Journal of Organometallic Chemistry, 150 (1978) 7—20

MERCURATION OF SOME STYRENES AND PHENYLCYCLOPROPANES. THE EFFECT OF THE AROMATIC NITRO GROUP ON REDUCTIVE DEMERCURATION WITH SODIUM BOROHYDRIDE

Yu.S. SHABAROV *, S.S. MOCHALOV, T.S. ORETSKAYA and V.V. KARPOVA

Department of Chemistry, M.V. Lomonosov Moscow State University, Moscow V-234 (U.S.S.R.)

(Received November 11th, 1977)

Summary

Mercuric acetate reacts with *o*- and *p*-nitrostyrenes and with nitrophenylcyclopropanes in methanol or glacial acetic acid to give β- and γ-mercurated nitroderivatives, respectively. In contrast to the nitrostyrenes, mercuration of the corresponding nitrophenylcyclopropanes only occurs in the presence of perchloric acid as catalyst. 2,4-Dinitrophenylcyclopropane does not react with mercuric acetate even under the catalysis conditions.

Aromatic nitro groups decelerate reductive demercuration of γ-mercurated alcohols and their derivatives with sodium borohydride to the extent that other fragments of the molecule may undergo reduction while the HgX function remains intact. This result may be explained by intermolecular coordination of the nitro group to the mercury atom, which reduces effective positive charge on the metal and hinders the attack by the reducing reagent.

Introduction

Phenylcyclopropane and its derivatives containing electron releasing substituents are known to undergo trimethylene ring opening under the action of mercuric acetate to give mercurated alcohols or their esters [1—3]. Electron withdrawing substituents in the phenyl nucleus decelerate the reaction, often to the extent that the corresponding adducts cannot be obtained even under reflux conditions [4].

In di- and polyphenylcyclopropanes, both electronic and steric factors greatly increase stability of the three-membered ring toward mercuric acetate, and the reaction goes predominantly in another direction, viz mercuration of the benzene nucleus [5—7].

On the other hand, *o*- and *p*-nitrophenylcyclopropanes, which are stable toward mercuration under the commonly used conditions, undergo cyclopro-

pane ring opening under the action of strong electrophiles such as concentrated sulphuric acid [8—10].

It is therefore reasonable to expect that increase in electrophilic power of the mercurating reagent * would favour mercuration of phenylcyclopropanes containing electron withdrawing substituents in the benzene nucleus.

TABLE 1

CONSTANTS, ANALYSES AND IR SPECTRA

Compound	M.p. (°C)	Analysis: found (calcd.)				IR spectra ν (cm⁻¹)
		C	H	N	Hg	
VI	105	27.62(27.91)	2.81(2.79)		45.25(45.63)	
VII	97	28.13(27.91)	2.91(2.79)		45.40(45.63)	
VIII	54—55	33.91(33.68)	3.61(3.50)		46.94(47.01)	1690(C=O)
IX	76	33.06(33.05)	3.80(3.81)		42.65(42.54)	
X	129	28.82(28.83)	2.64(2.62)		43.57(43.78)	1725(C=O)
XI	117	28.81(28.83)	2.62(2.62)		43.63(43.78)	1720(C=O)
XII	134	33.40(33.60)	3.53(3.60)		39.87(40.16)	
XIII	91(1) [a]	44.14(42.78)	4.43(4.38)	5.16(5.11)		
XIV	27	43.95(43.78)	4.55(4.38)	5.19(5.11)		
XV	[b]	49.34(49.36)	5.81(5.61)	4.70(4.43)		
XVI	26	44.03(43.71)	3.98(3.97)	4.79(4.64)		
XVII	35	44.08(43.71)	3.94(3.97)	4.85(4.64)		
XVIII	[b]	48.61(48.83)	5.21(5.23)	4.05(4.07)		1748(C=O)
XX	[b]	33.12(33.19)	3.29(3.40)		41.98(42.72)	
XXI	[b]	49.79(49.68)	5.07(5.09)	4.41(4.45)		
XXII	[b]	33.58(33.73)	3.15(3.21)		39.89(40.24)	
XXIII	[b]	48.86(49.12)	4.60(4.68)	4.08(4.09)		
XXIV	86—89 (dec.)	49.50(49.68)	5.16(5.09)	4.56(4.46)		
XXV	[b]	52.30(52.34)	5.34(5.36)	4.67(4.69)		
XXVIII	94	25.92(25.93)	2.39(2.40)		48.42(48.26)	
XXIX	108.5	26.04(25.93)	2.58(2.40)		48.07(48.26)	
XXXVI	118(10)	61.29(61.54)	6.59(6.66)	7.21(7.17)		
XXXVII	121(10)	61.34(61.54)	6.49(6.66)	7.32(7.17)		
XXXVIII	[b]	65.59(65.82)	7.99(8.01)	6.14(5.91)		
XXXIX	[b]	66.38(66.38)	7.20(7.23)	6.12(5.96)		
XL	82	25.87(25.96)	2.35(2.40)		48.29(48.26)	3250(OH)
XLI	84	25.89(25.96)	2.31(2.40)		48.34(48.26)	3250(OH)
XLII	[b]	31.28(31.44)	3.52(3.49)		43.71(43.84)	3245(OH)
XLIII	[b]	31.85(31.57)	3.10(3.07)		44.19(44.03)	3250(OH)
XLIV [c]	76	37.04(37.04)	3.82(3.76)		44.22(44.32)	1725(C=O)
XLV [c]	135(20)	77.10(77.04)	8.41(8.26)			1745(C=O)
XLVI	[b]	34.91(35.03)	3.72(3.64)		48.59(48.85)	3250(OH)
XLVII		75.12(75.00)	8.40(8.33)			1690(C=O)
XLVIII	[b]	48.51(49.40)	5.12(5.14)		34.18(34.48)	1690(C=O)
XLIX [b]	[b]	33.75(33.53)	3.89(3.96)		46.53(46.80)	3450(OH)
L	[b]	48.91(49.06)	5.82(5.79)		34.02(34.24)	3450(OH)

[a] Boiling points under vacuum are given. [b] The compounds represent viscous oils. [c] Compounds XLIV and XLV were prepared according to the known procedures [3].

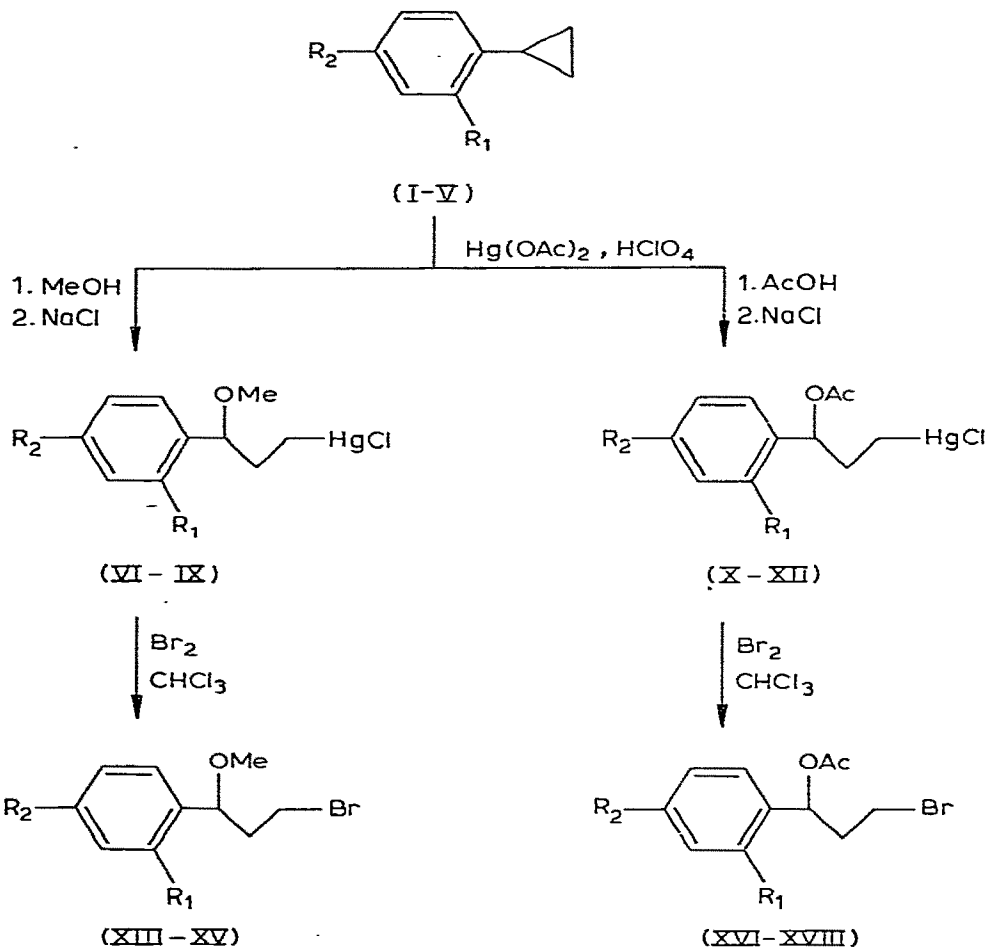
* Thus, the rate of mercuration of the aromatic nucleus of substituted benzenes increases considerably in the presence of perchloric acid as catalyst [11—13].

Discussion

Mercuration

The present paper describes the behaviour of nitro- and *p*-acetyl-phenylcyclopropanes, and *o*- and *p*-nitrostyrenes in reactions with mercuric acetate under various conditions. Constants, analytical and IR spectral data for the com-

SCHEME 1



$R_1 = NO_2$, $R_2 = H$ (I, VI, X, XIII, XVI); $R_1 = H$, $R_2 = NO_2$ (II, VII, XI, XIV, XVII); $R_1 = H$, $R_2 = COCH_3$ (III, VIII); $R_1 = NO_2$, $R_2 = i\text{-}C_3H_7$ (V, IX, XII, XV, XVIII); $R_1 = R_2 = NO_2$ (IV).

pounds studied are given in Table 1. The mercuration of phenylcyclopropanes containing only one electron-withdrawing substituent in the benzene ring (I—III) may be carried out in methanol as well as glacial acetic acid in the presence of catalytic amounts of perchloric acid. The reaction even goes at room

TABLE 2

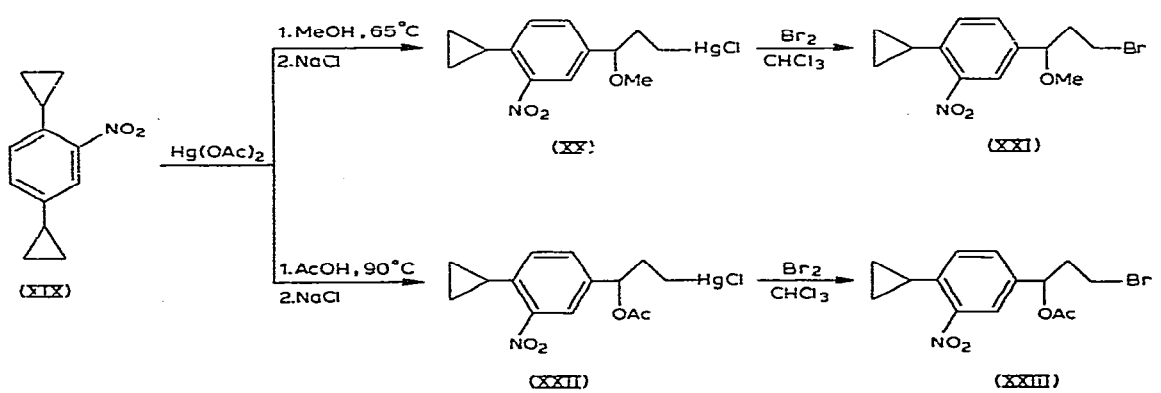
MERCURATION CONDITIONS AND PRODUCT YIELDS

Compound	Solvent	Reaction temperature (°C)	Reaction product	Yield [a] (%)	Recovery of the initial compound
I [b]	CH_3OH	65	VI	70	57
I [b]	CH_3COOH	20	X	63	31
I [b]	CH_3COOH	90	X	61	18
II [b]	CH_3OH	65	VII	72	22
II [b]	CH_3COOH	20	XI	83	40
II [b]	CH_3COOH	90	XI	90	19.5
III [b]	CH_3OH	65	VIII	92	40
V [b]	CH_3OH	65	IX	91	30
V [b]	CH_3COOH	20	XII	86	43.3
V [b]	CH_3COOH	90	XII	85.5	23
XIX	CH_3OH	65	XX	93.7	65
XIX [b]	CH_3OH	65	XX	96	10
XIX	CH_3COOH	95	XXII	71	25
XIX [b]	CH_3COOH	95	XXII	83.3	
XXIV	CH_3OH	95	XXVI	92	
XXIV	CH_3COOH	20			95.5
XXV	CH_3OH	65	XXVII	94	
XXV	CH_3COOH	20			97

[a] The yields are based on reacted initial compound. [b] Mercuration in the presence of perchloric acid as catalyst.

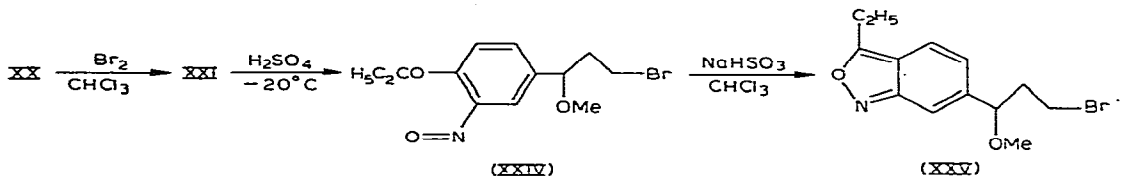
temperature to give the corresponding derivatives of γ-mercurated alcohols (VI—VIII, X, XI), however, in the yields not exceeding 20%. Increase of the reaction temperature up to 65°C in methanol and up to 90°C in acetic acid does not change the reaction direction but increases the extents of conversion (see Table 2).

The introduction of the iso-propyl group in the position *para* to the smaller cycle in compound I has no marked effect on the reaction rate (see Scheme 1) and Table 2), whereas the structure analogue of 2-nitro-4-isopropylphenylcyclopropane (V), 2-nitro-1,4-dicyclopropylbenzene (XIX), reacts with mercuric acetate much more readily and even in the absence of the catalyst ($HClO_4$). In the latter case the reaction requires heating however; the introduction of the catalyst does not change the reaction direction but considerably accelerates the process.



(XIX) (XX) (XXI) (XXII) (XXIII)

It is important that 2-nitro-1,4-dicyclopropylbenzene (XIX) reacts with mercuric acetate at the cyclopropane ring furthest from the nitro group. This follows from spectroscopic evidence and from the fact that the mercuration product, 3-(2-nitro-4-cyclopropylphenyl)-3-methoxy-1-chloromercuripropane (XX), may be converted into the corresponding anthranil (XXV).



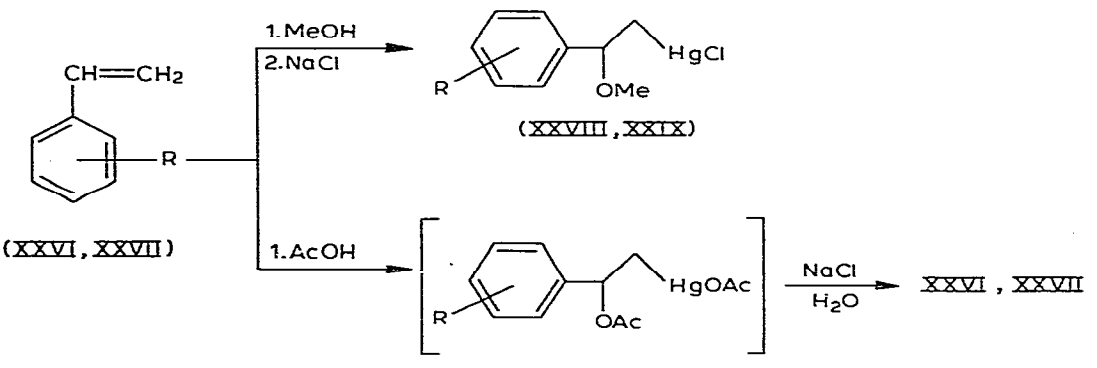
(XXIV) (XXV)

It thus appears that the *o*-nitro substituent which causes opening of the adjacent three-membered cycle in isomerization of compound XIX in the presence of sulphuric acid [9] has no such action in the mercuration reaction. The direction of the latter well fits the data on the smaller cycle reactivity in phenylcyclopropanes as depending on the nature and position of substituents in the aromatic nucleus [3,14]: the ring opening occurs with the three-membered cycle that is less subject to the electron withdrawing action by the nitro group.

This result cannot however be explained solely in terms of polar interactions; other factors may be the nature of the electrophile (its reactivity and bulk) and the conditions.

2,4-Dinitrophenylcyclopropane (IV) remains unreacted under the conditions studied: the presence of two strong electron acceptors in the phenyl nucleus blocks mercuration of the three-membered cycle with mercuric acetate, even under heating and in the presence of perchloric acid.

o- and *p*-nitrostyrenes (XXVI, XXVII) are far more reactive toward mercuric acetate than *o*- and *p*-nitrophenylcyclopropanes (I, II): the addition of mercuric acetate at the double bond practically goes under the conditions of mercuration of unsubstituted phenylcyclopropane [14]. Mercuration of nitrostyrenes in methanol leads to stable products (XXVIII, XXIX) that can be isolated from the reaction mixtures. On the contrary, the adducts formed in acetic acid undergo conversion to the initial nitrostyrenes during isolation.



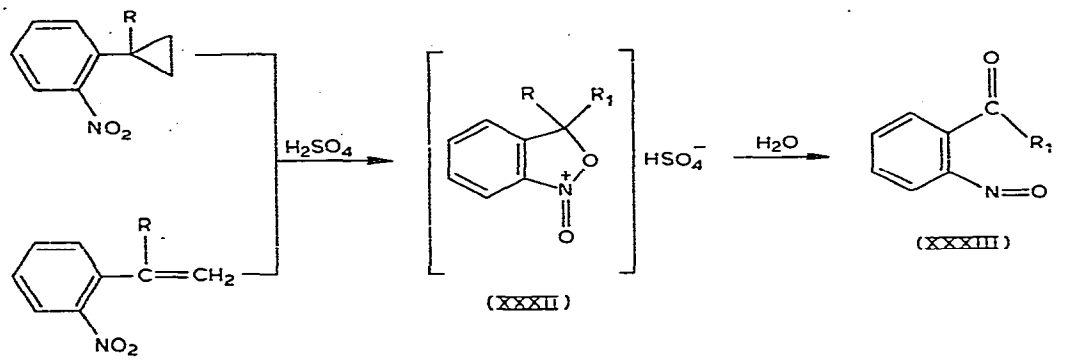
R = *o*-NO_2 (XXVI, XXVIII, XXX); R = *p*-NO_2 (XXVII, XXIX, XXXI)

The formation of adducts (XXX, XXXI) was proved by spectroscopic measurements: the proton NMR spectrum of the reaction mixture recorded in the 24 h after the beginning of the reaction in acitic acid revealed the presence of benzylic protons (t, 5.8 ppm) of β-mercurated acetates (XXX, XXXI), while the signals corresponding to the vinyl protons of the initial nitrostyrenes (XXVI, XXVII) were absent from the spectra. The absence of the UV maxima at 312 nm characteristic of *o*- and *p*-nitrostyrenes also showed that the initial compounds were fully consumed in the reaction with mercuric acetate.

It may well be that compounds XXX and XXXI undergo rapid deacetoxymercuration when reaction mixtures from mercuration in acetic acid are treated with solutions of sodium chloride, similar to what occurs with 2-hydroxymethylmercury chloride [15].

Nitroso organomercury compounds

The interaction of the cyclopropane ring in *o*-nitrophenylcyclopropanes and of the double bond in *o*-nitrostyrenes with strong protic acids leads to carbonium ions. In the absence of nucleophiles, these may undergo conversion to the more stable cyclic cations (XXXII) via intramolecular reaction at the nitro group [16]. These cations give nitrosoketones (XXXIII) [8] or form stable salts (oxaazoniolynes XXXII) [17] depending on whether there are mobile hydrogen atoms (R = H) or two alkyl radicals (R and R′ = Alk) in the molecule.



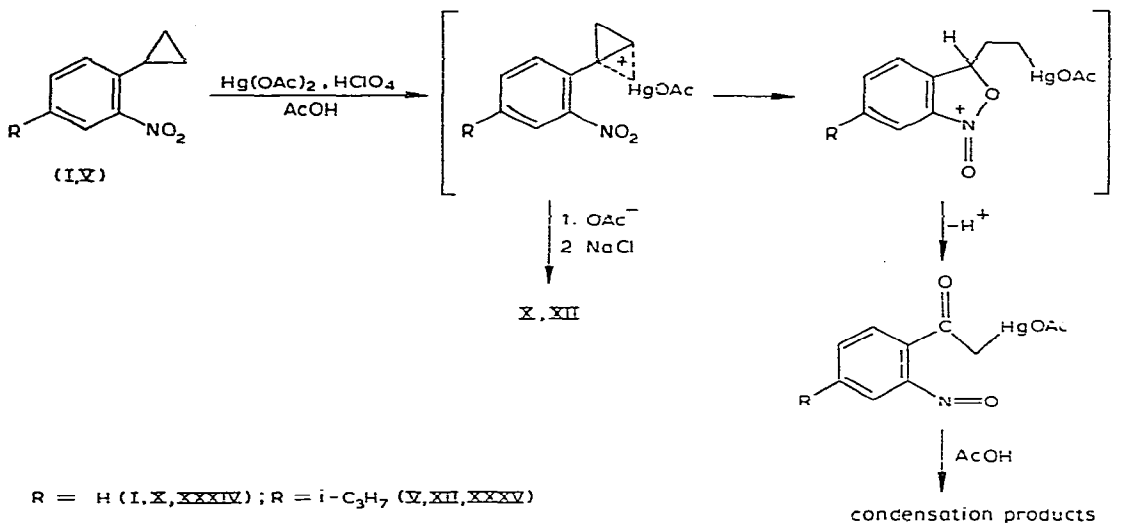
(XXXII) (XXXIII)

It is therefore natural to expect that so strong an electrophile as mercuric acetate would cause similar transformations in *o*-nitrophenylcyclopropanes and *o*-nitrostyrenes.

In fact, mercury-containing nitroso compounds (XXIV, XXXV) do occur in mercuration of 2-nitro-(I) and 2-nitro-4-isopropyl-(V) -phenylcyclopropanes in glacial acetic acid. This follows from the UV data on the reaction mixtures obtained at the initial stage of the process. Both solutions showed absorption maxima at about 740 nm (ϵ = 35) characteristic of aromatic nitroso compounds. All attempts at isolation of mercury-containing nitroso derivatives however proved a failure: it is likely that the compounds undergo further conversions under the action of the acid present in the reaction mixture to give complex product mixtures *. Thus, the interaction of *o*-nitrophenylcyclopropanes with mercuric

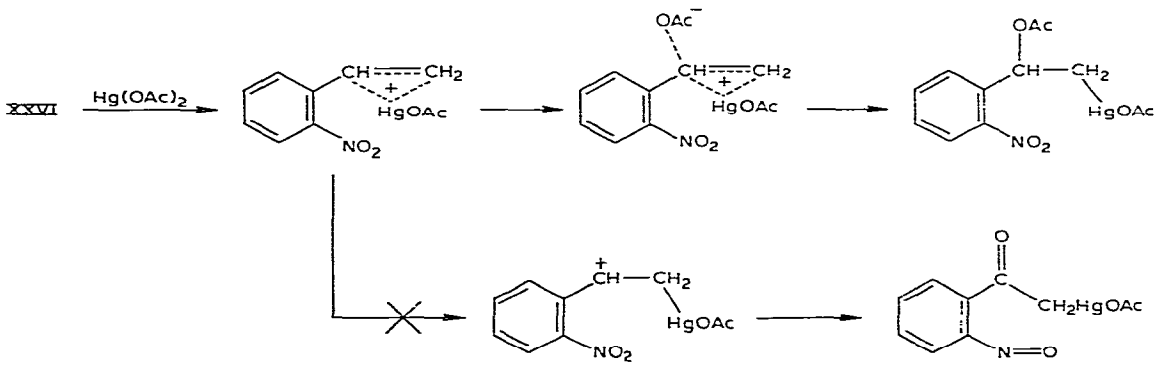
* It has been shown by special experiments that nitroso compounds of the type XXXIV and XXXV but containing no mercury give multicomponent mixtures in acetic acid solutions [18].

acetate seemingly proceeds by two paths:



Unlike with *o*-nitrophenylcyclopropanes (I, V), the reaction of *o*-nitrostyrene (XXVI) with mercuric acetate gives no nitroso compounds, though the initial compounds undergoes the usual rearrangement in the presence of sulphuric acid [8].

This result may be rationalized if one consideres that the addition of mercuric acetate at the *o*-nitrostyrene double bond occurs with participation of mercurinium ions [19]. It may well be that the benzyl carbon atom of the mercurinium ion undergoes the nucleophilic attack by the anion present in the reaction mixture prior to the formation of the open carbonium ion. The formation of the latter is prerequisite for the action of the nitro group as internal nucleophile followed by rearrangement to a nitroso compound.



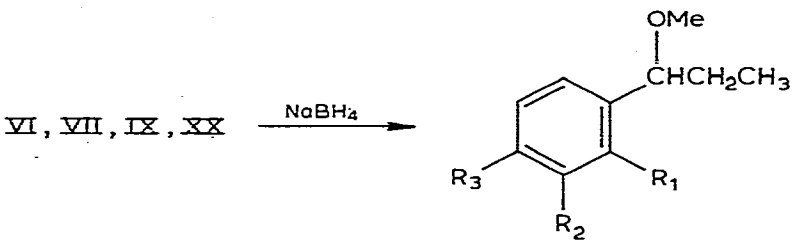
Similar reasons explain why nitroso compounds do not occur in reactions carried out in methanol, both with *o*-nitrostyrene (XXVI) and *o*-nitrophenylcyclopropanes (I, V). Methanol is the stronger nucleophile, which, we believe, is the determining factor, and the carbonium centre formed from the mercurinium ion reacts more readily with an external nucleophile (methanol) than it does with the internal one (the nitro function).

Reduction of nitroarylmercury chlorides with sodium borohydride

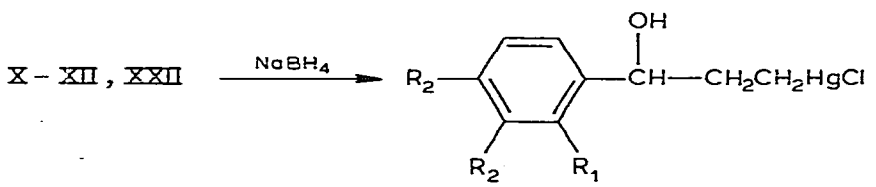
Reductive demercuration is widely used for synthetic purposes [20—22] and for structure assignments of organomercury compounds formed in mercuration reactions [3,23—25]. Most frequently, reduction is carried out with sodium borohydride. This reagent can be applied to eliminate the mercurated function even in the presence of other groupings that can undergo reduction [3,23,24,26].

The results obtained in this work show that the aromatic nitro group may suppress reactivity of mercury toward sodium borohydride to the extent that other fragments of the molecule undergo conversions under the action of this reagent while the mercurated function remains intact. In the absence of other reducible groupings, demercuration still occurs, though at greatly reduced rates

Thus, methoxy derivatives (VI, VII, IX, XX) containing no fragments liable to reduction other than the mercurated function undergo the usual demercuration under the action of various amounts of sodium borohydride (1 to 3 mol per mol of the mercury derivative), but at lower rates * than their structure analogues containing no nitro groups [3]. With the corresponding acetoxy derivatives (X—XII, XXII), the reduction of the acetoxy rather than mercury-containing function occurs to give mercurated nitroaromatic alcohols.



(XXXVI – XXXIX)



(XL – XLIII)

$R^1 = NO_2, R^2 = R^3 = H$ (VI, X, XXXVI, XL); $R^1 = R^2 = H, R^3 = NO_2$ (VII, XI, XXXVII, XLI); $R^1 = NO_2, R^2 = H, R^3 = i\text{-}C_3H_7$ (IX, XII, XXXVIII, XLII);
$R^1 = H, R^2 = NO_2, R^3 = cyclo\text{-}C_3H_5$ (XX, XXII, XXXIX, XLIII).

As the reduction of both ethers and esters derived from γ-mercurated alcohols containing no nitro groups always involves the Hg—C bond [23—26], the

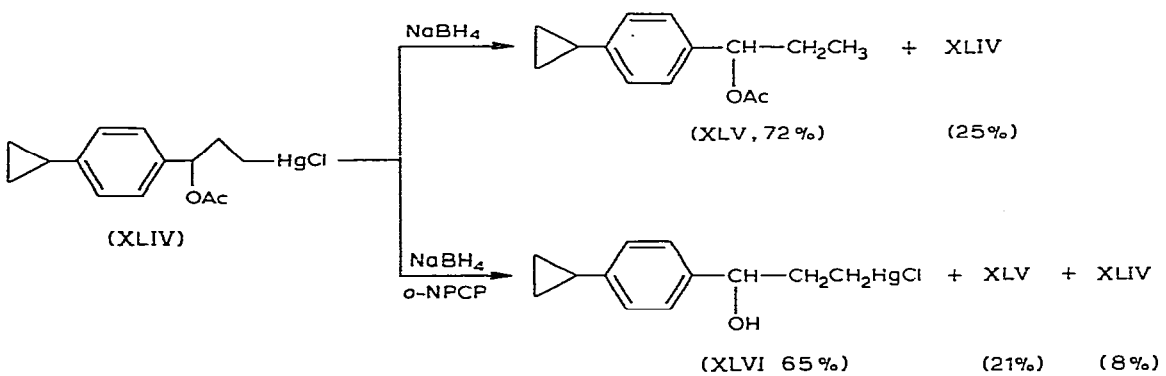
* Large proportions of the initial compounds (VI, VII, IX, XX) remained unreacted under the standard conditions (see Table 4).

results described above show that the nitro group affects either reducibility of the mercurated function or reactivity of sodium borohydride.

The latter explanation is unlikely, firstly because the nitro function is known to have no effect on the reducing power of sodium borohydride in its reactions with, say nitroarylketones [27], and secondly because the product yields from the reduction of ethers (VI, VII, IX, XX) as well as of acetoxyderivatives (X—XII, XXII) are almost independent of the reagent ratio.

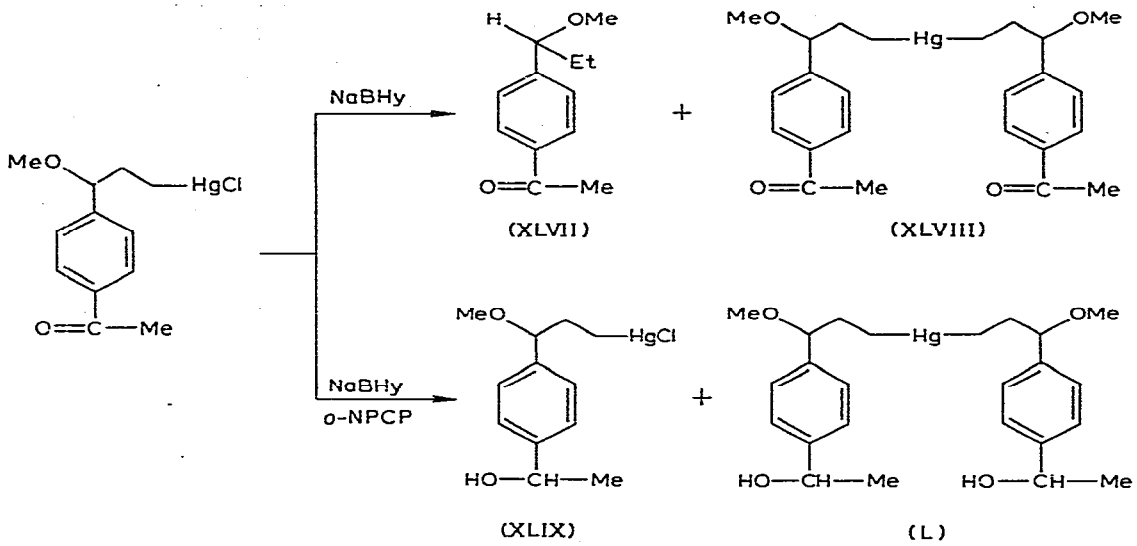
On the other hand, the reduction of organomercury compounds with sodium borohydride has been proven to proceed via hydride transfer from the reducing agent to the mercury atom as the first step [28,29]. Taking into consideration that, according to the literature data [30], the nitro group may form coordination bonds with mercury, a suggestion may be made that the effective positive charge on mercury in nitroaromatic derivatives of mercurated alcohols (X—XII, XIII) may be lowered by the coordination bonding to the extent that the hydride ion cannot interact with mercury or interacts only slowly under the conditions studied. There are grounds to believe that the coordination bonding is mainly of the intermolecular type *. Firstly, the reduction of *o*- and *p*-nitrophenylmercuric acetates (X, XI) to the corresponding hydroxymercury derivatives (XL, XLI) proceeds in the same yields. Secondly, the results obtained in the reduction of mercury derivatives containing no nitro groups in the presence and in the absence of nitroaromatic compounds support the suggestion of intermolecular bonding.

Thus, the interaction of 3-(4-cyclopropylphenyl)-3-acetoxy-1-chloromercuripropane (XLIV) with sodium borohydride leads to various products depending on the presence or absence of nitroaromatic compounds in the reaction mixture. In the absence of nitro compounds, acetoxymercury chloride (XLIV) gives the corresponding demercuration product (XLV) in a 72% yield (28% of the initial compound remains unreacted). With an equimolar mixture of compound XLIV and *o*-nitrophenylcyclopropane (*o*-NPCP), the yield of the demercuration product decreases drastically, and the formation of the corresponding carbinol (XLVI) becomes the predominant reaction direction.



* Such coordination bonds may also occur in methyl esters (XI, VII, IV, XX). Nevertheless, the reduction of the mercurated function occurs, though at a reduced rate, in these compounds, because the ether bond undergoes reduction with sodium borohydride under more forcing conditions than those used in this work.

The reduction of 3-(4-acetylphenyl)-3-methoxy-1-chloromercuripropane (VIII) with sodium borohydride in the presence and in the absence of aromatic nitro groups provides another example of the same kind. Under the conditions applied (methanol solution, and in the presence of *o*-nitrophenylcyclopropane), compound VIII remains completely unreacted. The reaction can only be carried out in ethanol *. In this case, the acetyl group of the aromatic nucleus undergoes reduction to yield mercury-containing carbinols (XLIX, L).



The ability of aromatic nitro groups to bar reduction of mercurated functions in organomercury compounds with sodium borohydride thus provides the possibility of selective reduction of functional groups in organomercury polyfunctional compounds.

Experimental

The proton NMR spectra were measured on a Varian T-60 spectrometer in $CDCl_3$ or CCl_4 using HMDS as external reference for organomercury compounds and as internal reference for all other compounds. The IR spectra of liquid films or Nujol mulls were obtained on a UR-10 instrument. The UV spectra were recorded on a Spekord spectrophotometer.

Except with organomercury compounds, GLC analyses were performed on a Tsvet-102 chromatograph, columns 3m × 4mm, 5% SE-30 on an N-AW-DMCS chromosorbent, gas carrier helium.

The initial *o*- and *p*-nitrostyrenes, nitroaryl- and *p*-acetylphenylcyclopropanes were prepared by the literature procedures: I, II [31], III [32], IV [10], V [33], XIX [9], XXVI [34,35], XXVII [34,36].

Mercuration of I—V, XIX, XXVI, XXVII (the standard procedure)

Mercury acetate (55 mmol) and, if necessary, 45% $HClO_4$ were added to a

* It should be mentioned that no reduction of acetophenone to the corresponding alcohol occurs under the action of sodium borohydride in a 3 : 1 methanol/ether mixture, while in ethanol the reaction proceeds in quantitative yield.

TABLE 3

BROMODEMERCURATION PRODUCT YIELDS

Compound	Reaction product	Yield [a] (%)	Recovery of the initial compound (%)
VI	XIII	75.5	20
VII	XIV	53	31
IX	XV	76	23
X	XVI	68	38
XI	XVII	65	17.5
XII	XVIII	56.6	21
XX	XXI	81.5	
XXII	XXIII	50.9	21.3

[a] The yields are based on reacted organomercury compounds.

solution of a nitrocompound (50 mmol) in 300 ml of a solvent. The mixture was stirred at the desired temperature for 50 h and poured into a 200 ml saturated solution of NaCl. The products were extracted with $CHCl_3$, neutralized by washing with NaCl solution, and dried over $MgSO_4$. The solvent was evaporated and the residue was separated on an Al_2O_3 column to give the unreacted initial compound (eluted with benzene) and an organomercury compound (eluted with chloroform). The results are given in Table 2.

Bromodemercuration of compounds VI, VII, IX, X—XIII, XX, XXII (the standard procedure)

A solution of Br_2 (26 mmol) in 10 ml $CHCl_3$ was added to a solution of an organomercury compound (25 mmol) in 30 ml dry $CHCl_3$ at 0°C. The mixture was kept for 48 h at that temperature and then poured into 100 ml saturated solution of $Na_2S_2O_3$. The organic layer was washed with water, dried over $MgSO_4$, and, after distilling off the solvent, separated on a column packed with Al_2O_3

TABLE 4

REDUCTION OF ORGANOMERCURY COMPOUNDS WITH SODIUM BOROHYDRIDE

Compound	Reaction product	Yield [a] (%)	Recovery of the initial compound (%)
VI	XXXVI	95	53
VII	XXXVII	97	49
VIII [b]			98
VIII	XLVII, XLVIII	45, 48	
VIII [b,c]	XLIX,	23, 65	20
IX	XXXVIII	80	40
X	XL	87	
XI	XLI	92	
XII	XLII	85.5	87.5
XX	XXXIX	94	38
XXII	XLIII	89	20
XLIV	XLV	72	25
XLIV	XLVI, XLV	65, 21	8

[a] The yields are based on reacted organomercury compounds. [b] The reaction was carried out in the presence of *o*-nitrophenylcyclopropane. [c] The reduction was carried out in ethanol.

TABLE 5

PROTON NMR SPECTRA

Compound	^{1}H chemical shift (δ (ppm))							
	Aromatic protons	$-\underline{CH}-CH_2-$	$-\underline{CH_2}-CH_2-$	$-CH_2-\underline{CH_2}$	$-CH_2-\underline{CH_3}$	$-OCH_3$	$-OCOCH_3$	$-OH$
VII	$H^{2,6}$ 7.2(d); $H^{3,5}$ 7.8(d)	4.0(1H,dd)	1.3—2.1(4H,m)			3.1(3H,s)		
VIII [a]	$H^{2,6}$ 7.3(d); $H^{3,5}$ 7.9(d)	4.1(1H,dd)	1.2—2.1(4H,m)			3.1(3H,s)		
XIII	7.2—8.0 (4H,m)	4.85(1H,dd)	2.0—2.5(2H,m)	3.2—3.8(2H,m)		3.1(3H,s)		
XIV	$H^{2,6}$ 7.3(d); $H^{3,5}$ 7.9(d)	4.35(1H,dd)	2.0—2.5(2H,m)	3.2—3.8(2H,m)		3.1(3H,s)		
XV [b]	7.2—7.6 (8H,m)	4.7(1H,dd)	1.9—2.3(2H,m)	3.1—3.6(2H,m)		3.0(3H,s)		
XVI	7.0—7.9 (4H,m)	6.2(1H,dd)	2.0—2.4(2H,m)	3.0—3.5(2H,m)			2.0(3H,s)	
XVII	$H^{2,6}$ 7.3; $H^{3,5}$ 7.9(d)	5.9(1H,dd)	2.0—2.5(2H,m)	3.0—3.5(2H,m)			2.0(3H,s)	
XVIII [b]	7.51—7.82 (3H,m)	6.2(1H,dd)	2.4—2.7(2H,m)	3.5(2H,t)			2.1(3H,s)	
XX [c]	H^2 7.7(d); H^5 7.1(d); H^6 7.4(dd)	4.3(1H,dd)	1.7—2.5(4H,m)			3.4(3H,s)		
XXI [c]	H^2 8.0(d); H^5 7.4(d); H^6 7.7(dd)	4.7(1H,dd)	2.1—2.6(2H,m)	3.5—3.9(2H,m)		3.5(3H,s)		
XXII [a]	H^2 8.2(d); H^5 7.4(d); H^6 7.9(dd)	6.1(2H,dd)	2.02—3.01(4H,m)				2.02(3H,s)	
XXIII [c]	H^2 8.0(d); H^5 7.4(d); H^6 7.7(dd)	6.15(1H,dd)	2.35—2.91(2H,m)	3.46—3.82(2H,m)			2.35(3H,s)	
XXVI	7.3—8.1(4H,m)	5.6(1H,dd)		2.3—2.6(2H,m)		3.2(3H,s)		
XXVII	$H^{2,6}$ 7.4(d); $H^{3,5}$ 8.0(d)	4.2(1H,dd)		2.3—2.6(2H,m)		3.2(3H,s)		
XXXVI	7.1—7.8(4H,m)	4.5(1H,dd)	1.3—1.8(1H,m); 1.9—2.1(1H,m)		1.0(3H,s)	3.1(3H,s)		
XXXVII	$H^{2,6}$ 7.2(d); $H^{3,5}$ 7.7(d)	4.65(1H,dd)	1.3—1.8(1H,m); 1.9—2.1(1H,m)		1.0(3H,s)	3.1(3H,s)		
XXXVIII [b]	7.0—7.8 (3H,m)	4.4(1H,dd)	1.55—2.33(3H,m)		0.9—1.8	3.1(3H,s)		
XXXIX [b]	H^2 8.2(d); H^5 7.4(d); H^6 7.9(dd)	3.9(1H,dd)	1.33—1.70(2H,m)		(3H,m)	3.1(3H,s)		
XLII [b]	7.5—7.8 (3H,m)	5.0(1H,dd)	1.7—2.2(4H,m)		0.44—1.15			4.0(1H,s)
XLIII [c]	H^2 8.2(d); H^5 7.4(d); H^6 7.9(dd)	4.4(1H,dd)	1.23—2.32(4H,m)		(3H,m)			3.2(1H,s)
XLVI [c]	$H^{2,6}$ 6.8(d); $H^{3,5}$ 7.0(d)	4.3(1H,dd)	1.2—1.8(4H,m)					2.9(1H,s)
XLVII [a]	$H^{2,6}$ 7.3(d); $H^{3,5}$ 7.9(d)	4.0(1H,dd)	1.3—1.8(2H,m)		0.85(3H,t)	3.1(3H,s)		
XLVIII [a]	$H^{2,6}$ 7.3(d); $H^{3,5}$ 7.9(d)	4.0(1H,dd)	1.9—2.2(2H,m)	0.7—1.0(2H,m)		3.1(3H,s)		
XLIX [d]	$H^{2,6}$ 7.15(d); $H^{3,5}$ 7.37(d)	3.9(1H,t)	1.9—2.3(2H,m)	0.5—0.9(2H,m)		3.1(3H,s)		
L [d]	$H^{2,6}$ 7.15(d); $H^{3,5}$ 7.37(d)	4.0(1H,t)	1.9—2.3(2H,m)	0.5—0.9(2H,m)		3.1(3H,s)		

[a] The acetyl proton signals in VIII, XLVII and XLVIII, δ (ppm): 2.5(3H,s). [b] The isopropyl group proton signals in XV, XVIII, XXXVIII abd XLII, δ (ppm): 1.3(6H, d), 3.2(1H, septet). [c] The cyclopropane ring proton signals in compounds XX—XXIII, XXXIX and XLIII, δ (ppm): 2.62(1H,m), 1.2(4H,m); in compound XLVI: 1.8(1H,m), 1.0(4H,m). [d] The *p*-α-oxyethyl group proton signals in compounds XLIX and L, δ (ppm); 4.8($C\underline{H}-CH_3$, 1H, q), 2.6($O\underline{H}$,1H,s), 1.4($CH-C\underline{H_3}$,3H,d).

to give the bromodemercuration products (eluted with benzene) and the starting organomercury compound (eluted with chloroform). The results are given in Table 3.

Isomerization of 1-(3-nitro-4-cyclopropylphenyl)-1-methoxy-3-bromopropane (XXI) under the action of concentrated sulphuric acid

Compound XXI (0.9 g) was added to 2 ml concentrated sulphuric acid at —20°C, the mixture was stirred at that temperature for 20 min and then poured into a mixture of ice (30 g) and water (30 ml). The products were extracted with $HCCl_3$, the organic layer was washed with water until it showed a neutral reaction, dried with $MgSO_4$ to give, after evaporating the solvent, 1-(3-nitroso-4-propylphenyl)-1-methoxy-3-bromopropane (XXIV) (0.7 g, 77.8%). Compound XXIV, m.p. 86—89°C, decomposes (from ethanol); UV spectrum: λ_{max} 745 nm (C—N=O); IR spectrum, ν, cm^{-1}: 1720 (C=O); mass spectrum: M^+ 313—315.

Cyclization of 1-(3-nitroso-4-propylphenyl)-1-methoxy-3-bromopropane.

A 40% solution of $NaHSO_3$ (3 ml) was added to a solution of compound XXIV (0.7 g) in 10 ml $CHCl_3$. The mixture was allowed to stand for 10—15 min, water and chloroform were then distilled off under vacuum, the residue was extracted with ether and dried with $MgSO_4$. After removing the solvent, the product was chromatographed on an Al_2O_3 column (eluent $CHCl_3$) to give 3-ethyl-7-(1-methoxy-3-bromopropyl)-anthranil (XXV) (0.4 g, 57.6%). Compound XXV, PMR spectrum (ppm): 1.82 (t, 3H, CH_3), 2.31—2.70 (m, 2H, $\underline{CH_2}$—CH_2Br), 3.51 (q, 2H, $\underline{CH_2}$—CH_3), 3.62 (s, 3H, OCH_3), 3.48—4.11 (m, 2H, CH_2Br), 4.65 (dd, 1H, $\underline{CH}$—OCH_3), 7.21 (dd, H^5), 7.73 (d, H^7), 7.83 (d, H^4) — the anthranil nucleus protons; mass spectrum: M^+ 297—299 (7%), 190 (100%). Analysis found: C, 52.30; H, 5.34; Br, 26.68; N, 4.57. $C_{13}H_{16}NO_2Br$ calcd.: C, 52.34; H, 5.36; Br, 26.80; N, 4.69%.

Reduction of organomercury compounds VI, VII—XII, XX, XXII, XLIV (the standard procedure)

An organomercury compound (7 mmol) was added dropwise to a stirred solution of $NaBH_4$ (20 mmol) and, with compounds VIII and XLIV, *o*-nitrophenyl cyclopropane (7 mmol) in 20 ml 3 : 1 methanol/ether. The mixture was vigorously stirred and refluxed in a water bath for 3 h, then poured into 20 ml 2 *N* HCl and extracted with $CHCl_3$ (2 × 30 ml). The organic layer was neutralized by washing with water and dried over $MgSO_4$. After removing the solvent, the products were chromatographed on an Al_2O_3 column or Cl_2O_3 plates and eluted with benzene to obtain compounds XXXVI—XXXIX and XL—XLIII. Compounds XL and XLI were viscous oils which crystallized on the addition of small amounts of benzene. Reduction of compound VIII in ethanol yielded a mixture of compounds XLIX and L. The results are given in Table 4.

References

1 R.Ya. Levina, V.N. Kostin and V.A. Tartakovskii, Zh. Obshchei Khim., 27 (1957) 881.
2 R.Ya. Levina, V.N. Kostin and K.S. Shanazarov, Zh. Obshchei Khim., 29 (1959) 40.
3 Yu.S. Shabarov, S.G. Bandaev and L.D. Sychkova, Zh. Org. Khim., 11 (1975) 1218.
4 R.Ya. Levina, Yu.S. Shabarov and V.K. Potapov, Zh. Obshchei Khim., 29 (1959) 3233.

5 Yu.S. Shabarov, L.D. Sychkova and S.G. Bandaev, J. Organometal. Chem., 99 (1975) 213.
6 Yu.S. Shabarov, L.D. Sychkova, S.G. Bandaev and O.A. Subbotin, Zh. Obshchei Khim., 45 (1975) 2300.
7 S.G. Bandaev, L.D. Sychkova, E.M. Volkov and Yu.S. Shabarov, Zh. Org. Khim., 12 (1976) 1005.
8 Yu.S. Shabarov, S.S. Mochalov and I.P. Stepanova, Dokl. Akad. Nauk SSSR, 189 (1969) 1028.
9 Yu.S. Shabarov, S.S. Mochalov and S.A. Ermishkina, Dokl. Akad. Nauk SSSR, 211 (1973) 1135.
10 Yu.S. Shabarov, S.S. Mochalov and O.M. Khryashchevskaya, Zh. Org. Khim., 6 (1970) 2434.
11 A.J. Kreage, M. Dubeck and H.C. Brown, J. Org. Chem., 32 (1967) 745.
12 H.C. Brown and C.W. McGary, J. Amer. Chem. Soc., 77 (1955) 2303.
13 H.C. Brown and G. Goldman, J. Amer. Chem. Soc., 84 (1962) 1650.
14 V.K. Potapov, Yu.S. Shabarov and R.Ya. Levina,, Zh. Obshchei Khim., 34 (1964) 2512.
15 F.C. Whitmore, Chem. Eng. News, 26 (1948) 672.
16 Yu.S. Shabarov, S.S. Mochalov, I.P. Stepanova and G.V. Aleksakhin, Dokl. Akad. Nauk SSSR, 207 (1972) 621.
17 Yu.S. Shabarov, S.S. Mochalov and V.I. Daineko, Zh. Org. Khim., 12 (1976) 1293.
18 Yu.S. Shabarov, T.S. Oretskaya and S.S. Mochalov, Zh. Obshchei Khim., 34 (1974) 1138.
19 J. Halpern and H.B. Tinker, J. Amer. Chem. Soc., 89 (1967) 6427.
20 H.C. Brown and W.J. Hammer, J. Amer. Chem. Soc., 89 (1967) 1524.
21 H.C. Brown and P.J. Geoghegan, J. Org. Chem., 35 (1970) 1844.
22 H.C. Brown and M.N. Rei, J. Amer. Chem. Soc., 91 (1969) 5646.
23 V.I. Sokolov, N.B. Rodina and O.A. Reutov, Zh. Obshchei Khim., 36 (1966) 955.
24 Yu.S. Shabarov, S.G. Bandaev, E.M. Volkov and L.D. Sychkova, Zh. Org. Khim., 12 (1976) 812.
25 Yu.S. Shabarov, S.N. Burenko and T.S. Shul'man, Zh. Obshchei Khim., 42 (1972) 1310.
26 H.B. Henbest and B. Nicholls, J. Chem. Soc. (London), (1959) 227.
27 W.G. Brown, J. Amer. Chem. Soc., 71 (1949) 3245.
28 F.G. Bordwell and M.L. Douglass, J. Amer. Chem. Soc., 88 (1966) 993.
29 D.J. Pasto and J.A. Gontraz, J. Amer. Chem. Soc., 91 (1969) 719.
30 A.K. Porkof'ev, Uspekhi Khim., 45 (1976) 1028.
31 Yu.S. Shabarov, V.K. Potapov and R.Ya. Levina, Zh. Obshchei Khim., 34 (1964) 3127.
32 H. Hart and G. Levitt, J. Org, Chem., 24 (1959) 1261.
33 S.S. Mochalov, T.S. Oretskaya, V.V. Karpova and Yu.S. Shabarov, Zh. Org. Khim., 13 (1977) 836.
34 R.H. Wiley and N.R. Smith, J. Amer. Chem. Soc., 72 (1950) 5198.
35 W.J. Dale and C.W. Strobel, J. Amer. Chem. Soc., 76 (1954) 6172.
36 R.W. Strassburg, R.A. Gregg and C. Walling, J. Amer. Chem. Soc., 69 (1947) 2141.