Oximes, O-Methyloximes and N-Methyloximes

of 2,6-Dimethyl-4-halogenobenzaldehyde

Preparation, Isomerization and Assignment of Configuration

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2,6-Dimethyl-4-bromoaniline was transformed to the hydrochloride and *via* diazotization to the correspondingly substituted benzonitrile and benzaldehyde. From the latter the 2,4-dinitrophenylhydrazone, the *syn*- and *anti*-oximes, the *syn*- and *anti*-O-methyloximes and the *anti*-N-methyloxime were prepared. The latter compound was isomerized to give a substance, which is provisionally assigned the *syn*-N-methyloxime structure. Furthermore, a dihydrogenated product, N-methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine, was detected.

An improved synthesis of 2,6-dimethyl-4-chloroaniline is described. From this compound were similarly prepared the corresponding hydrochloride, nitrile, aldehyde, 2,4-dinitrophenylhydrazone, *syn*-oxime, *syn*-O-methyloxime and *anti*-N-methyloxime.

The assignment of the molecular structures was achieved by chemical methods and by IR- and PMR-spectroscopy.

The molecular and crystal structures of *syn*- and *anti*-*p*-chlorobenzaldoximes have previously been determined by X-ray analyses in this laboratory.[1] The results indicated, that steric hindrance of coplanarity of the C=N bond with the benzene ring resulted in deformation of the valency angles and also of the bond lengths in the C=N—O system. The evidence however was not conclusive.

In order to use the X-ray diffraction method in further investigations on the character of deformation in the bond system of aromatic oximes possessing no planar configuration due to steric hindrance, the below mentioned compounds were synthesized. A family of compounds such as (III)-(VIII) has not earlier been known. The preparation of these substances therefore opens up the possibility of elucidating the influence not only of the aromatic moiety but also of the oxime moiety on the bond system.

SYNTHESES

The oximes as well as the O- and N-methyloximes of 2,6-dimethyl-4-bromobenzaldehyde were prepared according to the following scheme (R = 2,6-dimethyl-4-bromophenyl):

2,6-Dimethyl-4-bromoaniline (I) after diazotization and subsequent reaction with formaldoxime[2] followed by acid hydrolysis yielded 2,6-dimethyl-4-bromobenzaldehyde (II). The aldehyde (II) was treated with excess of hydroxylamine to give *syn*-2,6-dimethyl-4-bromobenzaldoxime (III). Rearrangement of (III) to give *anti*-2,6-dimethyl-4-bromobenzaldoxime (IV) was effectuated by treatment with hydrogen chloride in dry ether followed by neutralization by alkali of the precipitate.

The aldehyde (II) was treated with excess of methoxyamine to give *syn*-2,6-dimethyl-4-bromobenzaldehyde-O-methyloxime (V). Following irradiation of (V) with unfiltered UV-light a 15 % yield of *anti*-2,6-dimethyl-4-bromobenzaldehyde-O-methyloxime (VI) was isolated by chromatography on silica gel. From the column a further compound was isolated which was identified as 2,6-dimethyl-4-bromobenzonitrile (IX). This compound is assumed to arise from a *trans*-elimination of methanol from (VI).

The aldehyde (II) was treated with excess of N-methylhydroxylamine to give *anti*-2,6-dimethyl-4-bromobenzaldehyde-N-methyloxime (VII). Purification by recrystallization was inprofitable whereas chromatography on silica gel yielded the pure *anti*-N-methyloxime (VII). From the column a further compound (X) melting at 131.5—133° was isolated.

This compound (X) proved to be N-methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine and may derive from a reduction of (VII) by the excess of N-methylhydroxylamine.

2,6-Dimethyl-4-chloroaniline (XI) prepared from 2,6-dimethylaniline according to Dadswell and Kenner[3] only gave a yield of 15 % whereas a method including halogenation of 2,6-dimethylaniline with sulphuryl chloride in

chloroform was investigated resulting in a yield of 56 %. Diazotization of (XI) and subsequent treatment with CuCN gave a high yield of 2,6-dimethyl-4-chlorobenzonitrile. Since the conventional Stephen reduction [4] of this compound was unsuccessful the amine (XI) was converted to the oxime and subsequently to the aldehyde, the 2,4-dinitrophenylhydrazone, the *syn*-oxime, the *syn*-O-methyloxime, and the *anti*-N-methyloxime by reactions analogous to those described above leading from I to II, III, V, and VII.

ASSIGNMENT OF STRUCTURE

Aromatic aldehydes normally yield *syn*-oximes when treated with hydroxylamine. Accordingly (III) is likely to have the *syn*-configuration. A further clue to the configuration is obtained on comparing the melting points, 113—114° for (III) and 172.5—173.5° for (IV). Assuming the usual dimerization of *syn*-benzaldoximes and chain formation of the *anti*-forms [1, p. 113] by hydrogen bonding the low melting compound (III) is expected to have the *syn*-configuration. Furthermore the oxime (IV) after addition of acetic anhydride and subsequent treatment with sodium carbonate furnished in good yield a compound (IX) having the IR-spectrum identical to that of 2,6-dimethyl-4-bromobenzonitrile prepared by diazotization of (I) and subsequent treatment with CuCN, which proves the *anti*-configuration of (IV). A similar treatment of (III) only yielded a trace of the nitrile (IX) implying the *syn*-configuration of (III).

The PMR-spectra of the two oximes are recorded in Table 1.

Table 1. τ-Values from PMR-spectra of the oximes (III) and (IV)

	a	b	c	d	Solvent
syn-oxime (III)	7.62	2.93	1.63	1.43	CDCl$_3$
anti-oxime (IV)	7.83	2.79	2.49	−1.14	(CH$_3$)$_2$SO*
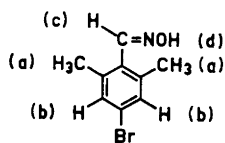
The hydrogen ratio determined from the peak areas of a, b, c, and d were 6:2:1:1. Stuart models of the *syn*- and *anti*-oximes (III) and (IV) clearly indicate that the *anti*-form is sterically hindered in attaining a planar configuration, whereas a relatively planar structure may be expected for the *syn*-oxime. As a consequence the (c)-proton of the *syn*-oxime to a larger extent than the corresponding proton of the *anti*-oxime is exposed to the effect from the ring current of the benzene ring.[5] This agrees with the finding that the chemical shift of the (c)-proton of the *syn*-oxime (III) is found at a lower field than the corresponding chemical shift of the *anti*-oxime (IV) (see Table 1).

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* No solvent effect was observed.

Further support to the assigned configuration of the compounds is to be found in the τ-values for the (a)-protons (see Table 1). Assuming the anisotropic effect of a C=N bond to be the same as the effect of a C=O bond a lowfield change of the chemical shift of the (a)-protons in the *syn*-O-methyloxime is expected due to the probable coplanarity of the C=N bond and the benzene ring which is not possible in the *anti*-oxime.[5, p. 124]

The treatment of aromatic aldehydes with methoxyamine normally yields *syn*-O-methyloximes analogous to the treatment with hydroxylamine. Accordingly, the *syn*-configuration of (V) and the *anti*-configuration of (VI) are proposed.

The melting points yield a weak support to these proposals. Since no association complicates matters with these compounds, one would expect the *trans*(*syn*)-compound to have the highest melting point. The m.p. of (V) is 36—36.5° and the m.p. of (VI) is 27.5—28.5° suggesting (V) to be the *syn*-O-methyloxime.

Table 2. τ-Values from PMR-spectra of the O-methyloximes (V) and (VI)

	a	d	b	c	Solvent
syn-O-methyl-oxime (V)	7.63	6.03	2.95	1.70	CDCl$_3$
anti-O-methyl-oxime (VI)	7.84	6.19	2.88	2.71	CDCl$_3$
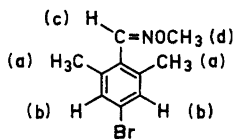
Further evidence for the configuration is obtained from the PMR-spectra (Table 2). The peak areas of a, d, b, and c gave the hydrogen ratio 6:3:2:1. A comparison of the τ-values of the (a)- and (b)- and especially the (c)-protons in Table 2 with the corresponding τ-values in Table 1 strongly indicates that (V) has the *syn*-configuration and that (VI) has the *anti*-configuration. Furthermore model considerations with these compounds exclude a planar configuration of the *anti*-compound.

The N-methyloxime (VII) was irradiated with unfiltered UV-light to give 10 % of a compound (VIII) giving analytical data concordant with the composition C$_{10}$H$_{12}$BrNO.

The N-methyloxime structure of (VII) and (VIII) were demonstrated as follows:

The compounds (VII) and (VIII) were treated with excess of lithium aluminium hydride in dry ether to give a compound having the IR-spectrum identical to the spectrum of N-methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine. Furthermore the compounds (VII) and (VIII) were boiled for 5 min with excess of concentrated hydrochloric acid and after cooling the mixtures were exhaustively extracted with chloroform which was proved to

contain 2,6-dimethyl-4-bromobenzaldehyde through thin-layer chromato-graphy using an authentic sample as a reference compound. The aqueous layers reduced Fehling's solution upon boiling implying the content of N-methylhydroxylamine.

The PMR-spectra of (VII) and (VIII) as well as that of *anti-p*-chlorobenzaldehyde-N-methyloxime (XII) were recorded to give the results shown in Table 3.

Table 3. τ-Values from PMR-spectra of the N-methyloximes (VII), (VIII), and (XII).

	a	d	b	c	Solvent
(VII)	7.76	6.14	2.80	2.52	CDCl$_3$
(VIII)	7.71	7.19	2.94	5.59	CDCl$_3$
(XII)	1.75;1.88	6.14	2.55;2.70	2.62	CDCl$_3$
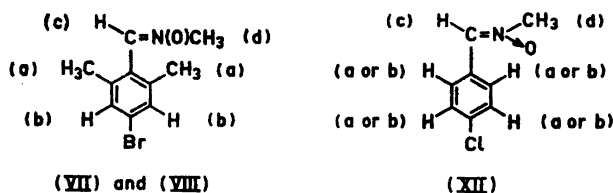
(VII) and (VIII)   (XII)

The configuration of (XII) is known to be *anti*.[6] Comparing the chemical shifts of the (c)-protons and the (d)-protons of (VII) and (VIII) in Table 3 with the corresponding chemical shifts of (XII) the *anti*-configuration of (VII) is clearly indicated.

anti-N-Methyl-*p*-chlorobenzaldoxime has been shown to rearrange by UV-irradiation to give *p*-chlorobenzmethylamide.[7] The possibility that (VIII) had been formed by a similar reaction was excluded, since the IR-spectrum did not show the strong carbonyl peak about 1700 cm^{-1} which is invariably found in amides and alkylamides.

The peak areas of the PMR-spectrum of (VIII) gave the hydrogen ratio of a:d:b:c = 6:3:2:1 which is consistent with (VIII) being the *syn*-N-methyloxime.

Two facts, however, seem to contradict the assumption, that (VII) and (VIII) are stereoisomers. One is the position of the PMR-signal of the (c)-proton in the compound (VIII) which is remarkably different from the signals of the (c)-protons in (VII) and (XII); the second is the great difference between the R_F-values (*viz.* 0.08 (VII) and 0.70 (VIII)) found by thin-layer chroma-tography on silica gel using chloroform-ethyl acetate 95:5 as developing solvent. These surprising results might be explained by assuming a dimer structure of (VIII), but a mass spectrum did not give evidence of any fragments of greater mass than the monomer molecular ion. Since dissociation of a presumed dimer might take place on volatilization of the compound, this experiment is not conclusive though it lends support to the proposed monomer structure. An unequivocal assignment of the structure of (VIII) can at present not be made, but an X-ray crystal structure determination will be attempted.*

The structure of the compound (X) was assigned as N-methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine. This compound might well be formed by dihydrogenation of the C=N bond in (VII), since an excess of the strongly reducing N-methylhydroxylamine was used for the preparation. The PMR-spectrum was in accordance with this assumption.

Table 4. τ-Values from the spectrum of the compound (X) dissolved in CDCl₃

a	e	c	d	b
7.72	7.48	6.33	*ca.* 3.57	2.85

The spectrum consisted of 5 signals (see Table 4). The hydrogen ratio determined by the integral curves was 6:3:2:1:2 and interpretation of the spectrum assigned the following possible structure:

(X)
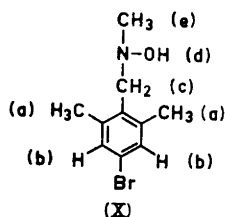
Furthermore the IR-spectrum of (X) was identical to that of N-methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine prepared from (VII) using lithium aluminium hydride as the reducing agent.

EXPERIMENTAL

2,6-Dimethyl-4-bromoaniline hydrochloride. The amine was prepared according to Noelting *et al.*[8] Yield of the hydrochloride 87 % melting at 203—204° (decomp.). (Found after drying at 50°/2 mm: Cl 14.90. Calc. for C₈H₁₁NBrCl: Cl 15.01).

2,6-Dimethyl-4-chloroaniline hydrochloride. A solution of 60.0 g (0.44 mole) of sulphuryl chloride in 100 ml of chloroform was placed in a 1-liter three-necked flask fitted with a separatory funnel, a mercury sealed mechanical stirrer, and a reflux condenser attached to a gas trap. Through the separatory funnel a solution of 24.3 g (0.20 mole) of 2,6-dimethylaniline (I) in 100 ml of chloroform was admitted over a period of 2 min with stirring which was continued for 5 min.

After addition of 100 ml of water the solution was stirred for 10 min and then steam distilled to remove the chloroform. After cooling to room temperature the residue was made alkaline by addition of a solution of 40 g (about 1 mole) of sodium hydroxide in 100 ml of water and steam distilled. Yield 17.3 g (56 %). Dissolved in 200 ml of dry ether the crude product was saturated with hydrogen chloride to give a hydrochloride appearing as very small colourless crystals. Yield 19.8 g (51 %), m.p. 239—239.5° (decomp.). (Found after drying at 50°/2 mm: Cl 37.09. Calc. for C₈H₁₁NCl₂: Cl 36.98).

Dissolved in a minimum of water the hydrochloride was decomposed by addition of excess of a 40 % solution of sodium hydroxide to give colourless crystals of the amine (II), m.p. 45.5—46° (Dadswell and Kenner,[3] m.p. 44—45°).

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* Note added in proof. Further work indicates that (VIII) is probably a 2-methyl-3-(4-bromo-2,6-dimethylphenyl)-oxaziridine; this structure is in accordance with all evidence hitherto obtained *cf.* Splitter, J. S. and Calvin, M. [*J. Chem. Soc.* **23** (1958) 651; **30** (1965) 3427] and Emmons, W.D. [*J. Am. Chem. Soc.* **79** (1957) 5739].

2,6-Dimethyl-4-bromobenzaldehyde (II). The preparation was similar to that described for *p*-chlorobenzaldehyde.[2] The crude product was purified through the bisulphite compound to give colourless crystals. Yield 13 %, m.p. 66.2—66.8°. (Found after drying at 50°/2 mm: C 50.84; H 4.41; Br 37.36. Calc. for C_9H_9BrO: C 50.73; H 4.23; Br 37.53). In another experiment the crude product was purified through vacuum distillation to give a yield of 33 % collected at 137—139°/12 mm.

2,6-Dimethyl-4-bromobenzaldehyde-2,4-dinitrophenylhydrazone. Red crystals, m.p. 285—285.5°. (Found after drying at 50°/2 mm: C 45.74; H 3.18; N 14.18. Calc. for $C_{15}H_{13}N_4O_4Br$: C 45.80; H 3.31; N 14.25).

2,6-Dimethyl-4-chlorobenzaldehyde was prepared and purified through the bisulphite compound just as (II). Colourless crystals. Yield 36 %, m.p. 55.5—56°. (Found after drying at 50°/2 mm: C 64.22; H 5.27; Cl 20.98. Calc. for C_9H_9OCl: C 64.09; H 5.34; Cl 21.07).

2,6-Dimethyl-4-chlorobenzaldehyde-2,4-dinitrophenylhydrazone. Red crystals, m.p. 269—270°. (Found after drying at 50°/2 mm: C 51.62; H 3.89; N 16.19. Calc. for $C_{15}H_{13}N_4O_4Cl$: C 51.65; H 3.73; N 16.07).

2,6-Dimethyl-4-bromobenzonitrile (IX). The preparation was similar to that described for *p*-tolunitrile.[9] Recrystallization from aqueous ethanol (35 %) gave colourless crystals. Yield 60 %, m.p. 69.5—70.5°. (Found after drying at 50°/2 mm: C 51.49; H 3.75; N 6.09. Calc. for C_9H_8NBr: C 51.43; H 3.81; N 6.67).

2,6-Dimethyl-4-chlorobenzonitrile. Prepared as the above compound (IX). Recrystallization from aqueous ethanol (30 %) gave colourless crystals. Yield 80 %, m.p. 62—62.5°. (Found after drying at 50°/2 mm: C 65.55; H 4.98; N 8.37. Calc. for C_9H_8NCl: C 65.45; H 4.85; N 8.46).

syn-2,6-Dimethyl-4-bromobenzaldoxime (III). A mixture of 0.5 g (0.0024 mole) of 2,6-dimethyl-4-bromobenzaldehyde (II), 1.25 g (0.0144 mole) of hydroxylamine hydrochloride and 2.6 g (0.0072 mole) of sodium carbonate in 35 ml of aqueous ethanol (40 %) was refluxed for 20 min, concentrated to about 10 ml and filtered after addition of 15 ml of 1 N sodium hydroxide. After addition of 5 ml of 4 N hydrochloric acid the filtrate was cooled on ice to give colourless crystals. Yield 64 %, m.p. 113—114°. (Found after drying at 50°/2 mm: N 6.08. Calc. for $C_9H_{10}NOBr$: N 6.14).

syn-2,6-Dimethyl-4-chlorobenzaldoxime. The preparation was similar to the above manner. Yield of colourless crystals 94 %, m.p. 119.5—120°. (Found after drying at 50°/2 mm: N 7.48. Calc. for $C_9H_{10}NOCl$: N 7.63).

anti-2,6-Dimethyl-4-bromobenzaldoxime (IV). 0.2 g of *syn*-2,6-dimethyl-4-bromobenzaldoxime (III) was dissolved in 20 ml of dry ether and dry hydrogen chloride was passed through for 30 min. The crystals were filtered off and suspended in 10 ml of water; excess of sodium carbonate was added and upon cooling in ice the crystals were filtered off and recrystallized from ethanol-water. Yield of colourless crystals 0.1 g (50 %), m.p. 172.5—173.5°. (Found after drying at 50°/2 mm: C 47.28; H 4.29; N 6.08. Calc. for $C_9H_{10}NOBr$: C 47.39; H 4.39; N 6.14).

syn-2,6-Dimethyl-4-bromobenzaldehyde-O-methyloxime (V). A mixture of 0.5 g (0.0024 mole) of 2,6-dimethyl-4-bromobenzaldehyde (II), 1.20 g (0.0144 mole) of methoxyamine hydrochloride and 2.06 g (0.0072 mole) of sodium carbonate in 40 ml of aqueous ethanol (50 %) was refluxed for 30 min. After concentration of the solution to about 10 ml, 10 ml of water were added and the solution was cooled in an ice and salt bath to give colourless crystals. Yield 80 %, m.p. 36—36.5°. (Found after drying at 20°/2 mm: C 49.43; H 5.02; N 5.90. Calc. for $C_{10}H_{12}NOBr$: C 49.61; H 4.96; N 5.79).

syn-2,6-Dimethyl-4-chlorobenzaldehyde-O-methyloxime. The preparation was similar to the above manner. Yield 80 %, m.p. 35.5—36°. (Found after drying at 20°/2 mm: C 61.00; H 6.22; N 6.96. Calc. for $C_{10}H_{12}NOCl$: C 60.75; H 6.08; N 7.09).

anti-2,6-Dimethyl-4-bromobenzaldehyde-O-methyloxime (VI). 0.8 g of *syn*-2,6-dimethyl-4-bromobenzaldehyde-O-methyloxime (V) dissolved in 50 ml of cyclohexane was placed in a quartz test-tube and irradiated with unfiltered UV-light (Tauch-lampe S 81/Pl 313, Quartzlampen Gesellschaft m.b.H. Hanau) for 20 h. The distance between the longitudinal axes of the test-tube and the lamp was 8 cm.

The solution was evaporated under reduced pressure and chromatographed on 40 g of silica gel (0.05—0.20 mm Merck) activated at 120° and mixed with 10 % of water. Petroleum ether-benzene 3:1 was used as developing solvent.

A compound was isolated having the approximate R_F-value 0.45 (thin-layer chromatography according to Tschesche *et al.*[10]) using benzene-chloroform 95:5 as developing

solvent. The compound was detected by spraying with ethanolic phosphomolybdic acid (10 %) and subsequent heating to 120° for 10 min. Recrystallization from petroleum ether cooled in CO_2/acetone yielded 0.12 g (15 %) of colourless crystals, m.p. 27.5—28.5°. (Found after drying at room temperature/2 mm: C 49.54; H 5.14; N 5.65. Calc. for $C_{10}H_{12}$BrNO: C 49.61; H 4.96; N 5.79).

anti-*2,6-Dimethyl-4-bromobenzaldehyde-N-methyloxime* (*VII*). A mixture of 0.5 g (0.0024 mole) of 2,6-dimethyl-4-bromobenzaldehyde (II), 0.25 g (0.0030 mole) of N-methylhydroxylamine hydrochloride and 0.43 g (0.0015 mole) of sodium carbonate in 40 ml of aqueous ethanol (50 %) was refluxed for 10 min. The solution was evaporated to dryness and extracted with 2 × 20 ml of chloroform. The combined extracts were evaporated to dryness.

Thin-layer chromatography in chloroform-ethyl acetate 95:5 indicated that the crude product was a mixture of at least 6 compounds (approximate R_F-values: 1) 0.97; 2) 0.82 (oxo-compound (II)); 3) 0.67; 4) 0.51; 5) 0.08; 6) 0.04). The compounds were detected by spraying with ethanolic phosphomolybdic acid (10 %) and subsequent heating to 120° for 10 min.

A similar mixture obtained from 2.5 g of the oxo-compound (II) was chromatographed on 100 g of silica gel (0.05—0.20 mm Merck) activated at 120° and mixed with 10 % of water. As eluent was used chloroform.

Recrystallized from water 1.0 g of (VII) (approximate R_F-value 0.08) was isolated as colourless needles, m.p. 177—178°. (Found after drying at 50°/2 mm: C 49.49; H 4.91; N 5.72; Br 33.21. Calc. for $C_{10}H_{12}$BrNO: C 49.61; H 4.96; N 5.79; Br 33.07).

Recrystallized from chloroform-ethyl acetate 59 mg of N-methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine (X) (approximate R_F-value 0.51) was isolated as colourless crystals, m.p. 131.5—133°.

anti-*2,6-Dimethyl-4-chlorobenzaldehyde-N-methyloxime*. The preparation was similar to that described for 2,6-dimethyl-4-bromobenzaldehyde-N-methyloxime (VII), except that the crude compound instead of purification by chromatography was recrystallized from water to give 59 % of colourless crystals, m.p. 177.5—178.5°. (Found after drying at 50°/2 mm: C 60.89; H 6.08; N 6.98; Cl 18.09. Calc. for $C_{10}H_{12}$NOCl: C 60.75; H 6.08; N 7.09; Cl 17.97).

syn-*2,6-Dimethyl-4-bromobenzaldehyde-N-methyloxime* (?) (*VIII*). 0.5 g of anti-2,6-dimethyl-4-bromobenzaldehyde-N-methyloxime (VII) dissolved in 60 ml of benzene was treated with UV-light as described for syn-2,6-dimethyl-4-bromobenzaldehyde-O-methyloxime (V).

The crude product was chromatographed on 25 g silica gel (0.05—0.20 mm Merck) activated at 120° and mixed with 10 % of water. Chloroform-benzene 1:1 was used as developing solvent. A compound was isolated with the approximate R_F-value of 0.70 (thin-layer chromatography using chloroform-ethyl acetate 95:5 as developing solvent). The compound was detected by spraying with ethanolic phosphomolybdic acid (10 % and subsequent heating to 120° for 10 min). Recrystallization from ethanol yielded 49 mg of colourless crystals, m.p. 88—89°. (Found after drying at 50°/2 mm: C 49.82; H 4.89; N 5.66. Calc. for $C_{10}H_{12}$NOBr: C 49.61; H 4.96; N 5.79).

N-*Methyl-N-(2,6-dimethyl-4-bromobenzyl)-hydroxylamine* (*X*). A mixture of 0.5 g (0.02 mole) of anti-2,6-dimethyl-4-bromobenzaldehyde-N-methyloxime (VII) and 0.1 g (0.026 mole) of lithium aluminium hydride in 30 ml of dry ether was refluxed for 15 min. The mixture was decomposed with 3 ml of water and the ethereal layer was separated. The residue was extracted with 3 × 10 ml of ether, and the combined extracts were dried (MgSO$_4$) and evaporated to dryness. The crystalline residue was recrystallized from ethanol-water to give 0.3 g of colourless needles, m.p. 131.5—132.5°. (Found after drying at 50°/2 mm: C 48.90; H 5.66; N 5.58; Br 32.64. Calc. for $C_{10}H_{14}$NOBr: C 49.18; H 5.74; N 5.74; Br 32.79).

The melting points have been determined with a hot stage microscope (Mikroskop-Heiztisch 350 Ernst Leitz G.m.b.H. Wetzlar).

The IR-spectra were recorded in potassium bromide discs on a Perkin-Elmer spectrophotometer, Model 21.

The PMR-spectra were made with a Varian A 60 NMR spectrophotometer operating at a fixed frequency of 60 Mc/s, using tetramethylsilane as internal standard.

The mass spectrum was determined on an Atlas CH 4 mass spectrometer fitted with an all metal inlet system which was maintained at 150°. The ion source temperature was 250°, the ionizing current was 35 μA and the ionizing potential was 70 eV.

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