindolines obtained as colourless crystals were confirmed by elemental analyses and ^{1}H nmr spectra (Table III) showing the usual features as reported in previous papers [8,10]. In contrast to the stable unsubstituted and 5-methylsubstituted epoxyisoindolines undergoing a retro Diels-Alder reaction at an elevated temperature [8,11] 5-nitro- and 5-halogeno-substituted analogues decomposed explosively at temperatures near 180°.

EXPERIMENTAL

Melting points are uncorrected. For tlc "Merck" silicca-GF or alumina GF glass plates were used. Columns for chromatographic separations and purifications were packed with "Fluka" silicagel or neutral alumina Grade I and eluted with solvents of analytical grade ("Kemika"). Proton nmr spectra in deuteriochloroform were obtained

with a Jeol JNM-FC 90Q spectrometer at 90 MHz and shifts (δ) are given in ppm relative to internal TMS, (s = singlet, bs = broadened singlet, d = doublet, t = triplet, q = quartet).

Azomethynes.

All furfurylidene-*p*-toluidines **I** except 5-methoxy-derivative **Ie** were prepared according to a reported [12] or a modified procedure and are exemplified by compounds **Ic** and **Ie**.

N-(5-Iodo-2-furfurylidene)-*p*-toluidine (**Ic**).

To 5-iodofurfural [13] (4.44 g, 0.02 mole) an equimolar quantity of *p*-toluidine (2.14 g, 0.02 mole) in 30 ml of ether was added and left at room temperature for 3 hours. The solvent was evaporated and the residue was recrystallized from petroleum ether (bp 40-70°). Azomethyne **Ic** (5.45 g, 88%) was obtained. An analytically pure sample, mp 79-80° was obtained by repeated recrystallization from petroleum ether; ^{1}H nmr (deuteriochloroform): δ 2.35 (3H, s) for CH_3, 6.71 (1H, d, J = 3.5 Hz) and 6.81 (1H, d, J = 3.5 Hz) for furanic H_4 and H_3, 7.16 (4H, s) for *p*-substituted phenyl and 8.19 (1H, s) for azomethyne -CH=.

Anal. Calcd. for $C_{12}H_{10}INO$: C, 46.32; H, 3.24; N, 4.50. Found: C, 46.22; H, 3.14; N, 4.73.

N-(5-Methoxy-2-furfurylidene)-*p*-toluidine (**Ie**).

To a solution of sodium methoxide prepared from 1.15 g (0.05 g-atom) of sodium and 60 ml of dry methanol, 9.35 g (0.03 mole) of *N*-(5-iodofurfurylidene)-*p*-toluidine **Ic** and 3.0 g of powdered cupric oxide were added. The reaction mixture was heated under reflux in methanol for 90 minutes. The solid obtained was filtered and the methanolic solution was diluted with an equal amount of water. The crude product (5.55 g, 86%) separated after cooling and was recrystallized from petroleum ether (bp 40-70°). The analytically pure sample melted at 87-88°; ^{1}H nmr (deuteriochloroform): δ 2.33 (3H, s) for CH_3, 3.91 (3H, s) for OCH_3, 5.34 (1H, d, J = 3.5 Hz) and 6.81 (1H, d, J = 3.5 Hz) for furan H_4 and H_3, 7.12 (4H, s) for *p*-substituted phenyl and 8.03 (1H, s) for azomethyne -CH=.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09. Found: C, 72.50; H, 5.99.

Secondary Amines.

General Procedure for **IIa-d**.

To a solution of azomethine **Ia-d** (0.02 mole) in 100 ml of methanol, 1.0 g (0.026 mole) of sodium borohydride was added portionwise during 2 hours at room temperature. Water (100 ml) was added and after cooling the crude amine was filtered. Pure crystalline amines **IIa-d** were obtained by recrystallization from the appropriate solvent.

N-(5-Chloro-2-furfuryl)-*p*-toluidine (**IIa**).

This compound was obtained in a yield of 91%, (methanol/water, 3:1), mp 50-52°; ^{1}H nmr (deuteriochloroform): δ 2.28 (3H, s) for CH_3, 3.59 (1H, bs, deuterium oxide exchangeable) for NH, 4.19 (2H, s) for CH_2, 6.03 (1H, d, J = 3.2 Hz) and 6.17 (1H, d, J = 3.2 Hz) for furanic H_4 and H_3, 6.55 (2H, d) and 6.97 (2H, d) $J_{A_2X_2}$ = 8.5 Hz for *p*-substituted phenyl.

Anal. Calcd. for $C_{12}H_{12}ClNO$: C, 65.01; H, 5.46; N, 6.32. Found: C, 65.30; H, 5.57; N, 6.14.

N-(5-Bromo-2-furfuryl)-*p*-toluidine (**IIb**).

This compound was obtained in a yield of 99%, (petroleum ether), mp 54-55°; ^{1}H nmr (deuteriochloroform): δ 2.22 (3H, s) for CH_3, 3.80 (1H, bs, deuterium oxide exchangeable) for NH, 4.22 (2H, s) for CH_2, 6.15 (1H, d, J = 3.5 Hz) and 6.19 (1H, d, J = 3.5 Hz) for furanic H_4 and H_3, 6.55 (2H, d) and 6.97 (2H, d), $J_{A_2X_2}$ = 8.5 Hz for *p*-substituted phenyl.

Anal. Calcd. for $C_{12}H_{12}BrNO$: C, 54.15; H, 4.55; N, 5.27. Found: C, 54.06; H, 4.73; N, 5.04.

N-(5-Iodo-2-furfuryl)-*p*-toluidine (**IIc**).

This compound was obtained in a yield of 99%, (methanol/water, 3:1), mp 33-34°; ^{1}H nmr (deuteriochloroform): δ 2.23 (3H, s) for CH_3, 3.55 (1H, bs, deuterium oxide exchangeable) for NH, 4.27 (2H, s) for CH_2, 6.43 (1H, d, J = 3.2 Hz) and 6.11 (1H, d, J = 3.2 Hz) for furanic H_4 and H_3, 6.55 (2H, d) and 6.98 (2H, d), $J_{A_2X_2}$ = 8.5 Hz for *p*-substituted phenyl.

Anal. Calcd. for $C_{12}H_{12}INO$: C, 46.02; H, 3.87; N, 4.48. Found: C, 46.30; H, 4.03; N, 4.71.

N-(5-Nitro-2-furfuryl)-*p*-toluidine (**IId**).

This compound was obtained in a yield of 90%, (methanol/water, 3:1), mp 65-66°, lit [14], mp 62-65°; ^{1}H nmr (deuteriochloroform): δ 2.23 (3H, s) for CH_3, 3.87 (1H, s, deuterium oxide exchangeable) for NH, 4.39 (2H, s) for CH_2, 7.21 (1H, d, J = 3.5 Hz) and 6.42 (1H, d, J = 3.5 Hz) for furan H_4 and H_3, 6.55 (2H, d) and 6.98 (2H, d), $J_{A_2X_2}$ = 8.2 Hz for *p*-substituted phenyl.

Anal. Calcd. for $C_{12}H_{12}N_2O_3$: C, 62.05; H, 5.21. Found: C, 61.79; H, 4.97.

N-(5-Methoxy-2-furfuryl)-*p*-toluidine (**IIe**).

This compound was prepared by substantially the same procedure from 2.6 g (0.012 mole) of **Ie**, but isolation of crude **IIe** was achieved by extraction with ether. Dried (magnesium sulfate) extracts were evaporated and purified by column chromatography (neutral alumina Grade I) using petroleum ether/ether (5:1) as the eluent. The pure amine **IIe** (2.5 g, 96%) was obtained as a light yellow oil sensitive to heating. Violent decomposition prevented distillation; ^{1}H nmr (deuteriochloroform): δ 2.21 (3H, s) for CH_3, 3.74 (3H, s) for OCH_3, 3.72 (1H, s, deuterium oxide exchangeable) for NH, 4.10 (2H, s) for CH_2, 5.00 (1H, d, J = 2.9 Hz) and 6.04 (1H, d, J = 2.9 Hz) for furan H_4 and H_3, 6.54 (2H, d) and 6.95 (2H, d), $J_{A_2X_2}$ = 8.2 Hz for *p*-substituted phenyl.

Tertiary Amines.

General Procedure for **IIIa-d** (Method A).

To an appropriate, freshly recrystallized or chromatographed secondary amine (0.01 mole) a slight surplus of allyl bromide (0.011 mole) was added and the mixture kept at room temperature for 20 hours. The crude hydrobromide of the tertiary amine was treated with 10 ml of methanol and 200 ml of 5% aqueous sodium hydroxide. The organic material was taken into ether, dried over anhydrous magnesium sulfate and the solvent evaporated. The oily residue was purified by column chromatography on silica using petroleum ether/ether (10:1) as the eluent. Pure tertiary amines **IIIa-d** were obtained as light yellow oils which were very sensitive to heating which prevented distillation due to explosive decomposition. Analytically pure samples were obtained by rechromatography on silica (Table I). The purity of amines **IIIa-d** was checked by tlc and was identified by ^{1}H nmr (Table II). As soon as separated, the oily amines spontaneously started to isomerize.

N-Allyl-*N*-(5-methoxy-2-furfuryl)-*p*-toluidine (**IIIe**). (Method B).

N-(5-Methoxy-2-furfuryl)-*p*-toluidine **IIe** (2.15 g, 0.01 mole) was added to a suspension of 2.0 g (0.08 mole) of powdered sodium hydride in 40 ml of dimethylformamide. The mixture was left at room temperature for 2 hours and then 3.0 g (0.025 mole) of allyl bromide was added and allowed to stand at room temperature for an additional 3 hours. The surplus of sodium hydride was removed by dropwise addition of methanol. The reaction mixture, after dilution with 400 ml of water, was extracted with ether and dried over magnesium sulfate. The solvent was evaporated and crude **IIIe** separated by column chromatography (Neutral alumina, Grade I) using petroleum ether (bp 30-50°) as the eluent, yield 2.1 g (82%). Pure **IIIe** was obtained by rechromatography as a light yellow oil sensitive to heating. The purity was checked by tlc and the compound identified by ^{1}H nmr spectra (Table II).

Isomerization to Epoxyisoindolines (Table I).

General Procedure.

About 2 g of the corresponding tertiary amine **IIIa-g** immediately after separation by column chromatography was transferred into a stoppered flask and allowed to isomerize by standing at 25° for 3 days. The semicrystalline mixture of starting amine **IIIa-g** and the isomeric cyclo-

addition product **IVa-g** was separated by column chromatography on silica (entries 1-3, 6, 7) or neutral alumina (entries 4 and 5) using the eluents specified in Table I. Recrystallization from ethanol gave colourless crystals **IVa-g** (Table I) identified by elemental analyses and by ^{1}H nmr spectra (Table III).

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[9c] The preparation of 5-methoxy derivatives includes transformation of 5-iodo-2-furfurylidene-*p*-toluidine (**Ic**) to 5-methoxy-2-furfurylidene-*p*-toluidine (**Ie**) by nucleophylic substitution with sodium methoxyde in the presence of cupric oxide.

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