Organometallic Chemistry

Mercuration of *B*(9)-substituted *meta*- and *ortho*-carboranes

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The mercuration of substituted $R_2C_2B_{10}H_9X$-9 type carboranes (where R = *m*-H, X = Cl, Br, I, Me; R = *o*-H, X = Me) was studied. It was found that mercury atoms add to the boron atoms in position 10 of *meta*-carboranes and in position 12 of *ortho*-carboranes, *i.e.*, to the boron atoms adjacent to the boron atom bonded to the X substituent. Symmetrical $(R_2C_2B_{10}H_8X)_2Hg$ type derivatives were obtained. It was shown that they can be used as starting materials in transmetallation reactions.

Key words: carboranes, mercury, mercuration.

In the chemistry of carboranes, the reactions of electrophilic substitution at the boron atoms have been studied in the most detail.[1,2] Among these reactions, the most promising for synthetic purposes is metallation (mercuration and thallation), which results in *B*(9)-metallated *o*- and *m*-carboranes, which are widely used as reagents for the synthesis of new *B*-substituted carboranes.[3] The effect of the substituents at the carbon atom of the caborane nucleus on mercuration has been studied qualitatively,[4] while the effect of these substituents on thallation has been studied quantitatively.[5] In the metallation of caboranes with substituents at the boron atom, only the mercuration of 9-phenyl-*o*- and -*m*-carboranes has been reported.[6] In this reaction, the replacement involves the phenyl fragment of the substrate, and the B—H bonds of the caborane nucleus remain untouched.

This work deals with the mercuration of *B*(9)-substituted *m*- and *o*-carboranes.

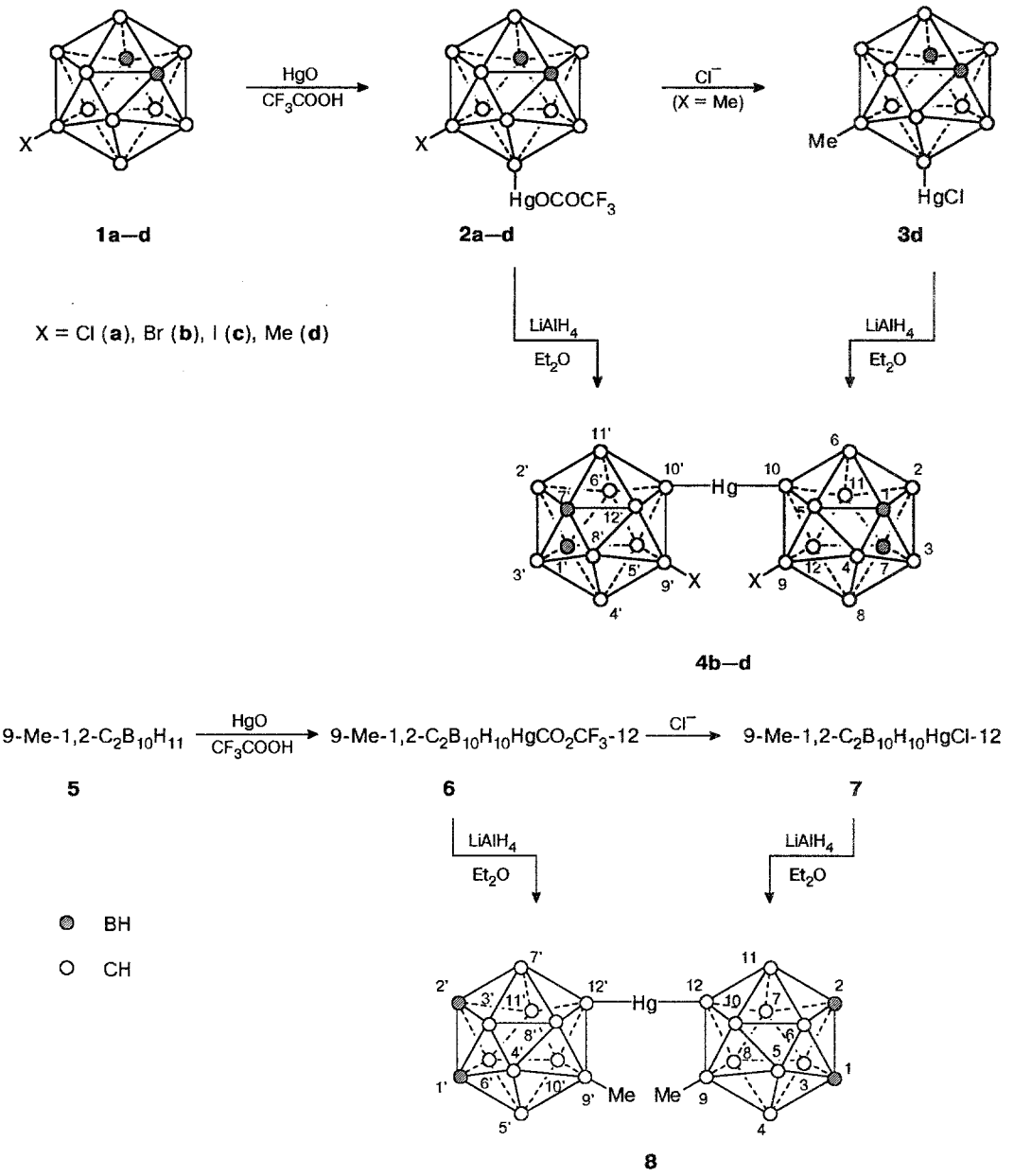
Results and Discussion

We found that 9-substituted *m*-carboranes enter the reaction of electrophilic mercuration when they are treated with mercury trifluoroacetate in trifluoroacetic acid (TFA). When the ratio between the reagents is 1 : 1, the reaction results in the products of the monomercuration of the caborane nucleus (Scheme 1).

It is known that halogenation[1,2] and mercuration[4] of carboranes occurs at the most nucleophilic 9 and 10 positions in *m*-carborane. In this connection, it is reasonable to expect that the mercury atom should replace the hydrogen atom in position 10 of carboranes **1a—d** (see Scheme 1). In fact, analysis of the ^{11}B and $^{11}B\{^1H\}$ NMR spectral data (Table 1) indicates the formation of 9-X-10-(HgO_2CCF_3)-1,7-$C_2B_{10}H_{10}$ (**2a—d**). It should be noted that the mercuration of **1a—c** occurs under more drastic conditions than the mercuration of the unsubstituted *m*-carborane,[4] which is, apparently, asso-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 743—747, April, 1995.
1066-5285/95/4404-0724 $12.50

Scheme 1



ciated with the electron-withdrawing nature of X in **1a—c**. It can be concluded that the relative reactivities of compounds **1a—c** change for the series of X in the following order: Cl ≈ Br > I. Thus, the mercuration of **1a—c** under standard conditions (a 1 : 1 molar ratio of the reagents, refluxing in TFA for 6 h) gave compounds **2a,b** in 45 and 50 % yields, respectively, whereas the yield of **2c** under the same conditions was 6 %. The use of a double excess of mercury trifluoroacetate and a longer duration of the reaction (15 h) made it possible to increase the yield of **2c** to 40 %. It is known that 9,10-diiodo-*m*-carborane is readily formed *via* the iodination of *m*-carborane with the I^+ electrophile, which is less electrophilic than $(CF_3CO_2)_2Hg$ in TFA (see Ref. 7). Therefore, it is reasonable to believe that not only the steric hindrances caused by the X substituents influence the reactivity of **1c** compared to that of **1a,b**. Probably, during the mercuration of **1c**, reversible coordinative interaction between iodine and the mercury atom occurs to decrease the reactivity of the latter, while the use of a double excess of $(CF_3CO_2)_2Hg$ increases the concentration of the free electrophile in solution. As expected, **1d** is mercurated more easily than **1a—c**, and the conversion of the substrate is completed after 4 h without heating.

It was shown using **2d** as an example that the

Table 1. Parameters of the ^{11}B NMR spectra of compounds **2—9**

Compound	δ	J_{B-H}/Hz (J_{B-Hg}/Hz)	Intensity	Assignment
2a	2.269	—	1	B(9)
	−4.90	162	2	B(5,12)
	−6.20	(2893)	1	B(10)
	−11.80	172	2	B(4,8)
	−13.03	164	2	B(6,11)
	−15.73	178	1	B(3)
	−21.31	181	1	B(2)
2b	−5.13	132	2	B(5,12)
	−5.13	(2856)	2	B(9,10)
	−11.43	173	2	B(4,8)
	−12.20	171	2	B(6,11)
	−15.05	187	1	B(2)
	−19.34	185	1	B(3)
2c	−3.87	(2940)	1	B(10)
	−3.87	110	2	B(5,12)
	−10.69	186	4	B(4,6,8,11)
	−14.00	188	1	B(3)
	−17.59	186	1	B(2)
	−22.40	—	1	B(9)
2d	1.08	—	1	B(9)
	−4.11	179	2	B(5,12)
	−6.32	(2858)	1	B(10)
	−11.04	177	2	B(4,8)
	−11.93	162	2	B(6,11)
	−14.46	177	1	B(3)
	−19.26	181	1	B(2)
3d	1.09	(2580)	1	B(10)
	−1.66	—	1	B(9)
	−8.77	174	2	B(5,12)
	−10.10	167	2	B(4,8)
	−11.80	171	2	B(6,11)
	−14.45	184	1	B(3)
	−19.18	181	1	B(2)
4b	28.60	(1231)	2	B(10,10')
	−3.76	—	2	B(9,9')
	−3.76	104	4	B(5,5', 12,12')
	−10.30	161	4	B(4,4',8,8')
4b	−12.53	122	4	B(6,6',11,11')
	−14.84	174	2	B(3,3')
	−19.18	182	2	B(2,2')
4c	28.83	(1446)	2	B(10,10')
	−3.44	185	4	B(5,5',12,12')
	−9.40	121	4	B(4,4',8,8')
	−10.97	188	4	B(6,6',11,11')
	−16.60	—	4	B(2,2',3,3')
	−21.21	(266)	2	B(9,9')
4d	31.92	(1156)	2	B(10,10')
	2.16	(197)	2	B(9,9')
	−3.59	163	4	B(5,5',12,12')
	−10.32	149	4	B(4,4',8,8')
	−12.03	124	4	B(6,6',11,11')
	−14.18	181	2	B(3,3')
	−18.09	191	2	B(2,2')
6	7.67	—	1	B(9)
	0.49	(2632)	1	B(12)
	−7.70	146	2	B(8,10)
	−13.45	120	6	B(4,5,3,6, 7,11)
7	7.73	—	1	B(9)
	5.11	(2518)	1	B(12)
	−6.92	150	2	B(8,10)
	−11.99	155	2	B(7,11)
	−12.64	176	4	B(3,4,5,6)
8	41.78	(1105)	2	B(12,12')
	8.97	—	2	B(9,9')
	−5.93	156	4	B(8,8',10,10')
	−10.36	125	4	B(7,7',11,11')
	−12.43	145	8	B(3,3',4,4', 5,5',6,6')
9	29.93	(1156)	2	B(9,9')
	−4.77	162	4	B(5,5',12,12')
	−8.57	150	2	B(10,10')
	−11.01	163	8	B(4,4',6,6', 8,8',11,11')
	−14.49	183	4	B(2,2',3,3')

trifluoroacetic ligand at the mercury atom can be easily exchanged for a chloride ion to form the corresponding chloromercury derivative (**3d**).

B(10)-Mercurated *m*-carboranes **2b—d**, as well as their *B*(9)-mercurated analogs,[8] are symmetrized under the action of $LiAlH_4$ in ether to yield compounds **4b—d**. Table 2 shows that the nature of the substituent at the boron atom in position 9 of the caborane nucleus does not have much effect on the yield of the symmetric product.

Under analogous conditions, the mercuration of 9-methyl-*o*-carborane (**5**) was studied. Unlike 9-substituted *m*-carboranes, this compound has a large nucleophilic zone for an electrophilic attack (first of all, the boron atoms in positions 12, 10, 8). Earlier, the isomeric composition of the products of the monomercuration of *o*-caborane was studied,[8] and the GLC data allowed one to conclude that the mercuration of the carborane icosahedron involves 85 % of the atoms in position 9 and 10 % of those in position 8, whereas the mercuration of 1-methyl-*o*-carborane occurs at positions 9(12) and 8(10) (90 and 10 %, respectively). These data as well as the presence of the substituent (Me) in position 9 of carborane **5** indicate that the main product of the mercuration of **5** is 9-Me-12-HgO_2CCF_3-1,2-$C_2B_{10}H_{10}$ (**6**) (according to the ^{11}B and $^{11}B\{^1H\}$ NMR spectral data). It was found that, similar to **2d**, compound **6** readily exchanges the trifluoroacetic ligand for a chlorine to form mercury chloride (**7**). The symmetrization of **6** and **7** under the action of $LiAlH_4$ in ether results in the formation of symmetric compound **8**.

When the data given in Table 1 are analyzed, it is worth noting that the introduction of donating (Me) as well as accepting (Cl, Br, I) substituents at the B(9)

Table 2. Characteristics of the obtained compounds

Compound	M.p. /°C	Yield (%)	Found (%) / Calculated					Molecular formula
			C	H	B	Hg	Hal	
2a	150—152	45	9.8	2.0	21.3	40.4		$C_4B_{10}H_{10}ClO_2HgF_3$
			9.8	2.2	21.9	40.8		
2b	198—201	50	9.3	2.2	20.0	37.1		$C_4B_{10}H_{10}BrO_2HgF_3$
			9.0	1.9	20.1	37.4		
2c	228—230	40	8.4	1.7	18.6	34.7		$C_4B_{10}H_{10}IO_2HgF_3$
			8.2	1.7	18.5	34.4		
2d	91—92	70	11.8	2.9	21.7	42.0	11.6	$C_5B_{10}H_{13}O_2HgF_3$
			12.8	2.8	22.9	42.6	12.1	
3d	193—195	80	9.8	3.4	27.3	49.9	10.0	$C_3B_{10}H_{13}HgCl$
			9.2	3.3	27.4	51.0	9.1	
4b	235—236	50	8.1	3.2	33.4	31.1	25.0	$C_4B_{20}H_{20}Br_2Hg$
			7.5	3.1	33.5	31.4	24.8	
4c	211—218	52	7.0	2.9	29.6	27.0	34.1	$C_4B_{20}H_{20}I_2Hg$
			6.5	2.7	29.3	27.2	34.4	
4d	144—146	50	13.7	4.3	41.3	41.0		$C_6B_{20}H_{26}Hg$
			14.0	5.0	42.0	39.0		
6	103—105	65	13.6	3.4	21.4	43.0		$C_5B_{10}H_{13}O_2HgF_3$
			12.8	2.8	22.9	42.6		
7	230—232	75	9.2	3.5	26.4	51.2		$C_3B_{10}H_{13}HgCl$
			9.2	3.3	27.4	51.0		
8	153—158	62	14.4	5.5	42.8	39.3		$C_6B_{20}H_{26}Hg$
			14.0	5.0	42.0	39.0		

atom has little effect on the deshielding of the neighboring B(10) atom bonded to Hg. Thus, the chemical shifts (CS) of the B(10) atom in carboranes **4b—d** fall within the 28—31 ppm interval, while the CS of the B(9) atom in $(1,7\text{-}C_2B_{10}H_{11})_2Hg$ (**9**) is 29.9 ppm (positions 9 and 10 in unsubstituted *m*-carborane are equivalent).

A comparison of the spectra of compounds **2** and **4** indicates that the replacement of the anion at the mercury atom with the corresponding donating B(10)-carboranyl ligand results in dramatic deshielding of the boron atoms in positions 10 and 10' and, probably, in the rehybridization of the orbitals of the boron atoms in the B—Hg—B bond system. Meanwhile, the $J_{^{11}B-^{199}Hg}$ decoupling constants for compounds **4b—d** are lower than those for compounds **2b—d** and **3d**.

It is known that 9-I- and 9-Me-carboranes may be used for the synthesis of 9-organosubstituted[9] carboranes and 9-carboranyl carbonic acids,[10] respectively. On the other hand, 9-mercurated carboranes are widely used in transmetallation reactions. Thus, compounds **2c,d**, **4c,d**, **6**, and **8** contain two potential reactive centers in positions 9 and 10 of the *m*-carborane nucleus and in positions 9 and 12 of the *o*-carborane nucleus.

We investigated the possibility of the replacement of Hg with Tl using compounds **2c** and **4c** as the starting compounds. It was found that a "one pot" procedure for the preparation of *B*(9)-thallated carboranes[11] *via* mercuration of the starting carborane by mercury trifluoroacetate in TFA and subsequent treatment of the reaction mixture with thallium(III) trifluoroacetate (TTFA) is not applicable to compound **2c** because a mixture of products that are difficult to separate is formed. The reaction of **2c** with TTFA in TFA and in ether proceeds analogously. However, transmetallation occurs smoothly in the reaction of **4c** with $TlCl_3$ in ether.

$$(9\text{-I-}1,7\text{-}C_2B_{10}H_{10}\text{-}10)_2Hg \xrightarrow{TlCl_3} \longrightarrow (9\text{-I-}1,7\text{-}C_2B_{10}H_{10}\text{-}10)TlCl_2 \quad (1)$$

10

Compound **10** obtained also contains two potential reactive centers in positions 9 and 10, and the Tl atom in boronthallated carboranes can be replaced with F, SCN, Se, and Te, as was described for *B*(9)-thallated carboranes.[12—14]

To perform our investigations, we looked for a convenient method for synthesizing the starting 9-halocarboranes **1a—c** and 9-iodine-*o*-carborane, which are used in mercuration reactions and for the synthesis of compounds **1d** and **5**. The most common methods for the synthesis of 9-halocarboranes are halogenation according to a known procedure[7] and (for the synthesis of **1c** and 9-iodo-*o*-carborane) treatment of *o*-carborane with I_2 in the presence of $AlCl_3$ in boiling methylene chloride as was described previously.[15] The bromodemercuration of (carborane-9-yl)mercurtrifluoroacetates

in CCl_4 yields 9-bromocarboranes in yields up to 45 %.[16] Therefore, mercuration of the corresponding carboranes followed by treatment with halogens without separation of the intermediate product can be proposed as a preparative method for the synthesis of 9-bromo(iodo)-*m*(*o*)-carboranes and 2-iodo-*p*-carborane.

$$RX \xrightarrow[2.\ X_2]{1.\ HgO,\ TFA} RH \qquad (2)$$

R = 9-*o*-carboranyl, 9-*m*-carboranyl, 2-*p*-carboranyl
X = Br, I

The yields of the halocarboranes obtained are given in Table 3.

Table 3. Yields of *B*-halocarboranes obtained by reaction (2)

R	X	Yield RX (%)
o-$C_2B_{10}H_{11}$-9	I	70
m-$C_2B_{10}H_{11}$-9	Br	68
m-$C_2B_{10}H_{11}$-9	I	72
p-$C_2B_{10}H_{11}$	I	80

Experimental

The ^{11}B NMR spectra were recorded on a Bruker WP-200SY instrument with working frequency 64.2 MHz (the external standard was $BF_3 \cdot OEt_2$). 9-Methyl-*o*- and 9-methyl-*m*-carboranes were obtained according to the known procedure,[7] and bis(1,7-dicarba-*closo*-dodecarborane-9-yl) mercury was synthesized as described previously.[3]

9-Chloro-*m*-carborane (1a). A flow of chlorine gas was passed through a solution of 4.86 g (0.01 mol) of $(m\text{-}C_2B_{10}H_{11})_2Hg$ in 70 mL of CCl_4 for 2.5 h. The precipitated residue was filtered, and the filtrate was washed with aqueous Na_2SO_3 and dried over $CaCl_2$. The solvent was distilled off and the solid residue was recrystallized from hexane to give 2.5 g (70 %) of **1a**, m.p. 214—217 °C.

General procedure for the bromination (iodination) of *o*-, *m*-, and *p*-carboranes. An equivalent amount of the starting carborane was added to a solution of 4.3 g (0.02 mol) of HgO in TFA. The mixture was stirred for several hours, with cooling to 10 °C in the case of *o*-carborane, with reflux in the case of *p*-carborane, and at 20 °C in the case of *m*-carborane. Then a 5 % excess of bromine (iodine) was added. The mixture was heated to reflux and HgX_2 was filtered. The solution was poured into water, and the precipitate was filtered, dried, and passed through a column with SiO_2, (the eluent was hexane). In the case of *p*-carborane, 2-iodo-*p*-carborane was crystallized from the reaction mixture after the elimination of HgI_2. The yields of the synthesized compounds are given in Table 3.

General procedure for the mercuration of compounds 1a—c. An equivalent amount of **1a—c** was added to a solution of 2.16 g (0.01 mol) of HgO in 50 mL of TFA. The suspension was stirred for 2 h at 20 °C and for an additional 6 h with reflux (the reaction was monitored by TLC on Silufol, the eluent was benzene/hexane, 4 : 1). For the synthesis of **2c**, a double excess of HgO was used (the time of boiling was 14 h). Compound **2d** was prepared without heating (the reaction time was 4 h). The reaction mixture was poured into distilled water, and the precipitate was fitered, dried over P_2O_5, and recrystallized from a benzene/hexane mixture. The yields of compounds **2a—d** and the results of elementary analysis are given in Table 2.

12-Trifluoroacetatomercuro-9-methyl-1,2-dicarba-*closo*-dodecaborane (6). 1.58 g (0.01 mol) of **5** was added to a solution of 2.16 g (0.01 mol) of HgO in TFA cooled to 5 °C. The mixture was stirred at 5 °C until most of the starting carborane was dissolved (~1.5 h) and then for 2 h at 20 °C. Further treatment was carried out similarly to the synthesis of compound **2d** (see Table 2).

10-Chloromercuro-9-methyl-1,7-dicarba-*closo*-dodecaborane (3d). A solution of 2.0 g (4.2 mmol) of **2d** in 70 mL of acetone was added to a solution of 5 g of NaCl in 100 mL of water. The precipitate was filtered, dried over P_2O_5, and recrystallized from acetone. **12-Chloromercuro-9-methyl-1,2-dicarba-*closo*-dodecaborane (7)** was prepared analogously. The constants of compounds **3d** and **7** are given in Table 2.

General procedure for the symmetrization of 2, 3d, 6, and 7. A solution of **2** or **6** was added dropwise to a suspension of $LiAlH_4$ in 70 mL of anhydrous ether (in the case of **3d** and **7**, a suspension in 50 mL of anhydrous ether was added). When addition was finished, the mixture was stirred for 1 h at 20 °C and for 2 h with reflux. Then the reaction mixture was cooled to 20 °C, and 100 mL of water was added dropwise. The organic layer was separated, washed with water (2 × 50 mL), and dried over Na_2SO_4. The ether was distilled off and the residue was recrystallized from a benzene—hexane mixture. (In the case of **4c**, the product was an oil, which was additionally purified by passing it through a layer of silica gel in benzene prior to crystallization.) The yields, melting points, and the results of elemental analysis are given in Table 2.

10-Dichlorothallium-9-iodo-1,7-dicarba-*closo*-dodecaborane (10). A solution of 0.5 g (1.6 mmol) of $TlCl_3$ in 50 mL of anhydrous ether was added dropwise to a solution of 1.2 g (1.5 mmol) of **4c** in 80 mL of anhydrous ether. The precipitate was filtered, washed with ether (2 × 25 mL), dried, and recrystallized from acetone to obtain 0.3 g (40 %) of compound **10**, m.p. 240—243 °C. Found (%): C, 4.6; H, 2.0; B, 20.5; Tl, 36.9. $C_2H_{10}Cl_2IB_{10}Tl$. Calculated (%): C, 4.4; H, 1.9; B, 19.8; Tl, 37.6. ^{11}B NMR (acetone), δ: −1.50 (B(10), $J_{^{11}B-^{205}Tl}$ = 10771 Hz); −5.11 (B(5,12), J_{B-H} = 189 Hz); −12.01 (B(3,4,6,8,11), J_{B-H} = 161 Hz); −15.8 (B(2), J_{B-H} = 184 Hz); −23.29 (B(9)).

This work was carried out with financial support from the Russian Foundation for Basic Research (Project No 93-03-18654) and the International Science Foundation (Grant NDM 000).

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Received December 3, 1993;
in revised form January 5, 1995