Journal of Organometallic Chemistry, 81 (1974) 309—320

STEREOCHEMICAL STUDIES

XIX. ON THE SPECIFIC DIRECTING EFFECT IN THE MERCURATION OF OLEFINS. STEREOCHEMISTRY OF THE METHOXYMERCURATION OF 1-CYANO-3-CYCLOHEXENE AND *trans*-1,2-DICYANO-4-CYCLOHEXENE

NICKOLAY S. ZEFIROV and L.G. GURVICH
Moscow State University, Department of Chemistry, Moscow 117234 (U.S.S.R.)
(Received June 12th, 1974)

Summary

The stereochemistry of the methoxymercuration of 1-cyano-3-cyclohexene and *trans*-1,2-dicyano-4-cyclohexene has been studied by NMR spectroscopy using partially deuterated model compounds. The configurations of the methoxymercurials formed suggest that the previously postulated "specific directing effect" (the preliminary coordination of a mercury ion with a functional group) should be discounted.

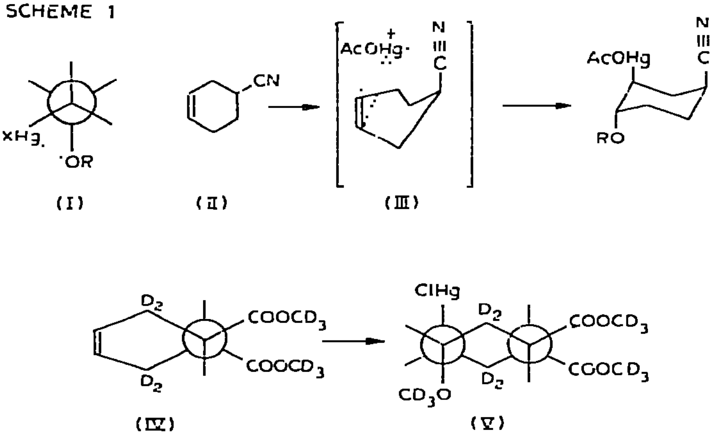
Introduction

The question of intramolecular coordination of functional groups with a metal atom, and with a mercury atom in particular, has already been reviewed [1-3]. This type of coordination was found in, for example, hydroxy- [4], acetoxy- [5] and alkoxy-mercurials [5, 6] and substituted 1-chloromercuri-3-halopropanes [7]. The Hg···OR coordination interaction in structure I (Scheme I) has been evaluated at about 0.7-0.9 kcal/mol [6, 8]. This value suggests that coordination may in some cases be considered to be an additional conformational factor, capable of stabilizing usually unstable conformers [6].

In this connection one important question may be posed. Can such coordination change the normal stereochemistry of reaction? We discuss this problem with application to the solvomercuration of olefins [3, 9]. First, it is evident, that the instances of kinetic or thermodynamic control in this reaction must be completely differentiated. The value of 0.7-0.9 kcal/mol for Hg···OR coordination is high enough to be a conformational energy, since thermodynamic control can lead to the strong predominance of an isomer which has a comparable coordinative interaction [8]. Second, if kinetic control operates in the *trans*-antiparallel addition reaction, coordination of functional groups in a product has no influence on the stereochemistry of the reaction. However, the situation may be changed if the olefin contains a substituent which is capable of preliminary coordination with an attacking mercury ion.

To the best of our knowledge this problem was first discussed by Henbest and Nicholls [10]. These authors found that the nitrile II reacts with mercuric salts with preliminary coordination of the mercury atom with the nitrile group (structure III, Scheme 1). Analogous stereochemistry has been found for a number of addition reactions of cyclohexenes containing OCH_3, OAc, COOR or CH_2OH substituents [10]. This observation stimulated a study of a number of model compounds [11-13] of the "specific directing effect", a concept which has been widely used in the interpretation of unusual stereochemical results.

SCHEME 1

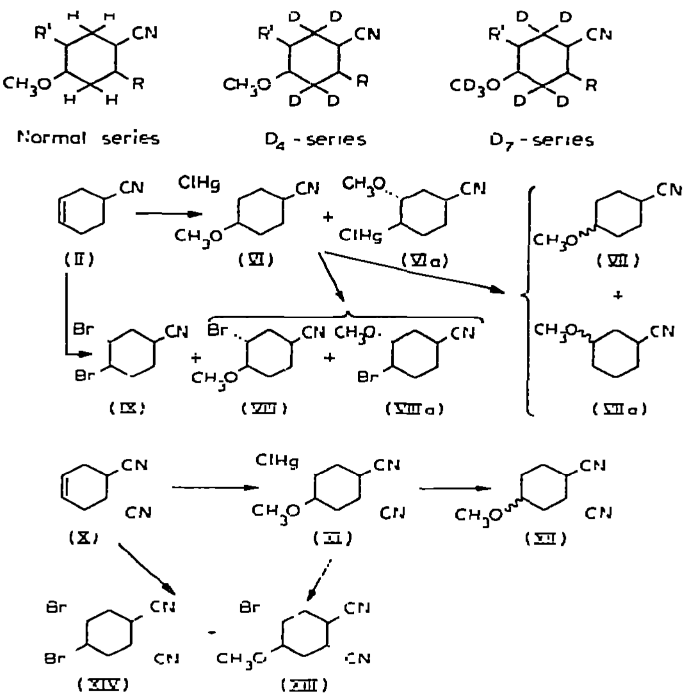


However, the problem of the changing reaction stereochemistry by preliminary coordination with functional groups has still not been unambiguously settled [11-19]. (The literature up to 1965 is discussed in ref. 3). We have already found [20] that methoxymercuration of the diester IV produces methoxymercurial V without preliminary coordination (Scheme 1), so the aim of the present paper is to reinvestigate this problem using the nitrile II and dinitrile X as model compounds (for a preliminary communication see ref. 21).

Results

Addition of mercuric acetate in MeOH to II and X gives the methoxymercurials VI and XI respectively (Scheme 2). Bromination of VI and XI in pyridine produces the methoxybromines VIII and XIII respectively. These compounds have also been obtained by the methoxybromination of II and X (Scheme 2). All experiments were carried out on partially deuterated compounds in order to simplify the NMR spectra. We prepared two series of compounds (Scheme 2): the D_4-series, in which the deuterium atoms are in the 3,3,6,6-positions of the six-membered ring, and the D_7-series, in which the methoxymercurations were carried out in CD_3OD. NMR data are shown in Tables 1 and 2.

SCHEME 2

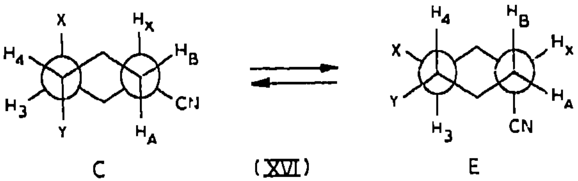


Two problems face us: (a) the configuration of the methoxybromines VIII and XIII and (b) structural isomerism of the methoxymercurial VI. It is known that methoxymercuration of 4-alkylcyclohexenes produces a mixture of isomers [22], but some examples of regioselectivity in analogous addition reactions have appeared [23]. In principle, a mixture of VI and VIa may be expected as a result of the methoxymercuration of II. Usual methods of structure determination are based on either conversion to halogen hydrines [3, 24] or reduction to alcohols (ethers) by sodium borohydride [8, 22]. According to "Jensen's rule" bromination occurs with retention of configuration in pyridine solution [25] and may thus be used for the determination of configuration of methoxymercurials [3, 24].

Bromination of VI proceeds to give a mixture of the methoxybromines VIII and VIIIa (69/31 from NMR data). The methoxybromination of II-D_4 gives a three component mixture (51/37/12). Comparison with the NMR spectra of methoxybromines VIII and VIIIa allows us to identify the two main components of this mixture. The minor component (12%) was identified as the dibromine IX, which was determined by a comparison of its NMR spectra with a specially prepared example of IX-D_4 (Table 1). The bromination of XI-D_7 proceeds to give a mixture of methoxybromine XIII-D_7 and dibromine XIV-D_4 (86/14). The methoxybromination of X-D_4 also produces a mixture of XIII-D_4 and XIV-D_4 (54/46). Dibromine XIV-D_4 was obtained by bromination of X-D_4. NMR data of the compounds obtained are listed in Table 2. The configurations and conformations of VIII, VIIIa and XIII may be assigned by using the J_{vic} values obtained from the NMR spectra. Inspection of the data in Tables 1 and 2 reveals that (a)

TABLE 1

NMR DATA OF 1-CYANO SUBSTITUTED COMPOUNDS



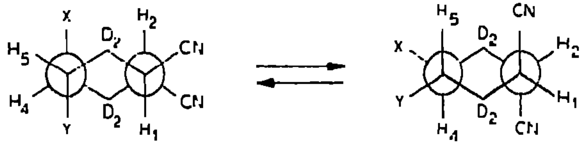
(XVI)

Compound	X	Y	Solvent	J_{34} (± 0.1 Hz)	$J_{AX} + J_{BX}$ (± 0.1 Hz)	J_{AX} (± 0.1 Hz)	Chemical shifts δ (± 0.005 ppm)					E (%)[a]		−ΔG (kcal/mol)
							H_X	H_A	H_B	H_3	H_4	from J_{34}	from $J_{AX} + J_{BX}$	
VI-D_7	HgCl	OCD_3	C_5H_5N	8.0[b]	10.5[b]	6.1	2.7_4	1.7_4	1.4_0	2.8_7	3.2_5	61.5	60.2	0.26
			CD_3CN	9.0[c]	9.2[c]		2.8_2			2.5_8	3.3_2	74.3	76.9	0.67
			CD_3NO_2	9.0	9.0	4.6_8	2.9_1	1.9_1	1.6_4	2.7_4	3.3_8	74.3	79.4	0.74
VIII-D_4 + VIIIa-D_4	Br	OCH_3	CCl_4	4.5	14.0		2.8_6			4.1_6	3.5_0	16.7	15.4	−0.97
	OCH_3	Br		4.7_5							4.2_2	20		−0.82
IX-D_4	Br	Br	CCl_4	3.5	15.5		2.9_7			4.5_5	4.4_4	10	(0)	

[a] Assuming J_{aa} 11, J_{ae} 4.2 and J_{ee} 3.2 Hz. [b] The same values have been found for VI-D_4; [c] ± 0.2 Hz.

TABLE 2

NMR DATA OF *trans*-1,2-DICYANO SUBSTITUTED COMPOUNDS



H (XVIII) K

Compound	X	Y	Solvent	J_{45} (± 0.1 Hz)	J_{12} (± 0.1 Hz)	Chemical shifts δ (± 0.005 ppm)				H (%)[a]		ΔG (kcal/mol)
						H_1[b]	H_2[b]	H_4	H_5	from J_{45}	from J_{45}	
XI-D_7	HgCl	OCD_3	CD_3NO_2	5.6	8.6	3.2_9	3.1_6	3.0	3.7_6	69.2	69.2	0.48
			C_5D_5N	5.3[c]	*d*	*d*	*d*	2.9_4	3.6_3		73.0	0.59
			CD_3CN	5.2[c]	9.0[c]	3.2_6	3.1_2	2.8_2	3.7_2	74.3	74.3	0.63
XIII-D_7 (from XI-D_7)	Br	OCD_3	$CHCl_3$	3.3	11.4	3.0_4	3.2	4.2_5	3.5	(100)		
XIII-D_4 (from X-D_4)	Br	OCH_3	$CHCl_3$	3.4	11.5	3.0	3.2	4.2_8	3.5_6	(100)		
XIV-D_4	Br	Br	CD_3CN			3.3_6	3.3_6	4.5_6	4.5_6			

[a] Assuming J_{aa} 11; J_{ee} 3.2 Hz. [b] Assignment is based on the electronegativity of the substituents assuming $E_{Br} > E_{OCH_3} > E_{HgX}$. [c] ± 0.2 Hz. [d] Unresolved singlet at δ 3.34 ppm.

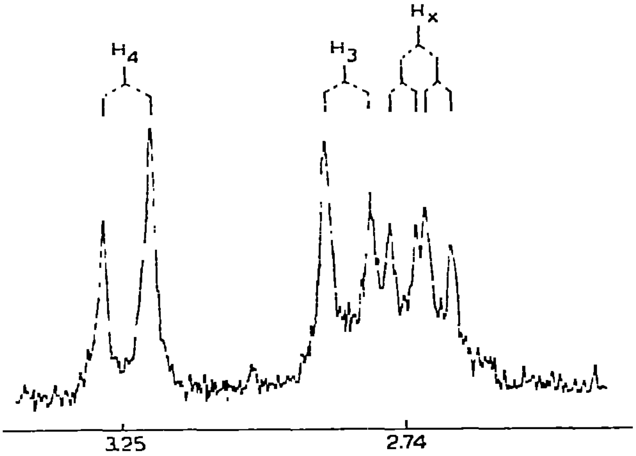


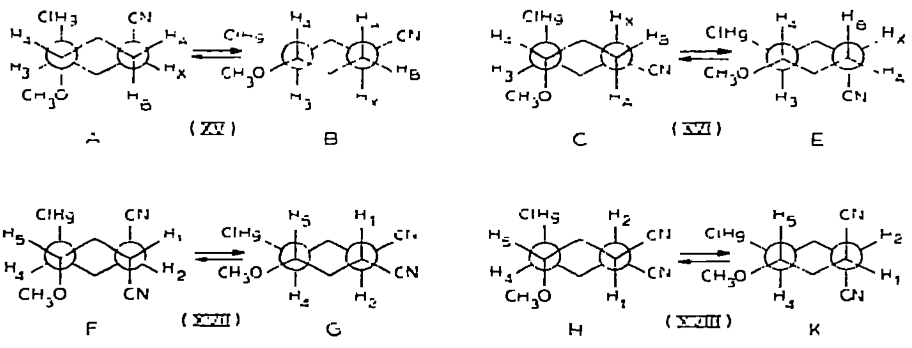
Fig. 1. The low-field part of the NMR spectrum of VI at 100 MHz.

conformation of type XVI-C must be assigned to the methoxybromines VIII and VIIIa, both of which have the same configuration and (b) methoxybromine XIII has conformation of the type XVIII-H.

We also achieved reductive demercuration of compounds VI and XI expecting to obtain the methoxynitriles VII and XII, but the NMR spectra of VII and VII-D_4 showed a mixture of products. GLC analysis also showed that the reduction product from VI contains three components (57/29/14). We then carried out a thorough investigation of the NMR spectra of methoxymercurial VI. As can be seen from Table 1 and Fig. 1 the NMR spectrum of VI-D_7 contains a set of signals due to a single isomer, the presence of the other isomer (10-15%) not being detected because of the very limited solubility of compound VI. However, the CH_3 group appears as a sharp singlet in the NMR spectrum of VI-D_4, indicating the presence of a single addition product. We must emphasise that this NMR investigation was carried out on an uncrystallized sample of VI-D_4 to avoid loss of the minor isomer during purification. The bromination and methoxybromination data therefore suggest that methoxymercurial VI is a mixture of isomers VI and VIa, while, on the other hand the NMR data strongly indicate that methoxymercuration occurs regioselectively to give a single isomer VI. This discrepancy however, can have no influence on the conclusions drawn regarding the stereochemistry. Indeed the configurations of methoxymercurials VI and XI were assigned using J_{vic} values (see below), and if the methoxymercurial VI were a mixture of isomers, the exact coincidence of their NMR spectra suggests that they have identical configurations. Thus we assume a single structure, VI, for the methoxymercurial obtained from the nitrile II; NMR data are more reliable since bromination of the mercurials VI and XI proceeds in a complicated manner which is shown by the formation of the dibromide XIV.

The most reliable determination of configurations was also made by using the NMR spectra (Tables 1 and 2). It is difficult to choose between configurations XV and XVI for the methoxymercurial VI and between configurations XVII and XVIII for compound XI (Scheme 3). Possible conformations for the various con-

SCHEME 3



figurations are also shown in Scheme 3. The choice between configurations XVII and XVIII is based on the following arguments. For compound XI to have the configuration XVII the coupling constants J_{12} and J_{45} (1), must be nearly equal irrespective of the position of the conformation equilibrium* and (2), must undergo symbathic changes in unison with the change of position of the conformational equilibrium F $\rightleftharpoons$ G; both J_{12} and J_{45} must increase with shift of the equilibrium towards conformation G and decrease with a shift towards F. On the other hand, for compound XI to have the configuraion XVIII J_{12} and J_{45} need not be equal. They are only equal at approximately equal concentrations of each of conformers H and K, and the changes of these coupling constants must be dissimilar, i.e. J_{12} must decrease and J_{45} must increase on going from H to K and vice versa. The same should also hold for the methoxymercurial VI. In this case the NMR spectrum must be of the ABX type, with all conformations including an additional and approximately equal contribution from either J_{ae} or J_{ea}.

As can be seen from Tables 1 and 2 the coupling constants discussed are clearly unequal, furthermore, they show slight, but clearly antibathic changes in different solvents. In the light of the above it is obvious that methoxymercurials VI and XI have the configurations XVI and XVIII respectively.

This conclusion becomes unequivocal after quantitative treatment of the conformational equilibrium of the methoxymercurials using the Eliel equation (see e.g. refs. 6, 26 and 27). The limiting or "standard" coupling constants of the respective conformations can be taken from the model compounds: for cyclohexane itself J_{aa} 13.12, J_{ae} 3.73, and J_{ee} 2.96 Hz [28]. However, examples where J_{aa} is about 13 Hz are extremely rare; usually it is about 11 Hz [26-28]. The close structural analogy of all compounds investigated permits us to treat the methoxybromines VIII and XIII and the diester V (J_{aa} 10.5, J_{ee} 3.9 Hz in CH_3CN [20]) as model compounds. J_{ee} values for these compounds are about 3.3 to 3.5 Hz and the slightly lower value of 3.2 Hz may thus be assumed as a "standard" value for J_{ee}. J_{ae} can be estimated as 4.3-4.5 Hz from J_{AX} + J_{BX} in the NMR spectra of IX (assuming J_{aa} is 11 Hz) and VI (taking J_{AX} into account). This value is probably slightly overestimated and it is reasonable to take 4.2 Hz as a "standard" J_{ae} value. Thus, analysis of the NMR spectra of the model compounds gives the

---

* A slight difference of coupling constants may be due to the difference in electronegativities of the substituents.

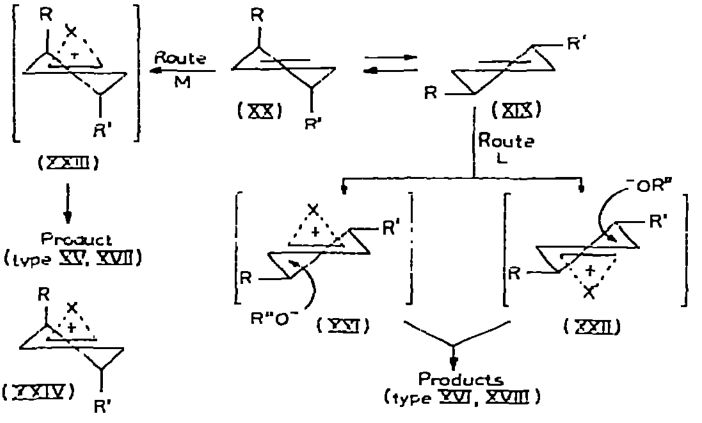
following "standard" coupling constants: J_{aa} 11, J_{ae} 4.2 and J_{ee} 3.2 Hz. These are in good agreement with the literature data [26-28]. Tables 1 and 2 list the conformational equilibrium positions calculated using these standard constants*.

All the results discussed permit us to conclude that the methoxymercurical VI has configuration of the type XVI with E as the predominant conformer; and methoxymercurial XI has configuration of the type XVIII but with the conformer H predominant.

Discussion

Methoxymercuration of substituted Δ^4-cyclohexenes are shown in Scheme 4

SCHEME 4



assuming *trans*-diaxial addition [3, 4, 7] and *quasi*-chair conformation of the transition states [29-31]. The approach of the reagent X^+ toward the reaction center involves generation of an interaction between the incoming X^+ and the remote functional group R. If this interaction is repulsive in nature the intermediates (or transition states) XXI and XXII would be more favourable than XXIV. In this case the reaction would proceed via equatorial conformation XIX (route L, Scheme 4). This case is generally referred to as involving "steric approach control" [32]. However, if this interaction were attractive in nature, the reaction would proceed via axial conformation XX and an intermediate XXIII (route M). Thus the occurrence of the addition reaction with or without preliminary attractive coordination of the reagent with the substituent must lead to products of differing configurations. The configurations of methoxymercurials V (Scheme 1), VI and XI (Schemes 2 and 3) suggest that methoxymercuration of the diester IV and nitriles II and X proceeds via route L (Scheme 4) without coordination of theXHg with the —COOR or —CN groups.

---

* The data on the position of the conformational equilibrium of VI, VIII, XI and XIII are rather unexpected when the very small value of $-\Delta G_{CN}$ (0.2 kcal/mol) is taken into account. This allows the following assumption to be made. In poly-substituted cyclohexanes of the types investigated, $-\Delta G_{CN}$ increases sharply up to approximately 1 kcal/mol. This novel conformational effect will be discussed in another publication.

An important question may be posed: Is this conclusion general or could any other factors be responsible for the absence of "the specific directing effect" in the reactions investigated? For example, the unfavourable position of the conformational equilibrium XIX ⇌ XX may be such a factor. Indeed the ratio of the reaction products via routes L and M may be found by using the following equation:

$$P_L/P_M = k_L \cdot K_{eq}/k_M$$

The influence of K_{eq} may be important if the conformational equilibium is stongly shifted (usually towards XIX [26]). In particular, one may expect strong predominance of the diequatorial conformation XIX for the diester IV [26, 33, 34], this factor is, however, unimportant for the nitriles II and X. Depending on the solvent, ΔG_{CN} for nitrile II lies between —0.1 and 0 kcal/mol [25, 26] and thus the energy difference of conformations XIX and XX is negligible. An increased proportion of the diaxial conformer has also been found for the dinitrile X (about 60% in $CDCl_3$ [27]). Thus nitriles II and X would be excellent model compounds with a minimum of conformational hindrance for route M; nevertheless the reaction proceeds via route L.

We believe that route M is impossible for the usual substituents such as OR. COOR and CN. Probably route M could only be followed in rare cases where substituents can generate a normal bond with the reagent as, for example, in —O—HgX or —COO—HgX. However, in the light of the results discussed in this article and the findings on the stereochemistry of oxymercuration of other cyclohexenes [15-18] and norbornenes [13, 19] it seems that strictly speaking there is no proven example of a change in the stereochemistry of the oxymercuration due to preliminary coordination with the substituent group. Thus, the concept of "specific directing effect" in the methoxymercuration reaction must be discounted or at least restricted to special cases.

Experimental

^{1}H NMR spectra were recorded on a Varian-XL-100 spectrometer. Deuterium decoupling was used in some experiments.

2,2,5,5-D$_4$-1-Cyano-3-cyclohexene (II-D$_4$)

A mixture of acrylnitrile (2.12 g, 0.04 mol), 1,1,4,4-D$_4$-butadiene (2.6 g, 0.05 mol), hydroquinone (20 mg) and toluene (6 ml) was heated at 130° during 12 h in a sealed tube and then distilled in vacuo. The nitrile II-D$_4$ was obtained in 56% yield as a liquid, b.p. 62°/8 mmHg, n_D^{20} 1.4730 (lit. [35] II: b.p. 83°/20 mmHg, n_D^{20} 1.4770).

3,3,6,6-D$_4$-trans-1,2-Dicyano-4-cyclohexene (X-D$_4$)

A mixture of fumarodinitrile (2.8 g, 0.04 mol), 1,1,4,4-D$_4$-butadiene (4 g, 0.07 mol), hydroquinone (20 mg) and toluene (10 mol) was heated at 110° during 24 h in a sealed tube, cooled and the precipitate collected. Recrystallization from EtOH yielded 3.9 g (89%) of X-D$_4$, m.p. 123-124° (lit. [36] X: m.p. 124-125°).

Methoxymercuration of II

Mercuric acetate (2.8 g, 0.01 mol) was added to a stirred solution of II (1 g, 0.01 mol) in MeOH (30 ml). The mixture was stirred at 60° until a test portion failed to give a precipitate of mercuric oxide on treatment with dilute aqueous sodium hydroxide (4-5 h). It was then filtered and about two-thirds of the MeOH was removed. The residue was treated with sodium chloride (0.53 g) in water. The precipitated oil crystallized during the azeotropic removal of water with benzene in vacuo. Methoxymercurial VI (2.5 g) had m.p. 141-143° (from acetone/methanol, 1/2) (lit. [10] m.p. 125-129°).

Methoxymercurials VI-D_4 (m.p. 146-148°) and VI-D_7 (m.p. 143-145°) were synthesized in an analogous manner. The mixed melting points of these mercurials showed no depression.

Methoxymercuration of X

Methoxymercurial XI (1.4 g, m.p. 190-191° from MeCN/MeOH, 1/1) was obtained analogously from dinitrile X (1 g, 0.007 mol) and mercuric acetate (1.8 g, 0.006 mol) in 30 ml of MeOH. (Found: C, 27.35; H, 2.84. $C_9H_{11}ClHgN_2O$ calcd.: C, 27.08; H, 2.76%.) The methoxymercurials XI-D_7 had m.p. 184—188°. A mixed melting point with another sample of XI showed no depression.

Methoxybromines VIII-VIIIa

(a). A solution of bromine (1.7 g, 0.01 mol) in 20 ml of dry pyridine was added dropwise to a solution of methoxymercurial VI (4 g, 0.01 mol) in 20 ml of pyridine. The mixture was stirred for 5 h and left standing overnight, the pyridine was removed in vacuo and the residue extracted several times with $CHCl_3$. The solvent was distilled off in vacuo and the resulting oil was chromatographed on alumina ($CHCl_3$/heptane, 1/1). The solvents were again removed and the residue was distilled in vacuo under nitrogen to give a mixture of VIII + VIIIa (1.2 g), b.p. 116-119°/1 mmHg, n_D^{24} 1.5024. (Found: C, 44.40; H, 5.65. $C_8H_{12}BrNO$ calcd.: C, 44.05; H, 5.55%.) A mixture of VIII-D_4 + VIIIa-D_4 had b.p. 110-112°/1 mmHg and n_D^{26} 1.5028.

(b) A solution of bromine (1.2 g, 0.008 mol) in 150 ml of MeOH was added dropwise to a stirred solution of II (or II-D_4) (0.8 g, 0.008 mol) in 500 ml of MeOH. The mixture was stirred for 2 h and left standing overnight. Sodium carbonate (0.4 g) was added and the solvent removed in vacuo. The residue was extracted with ether, after which evaporation of the dry extract and distillation under nitrogen gave 1 g (62%) of methoxybromination products.

Methoxybromine XIII

(a). The procedure used was similar to that for the bromination of VI with the exception that purification was accomplished by chromatography on alumina ($CHCl_3$). Methoxybromine XIII (1 g, 56%; m.p. 142-144° from MeOH) was obtained from 3 g (0.007 mol) of XI in 20 ml of pyridine and 3 g (0.007 mol) of bromine in 15 ml of pyridine. Methoxybromines XIII-D_4 and XIII-D_7 had m.p.'s 142-144° and 136-138° respectively. (Found: C, 44.42; H, 4.85. $C_9H_{11}BrN_2O$ calcd.: C, 44.44; H, 4.54%.)

(b) By methoxybromination of X the procedure used was similar to that for the methoxybromination of II with the exception that the residue, after removal of MeOH, was dissolved in $CHCl_3$, and the resulting solid was recrystallized from MeOH.

Reduction of mercurials VI and XI

A solution of sodium borohydride (1.6 g, 0.04 mol) in 25 ml of 1 *M* aqueous KOH was added dropwise to a stirred solution of VI (16 g, 0.04 mol) in 100 ml of 1 *M* aqueous KOH. The mixture was stirred at 60° for 30 min, cooled, filtered and extracted thoroughly with CCl_4. The solvent was removed and the residue was distilled in vacuo under nitrogen to give VII and VIIa (4.6 g; b.p. 68–70°/ 1-1.5 mmHg; n_D^{20} 1.4570). (Found: C, 69.12; H, 9.49; N, 10.06. $C_8H_{13}NO$ calcd.: C, 69.06; H, 9.35; N, 10.08%.)

XII (0.8 g; b.p. 125-126°/1 mmHg; n_D^{20} 1.4780) was obtained in an analogous manner from 6.5 g of XI and 0.6 g of $NaBH_4$. (Found: C, 65.67; H, 7.70. $C_9H_{12}N_2O$ calcd.: C, 65.82; H, 7.36%.)

Dibromine IX

To a solution of 1.5 g (0.015 mol) of II-D_4 in 30 ml of $CHCl_3$ at 0° was added slowly 2.1 g (0.015 mol) of bromine. The solvent was removed and the residue was distilled in vacuo under nitrogen to give IX-D_4 (2.2 g, 60%; b.p. 126°/1 mmHg, m.p. 64-65°) (lit. [37] IX: b.p. 192°/4 mmHg, m.p. 63.5°).

Dibromine XIV

Bromine (1.2 g, 0.007 mol) was added dropwise at 0° to a solution of X (1.0 g, 0.007 mol) in 20 ml of $CHCl_3$. The usual workup gave 1.5 g (68%) of XIV, m.p. 222-223° (from MeOH/MeCN, 2/1). (Found: C, 32.84; H, 2.96. $C_8H_8Br_2N_2$ calcd.: C, 32.87; H, 2.76%.) The dibromine XIV-D_4 had m.p. 228-230°.

Acknowledgement

We are extremely grateful to Prof. P. von R. Schleyer for the gift of deuterated solvents for NMR.

References

1 A.K. Prokof'ev, V.I. Bregadze and O.Yu. Okhlobystin, Usp. Khim., 39 (1970) 412.
2 I.P. Beletskaya, K.P. Butin, A.N. Ryabtsev and O.A. Reutov, J. Organometal. Chem., 59 (1973) 1.
3 N.S. Zefirov, Usp. Khim., 34 (1965) 1272.
4 T. Traylor and A. Baker, J. Amer. Chem. Soc., 85 (1963) 2746.
5 R.F. Richter, J.C. Philips and R.D. Bach, Tetrahedron Lett., (1972) 4327.
6 N.S. Zefirov and N.M. Schechtman, Dokl. Akad. Nauk SSSR, 177 (1967) 842.
7 E.F. Kiefer, W.L. Waters and D.A. Carlson, J. Amer. Chem. Soc., 90 (1968) 5127.
8 S. Bentham, P. Chamberlain and G.H. Whitham, J. Chem. Soc., Chem. Commun., (1970) 1528.
9 W. Kitching, Organometal. Chem., Rev., 3 (1968) 61.
10 H.B. Nenbest and B. Nicholls, J. Chem. Soc., (1959) 227.
11 M. Abercrombie, A. Rodgman, K. Bharucha and G. Wright, Can. J. Chem., 37 (1959) 1328.
12 K. McNeely, A. Rodgman and G. Wright, J. Org. Chem., 20 (1955) 714.
13 A. Factor and T.G. Traylor, J. Org. Chem., 33 (1968) 2607.
14 J. Roussel, J.J. Pene, J.P. Lavat and A. Lattes, Tetrahedron, 28 (1972) 701.
15 M.T. Johnson and B. Rickborn, J. Org. Chem., 34 (1969) 2718.
16 S. Moon and B.H. Waxman, Chem. Commun., (1967) 1283.
17 S. Moon, C. Ganz and B.H. Waxman, Chem. Commun., (1969) 866.

18 J. Klein and R. Levene, Tetrahedron Lett., (1969) 4833.
19 F.R. Jensen and J.J. Miller, Tetrahedron Lett., (1966) 4861.
20 N.S. Zefirov, V.N. Chekulaeva, N.D. Antonova and L.G. Gurvich, Dokl. Akad. Nauk SSSR, 192 (1970) 567.
21 N.S. Zefirov and L.G. Gurvich, Zh. Org. Khim., 10 (1974) 127.
22 D.J. Pasto and J.A. Gontarz, J. Amer. Chem. Soc., 93 (1971) 6902, 6909.
23 J. Klein, E. Dunkleblum and D. Abrahami, J. Org. Chem., 32 (1967) 935.
24 Yu.K. Yur'ev, N.S. Zefirov and L.P. Prikazchikova, Zh. Obshch. Khim., 33 (1963) 1793.
25 F.R. Jensen and L.H. Gale, J. Amer. Chem. Soc., 82 (1960) 148.
26 N.S. Zefirov, V.N. Chekulaeva and A.I. Belozerov, Tetrahedron, 25 (1969) 1997.
27 J.P. Aycard, H. Bodot, R. Garnier, R. Lauricella and G. Pauzard, Org. Magn. Resonance, 2 (1970) 7.
28 E.W. Garbish and M.G. Griffiths, J. Amer. Chem. Soc., 90 (1968) 6543.
29 G. Bellucci, F. Marioni and A. Marsili, Tetraherdon, 28 (1972) 3393.
30 R.L. Barili, G. Bellucci, F. Marioni, I. Morelli and V. Scartoni, J. Org. Chem., 37 (1972) 4353.
31 P.L. Barili, G. Bellucci, G. Berti, F. Marioni, A. Marsili and I. Morelli, Chem. Commun., (1970) 1437.
32 W.G. Dauben, G.J. Fonken and D.S. Noyce, J. Amer. Chem. Soc., 78 (1956) 2579.
33 N.S. Zefirov, N.M. Viktorova, S.P. Knyasev and N.M. Sergeev, Tetrahedron Lett., (1972) 1091.
34 N.S. Zefirov, N.M. Sergeev, V.N. Chekulaeva and L.G. Gurvich, Dokl. Akad. Nauk SSSR, 190 (1970) 345.
35 A.A. Petrov and N.P. Sopov, Zh. Obshch. Khim., 17 (1947) 2228.
36 V.G. Yashunski, A.P. Terent'ev and Ya.G. Nechlin, Zh. Obshch. Khim., 26 (1956) 723.
37 A.P. Terent'ev, A.N. Kost and S.M. Gurvich, Vestnik Moscow Univ., 6 (1951) 79.