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Dedicated to Full Member of the Russian Academy of Sciences
A.I. Konovalov on His 70th Anniversary

Catalytic Olefination. Estimation of the Reactivity of Polyhaloalkanes

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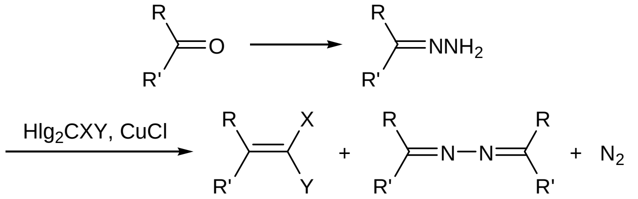
Abstract—Global electrophilicity indices and carbon–halogen bond energies of a wide series of halogen derivatives were calculated in terms of the density functional theory (DFT). The calculated values were used to estimate the reactivity of halogen derivatives under conditions of catalytic olefination. Reactions of N-unsubstituted hydrazones with polyhaloalkanes in the presence of CuCl afforded substituted alkenes. The relation between the structure of polyhaloalkanes and their reactivity was studied using the reaction with 4-chlorobenzaldehyde hydrazone as an example. It was found that increase in the global electrophilicity index and decrease in the C–Hlg bond energy are accompanied by increase in the "olefinating" power of halogen derivatives.

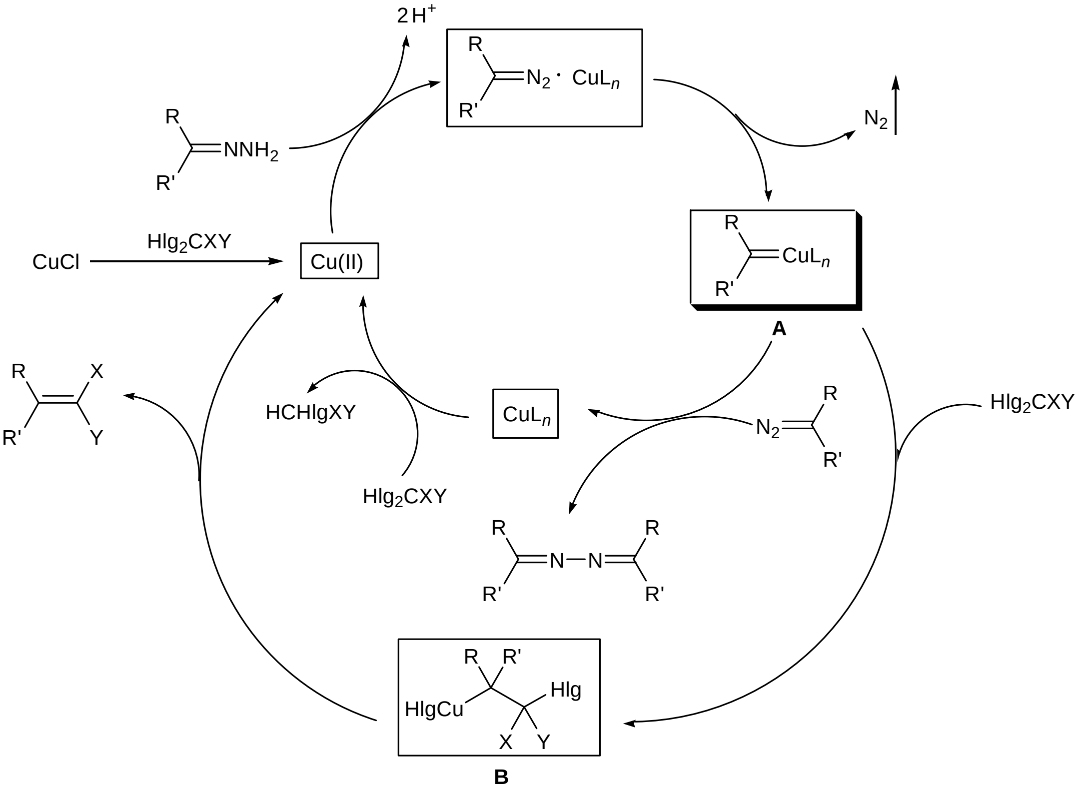
The present work continues the series of our studies on catalytic olefination. Building up of new carbon–carbon bonds is one of the most important transformations in organic synthesis. Olefination of carbonyl compounds, i.e., the conversion of C=O group into double C=C bond has found increasing application in the synthesis of substituted alkenes [1, 2]. Up to now, numerous olefination methods utilizing various reagents have been developed [1, 2]. Among these, the Wittig reaction and its versions [3], Julia olefination [4], and Peterson reaction [5] are used most widely in the synthetic practice. However, these procedures require large amounts of organometallic compounds, and the reactions are carried out as a rule in an inert atmosphere in dry solvents. Therefore, search for alternative methods for olefination of carbonyl compounds, specifically catalytic ones, remains an important problem. We have discovered a catalytic olefination process which implies reaction of hydrazones with geminal dihalo derivatives Hlg_2CXY in the presence of a catalytic amount of CuCl (Scheme 1) [6]. As a result, hydrazones are converted into the corresponding alkenes, and symmetric azines are formed as by-products. The discovered reaction is more advantageous than the classical olefination methods, which makes it a convenient tool in organic synthesis. On the basis of the catalytic olefination, promising procedures for the preparation of dichloroalkenes [7], dibromoalkenes [8], vinyl halides [9], and fluorine-containing unsaturated compounds were developed [10]. In the present work we examined the relative reactivity of various polyhalogenated compounds and tried to find parameters which can be used to predict their reactivity.

Scheme 1.



Scheme 2 illustrates the general mechanism of the catalytic olefination, proposed by us previously [7, 11]. The reaction is initiated by oxidation of CuCl with halogen-containing compound $CHlg_2XY$; copper(II) thus formed oxidizes hydrazone to give diazoalkane. The latter undergoes copper-catalyzed decomposition with elimination of nitrogen, leading to copper–carbene complex **A** which is the key intermediate in the catalytic olefination. Further transformations of complex **A** follow two pathways. The reaction with

Scheme 2.



$CHlg_2XY$ results in formation of substituted alkene and regeneration of Cu(II) as catalyst (outer cycle). Aldehyde (ketone) azine is formed as by-product via reaction of the copper–carbene complex with another diazoalkane molecule (inner cycle). Concomitant low-valence copper compounds should be oxidized with polyhaloalkanes to give products of partial reduction of the latter.

Both catalytic cycles, outer and inner, involve the same states of copper catalyst. The ratio of the hydrazone transformation products, alkenes and azines, depends on the relative contributions of concurrent transformations of complex **A**. In keeping with the proposed mechanism, the “olefinating” reactivity of polyhaloalkanes should be determined by their reaction with complex **A**, which leads to organocopper intermediates **B**, i.e., by their ability to act as electron acceptors, and by the strength of the carbon–halogen bond which is broken as a result of oxidative addition of the copper–carbene complex to the halogen-containing reagent. Increase in the olefinating power of polyhaloalkanes should lead to increase in the yield of the target products (alkenes) and decrease in the yield of by-products (azines), for these reaction pathways compete with each other.

On the basis of the proposed model of the reaction of copper–carbene complexes with polyhaloalkanes we performed calculations which allowed us to predict with high accuracy chemo- and stereoselectivity in the formation of alkenes [11]. In the present work we applied this model to prediction of the olefinating power of various halogen-containing compounds, which are potential reagents for the catalytic olefination, by estimating their electrophilicity and the energy of the carbon–halogen bond therein.

It is known that polyhaloalkanes behave as electrophiles in reactions with electron donors [12]. Previously, qualitative correlations were revealed between the reactivity of polyhaloalkanes and such parameters as half-wave potential of electrochemical reduction, electron affinity, bond energy, and energy of the lowest unoccupied molecular orbital (LUMO) [13]. As a rule, electron affinity rises with increase in the number of halogen atoms (except for polyfluorinated compounds) [14]. In the recent time, global electrophilicity index ω is used to characterize the reactivity of chemical compounds. It is a semiempirical parameter which reflects the gain in energy upon electron transfer to the LUMO of a molecule under study [15]. The global reactivity index is calculated by the formula $\omega = \mu^2/2\eta$, where μ

Table 1. Global electrophilicity indices and energies of the lowest unoccupied (LUMO) and highest occupied molecular orbitals (HOMO) of polyhaloalkanes

Reagent	$-E_{\mathrm{HOMO}}$, eV	$-E_{\mathrm{LUMO}}$, eV	ω, eV
CBr_3NO_2	7.24	3.93	4.70
CCl_3COCF_3	7.48	3.94	4.60
CBr_4	7.02	3.73	4.38
CCl_3NO_2	7.61	3.86	4.38
CBr_3Cl	7.02	3.59	4.10
CBr_2Cl_2	7.13	3.43	3.76
CCl_3CHO	7.06	3.27	3.52
$CHBr_2CN$	7.50	3.26	3.42
$CBrCl_3$	7.34	3.22	3.39
CBr_3COMe	6.63	3.12	3.38
$CHBr_2COMe$	6.46	3.03	3.29
$CHBr_3$	6.91	3.03	3.19
CBr_2F_2	7.35	2.98	3.06
CCl_4	7.73	2.99	3.03
CCl_3CN	8.09	2.96	2.98
$CHBr_2CO_2Me$	6.87	2.88	2.97
$CHCl_2COMe$	6.47	2.80	2.93
$CHBr_2Cl$	7.03	2.85	2.92
CH_2BrCN	7.44	2.74	2.76
$CHCl_2CN$	8.12	2.69	2.69
$CHBr_2SO_2Me$	7.13	2.66	2.68
$CHBrCl_2$	7.21	2.62	2.64
CCl_3CO_2Me	7.03	2.61	2.63
CCl_3F	7.76	2.62	2.62
CH_2BrCO_2Me	6.57	2.58	2.62
CCl_3SO_2Me	7.41	2.57	2.57
$CHCl_2COOMe$	6.92	2.51	2.52
CCl_3CF_3	7.84	2.52	2.52
$CH_2BrCOMe$	6.15	2.46	2.51
$CF_3CHBrCl$	7.49	2.43	2.43
CCl_3CCl_3	7.46	2.43	2.43
CCl_3CCl_2H	7.42	2.38	2.39
CCl_3OMe	7.30	2.35	2.35
CCl_3CONH_2	6.70	2.34	2.34
$PhCHBr_2$	6.38	2.30	2.31
CCl_3CH_2OH	7.19	2.25	2.26
$CHCl_3$	7.53	2.25	2.26
CH_2Br_2	6.97	2.24	2.24
CCl_2F_2	8.04	2.18	2.23
CCl_3CONMe_2	6.34	2.21	2.21
CCl_2FCClF_2	8.08	2.15	2.21
$PhCH_2Br$	6.31	2.13	2.13
$CClF_3$	8.55	1.50	1.79
CH_2Cl_2	7.37	1.52	1.69
CH_3Br	6.68	1.33	1.50
CH_4	9.42	0.36	1.32
CH_3Cl	7.09	0.84	1.26

is the electronic chemical potential [$\mu = 1/2(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}})$], and η is the chemical hardness ($\eta = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$). The parameter ω takes into account both acceptor and donor properties of a molecule and correlates well with the experimental data on the electrophilicity of various compounds [15].

We calculated the energies of frontier molecular orbitals (LUMO and HOMO), global electrophilicity indices (Table 1), and energies of the carbon–halogen bond (Table 2) for a series of halogen-containing compounds in terms of the density functional theory (DFT) using PBE 96 functional [16]; the calculations were performed with the aid of PRIRODA software [17]. In the DFT/PBE calculations we used a large basis set consisting of contracted Gauss type basis functions with the following contraction schemes: (5.3×1/3×1/2×1) for hydrogen atoms, 7.7×1/5.3×1/3×1/2×1) for carbon, (7.7×1/5.3×1/3×1/2×1) for fluorine, (8.12×1/7.8×1/3×1/2×1) for chlorine, and (8.17×1/6.13×1/6.8×1/3×1) for bromine. The calculated global electrophilicity indices and C–Hlg bond energies showed some relations with the reagent nature. The energy of the carbon–halogen bond in halomethanes CH_nHlg_{4-n} changes over a wide range, depending on the number of the halogen atoms (Table 2). It is seen that the energy of the C–Hlg bond decreases with rise in the degree of halogenation; correspondingly, dissociation of the carbon–halogen bond becomes easier. In going from trihalomethanes $CHBr_nCl_{3-n}$ to tetrahalomethanes CBr_nCl_{4-n} the energy of the C–Br and C–Cl bonds decreases by 8–10 kcal/mol.

The calculation results suggest that the reactivities of such tetrahalomethanes as CBr_4, CBr_2Cl_2, and $CBrCl_3$ should be almost similar, for the reactivity of these compounds is determined by the strength of the weakest C–Br bond which is broken first upon

Table 2. Energies of C–Hlg bonds (kcal/mol) in polyhaloalkanes

Reagent	C–Br	C–Cl	Reagent	C–Br	C–Cl
CCl_3COCCl_3		54.28	$PhCHBr_2$	56.30	
CCl_3COCF_3		55.45	CBr_3OMe	59.44	
CCl_3CN		58.38	$PhCH_2Br$	63.14	
CCl_3CO_2Me		61.73	CH_2BrCN	62.28	
CCl_3CONH_2		62.85	$CH_2BrCOMe$	65.83	
CCl_3NO_2		63.00	CH_2BrCO_2Me	65.93	
CCl_3CONMe_2		63.48	CH_2BrNO_2	68.78	
CH_2ClCN		72.61	CCl_4		67.07
CCl_3OMe		72.74	CCl_3F		74.32
$CH_2ClCOMe$		76.96	CCl_2F_2		80.74
CH_2ClCO_2Me		77.10	CBr_2F_2	66.93	
CH_2ClNO_2		80.64	$CHBr_3$	63.19	
CBr_3CN	46.91		$CHBr_2Cl$	63.28	75.18
CBr_3CO_2Me	49.35		$CHBrCl_2$	63.31	75.30
CBr_3COCF_3	44.13		$CHCl_3$		75.35
CBr_3CONH_2	50.76		CH_2Br_2	71.15	
CBr_3CONMe_2	50.86		CH_2Cl_2		82.51
CBr_3NO_2	49.56		CCl_3CCl_3		65.82
CBr_4	53.67		CCl_3CCl_2H		66.47 (CCl_3), 73.49 (CCl_2H)
CBr_3Cl	54.09	65.89	CCl_3CF_3		68.86
CBr_2Cl_2	54.49	66.31	CCl_2FCClF_2		76.33 (CCl_2F), 82.95 ($CClF_2$)
$CBrCl_3$	54.87	66.71			

oxidative addition of the copper–carbene complex. On the other hand, the reactivity of CCl_4 under conditions of the catalytic olefination should be considerably lower. Such trihalomethanes as $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ should also be characterized by similar reactivities, for the energy of the C–Br bond in these compounds is almost the same. The reactivity of chloroform ($E_{C–Cl}$ = 75.35 kcal/mol) and dihalomethanes should be much lower than the reactivity of bromine-containing trihalomethanes and CCl_4.

As applied to other halogen-containing compounds of the general formula $CH_nHlg_{3-n}G$ where G is a functional group, introduction of electron-acceptor substituents leads to an appreciable decrease in the energy of the C–Cl and C–Br bonds. Replacement of chlorine or bromine by fluorine increases the strength of the carbon–halogen bond. In all $CH_nHlg_{3-n}G$ compounds, the C–Cl bond is slightly stronger than C–Br (by several kcal/mol).

The global electrophilicity indices of the corresponding halogen derivatives increase in parallel with decrease in the carbon–halogen bond energy; therefore, both these parameters equally predict the relative reactivity.

In order to obtain experimental proofs for the hypothesis that the global electrophilicity index and the

Scheme 3.

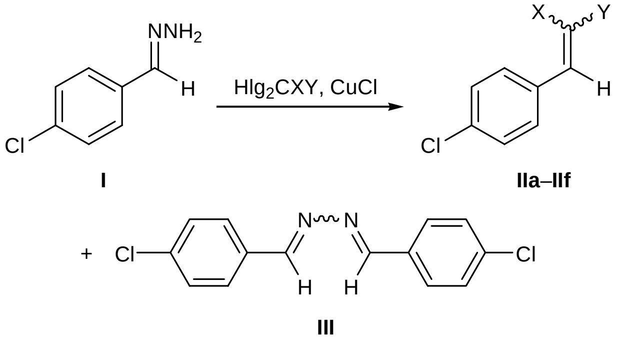


Table 3. Reactions of polyhaloalkanes with 4-chlorobenzaldehyde hydrazone (**I**)

Reagent	Yield, %			
	alkene[a]		azine **III**	overall
CBr_4	ArCH=CBr_2 (**IIa**)	89	7	96
$CBrCl_3$	ArCH=CCl_2 (**IIb**)	71	20	91
CCl_4	ArCH=CCl_2 (**IIb**)	82	17	99
$CHBr_3$	ArCH=CHBr (**IIc**)	67	26	93
$CHBrCl_2$	ArCH=CHCl (**IId**)	44	52	96
$CHCl_3$	ArCH=CHCl (**IId**)	0	52	52
CH_2Br_2	–	0	78	78
CH_2Cl_2	–	0	63	63
CCl_3CF_3	ArCH=$CClCF_3$ (**IIe**)	63	21	84
CCl_2FCClF_2	ArCH=$CFCClF_2$ (**IIf**)	20	21	41

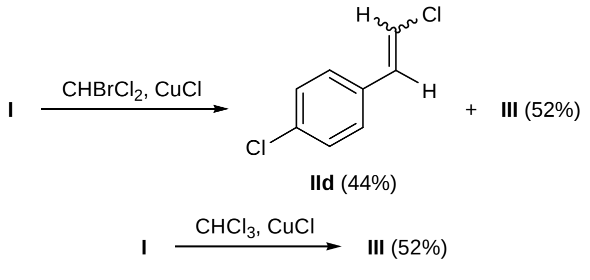
[a] Ar = 4-ClC_6H_4.

energy of the carbon–halogen bond can be used as parameters for prediction of the behavior of polyhaloalkanes in the catalytic olefination and for estimation of their olefinating power, we examined reactions of a series of polyhaloalkanes with 4-chlorobenzaldehyde hydrazone (**I**) as model compound (Scheme 3). The reactions were performed in DMSO in the presence of aqueous ammonia.

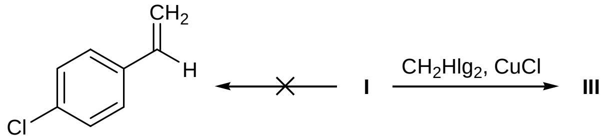
In all cases, the only products were the corresponding alkenes **IIa**–**IIf** and 4-chlorobenzaldehyde azine (**III**) (Table 3). The examined tetrahalomethanes CBr_nCl_{4-n} turned out to be excellent olefinating agents, and the corresponding β,β-dihalostyrenes were isolated in high yields (71–89%); the yield of the target product almost did not depend on the number of bromine atoms in the reagent molecule. Compound **III** was formed as the minor product, and the overall yield of products **II** and **III** was nearly quantitative. In the reaction with CBr_4, dibromostyrene **IIa** was isolated, and from bromotrichloromethane and CCl_4 we obtained dichlorostyrene **IIb**.

Bromoform can be used as C_1 building block in the catalytic olefination. Its reaction with hydrazone **I** yields vinyl bromide **IIc**. No expected β-chlorostyrene **IId** was detected in the reaction of hydrazone **I** with chloroform (Scheme 4), presumably due to the low global electrophilicity index and appreciably higher C–Cl bond energy, as compared to tetrahalomethanes. In this case, the only reaction product was aldehyde azine **III** (yield 52%). Replacement of one chlorine atom by bromine ($CHBrCl_2$) gives rise to stereoselective formation of β-chlorostyrene (**IId**) in a good yield, the *E* isomer prevailing. Thus the use of bromodichloromethane as olefinating agent provides a convenient preparative procedure for the synthesis of β-chlorostyrenes. Our experimental results convincingly prove that the strength of the carbon–halogen bond is an important factor determining the reactivity of polyhaloalkanes in the catalytic olefination.

Scheme 4.



Scheme 5.

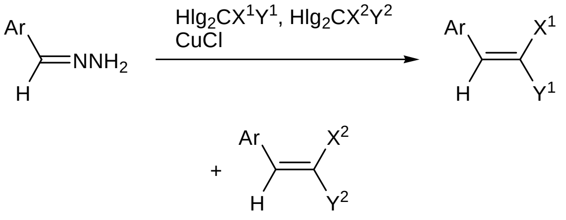


Hlg = Cl, 78%; Br, 63%.

Dihalomethanes CH_2Hlg_2 (Hlg = I, Br, Cl) turned out to be inactive in the catalytic olefination, and the expected 4-chlorostyrene was not detected (Scheme 5). Isomeric Freons of the general formula $C_2Cl_3F_3$ react with 4-chlorobenzaldehyde hydrazone (**I**) to afford fluorine-containing alkenes **IIe** and **IIf**. 1,1,1-Trichloro-2,2,2-trifluoroethane CCl_3CF_3 (Freon 113a) is much more reactive than isomeric CCl_2FCClF_2. Alkene **IIe** was isolated in 63% yield, while the yield of **IIf** was as poor as 20%. This is explained by the fact that in the key olefination stage, i.e., insertion of the copper–carbene complex at the carbon–halogen bond, the reactivity of the trichloromethyl moiety is considerably higher than the reactivity of the dichlorofluoromethyl group: the energy of the C–Cl bond in CCl_3CF_3 is much lower while the global electrophilicity index is higher than in CCl_2FCClF_2.

Thus the reactivity of polyhalogenated compounds, predicted on the basis of the global electrophilicity indices and carbon–halogen bond energies, is fully consistent with the obtained experimental results. Reagents possessing a higher global electrophilicity index relative to chloroform (chlorine-containing compounds) or methylene bromide (bromine-containing reagents) should be active in the catalytic olefination, and the corresponding alkenes should be formed.

Scheme 6.



Ar = 4-ClC_6H_4.

We also examined the relative olefinating power of a series of polyhaloalkanes. For this purpose, model hydrazone **I** was treated with a mixture of halogenated reagents under standard catalytic olefination conditions (Scheme 6). Taking into account that each of the polyhaloalkanes used is a good olefinating agent, the relative reactivity can be estimated from the ratio of two different alkenes formed as a result of the competing reactions (Table 4). In the reaction of **I** with a mixture of CBr_4 and CCl_4, the only product was β,β-dibromostyrene (**IIa**). This means that the reactivity of CBr_4 is much higher than the reactivity of CCl_4, in keeping with the energies of the C–Cl and C–Br bonds and global electrophilicity indices of the reagents. Comparison of the reactivities of the pairs CCl_4/CCl_3CF_3 and $CBr_4/CHBr_3$ convincingly proves higher reactivity of tetrahaloalkanes as compared to trihaloalkanes. Bromoform and bromodichloromethane showed comparable reactivities: β-bromostyrene (**IIc**) and β-chlorostyrene (**IId**) were formed at a ratio of 3:2, which is consistent with fairly similar energies of the C–Br bond in bromoform and bromodichloromethane. Analogous results were obtained with a mixture of CBr_4 and $CBrCl_3$ in support of our assumption that polyhalomethanes with similar energies of the weakest carbon–halogen bond should be characterized by similar reactivities. The examined polyhaloalkanes can be arranged into the following series according to their reactivity toward 4-chlorobenzaldehyde hydrazone (**I**) in the system DMSO–aqueous ammonia: $CBr_4 \approx CBrCl_3 \gg CCl_4 > CHBr_3 \approx CHBrCl_2 > CCl_3CF_3$. This series agrees with the calculated global electrophilicity indices (Table 1) and C–Hlg bond energies (Table 2).

Thus we have developed a model of alkene formation in the catalytic olefination, which makes it possible to estimate and predict the olefinating power of halogen-containing compounds on the basis of their global electrophilicity indices and energies of the carbon–halogen bonds.

Table 4. Competing reactions of polyhaloalkanes with 4-chlorobenzaldehyde hydrazone (**I**)

Reagents	Products (ratio)[a]	Overall yield of alkenes, %
CBr_4/CCl_4	**IIa**	65
$CBr_4/CHBr_3$	**IIa**/**IIc** (50/1)	98
$CCl_4/CHBr_3$	**IIb**/**IIc** (6/1)	72
CCl_4/CCl_3CF_3	**IIb**/**IIe** (33/1)	63
$CHBr_3/CHBrCl_2$	**IIc**/**IId** (3/2)	74
$CBr_4/CBrCl_3$	**IIa**/**IIb** (2/3)	84

[a] Determined by ^1H NMR spectroscopy.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian VXR-400 spectrometer at 400 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Kieselgel 60 F_{254} plates (Merck) were used for thin-layer chromatography, and column chromatography was performed on silica gel (63–200 mesh, Merck). 4-Chlorobenzaldehyde hydrazone (**I**) was synthesized according to known procedure [7]. Commercial polyhaloalkanes were used without additional purification.

Typical procedure for reactions of 4-chlorobenzaldehyde hydrazone (I) with polyhaloalkanes in DMSO. Aqueous ammonia, 0.68 ml (a 25% solution) and 20 mg (0.2 mmol) of freshly purified copper(I) chloride were added to a solution of 2 mmol (309 mg) of freshly prepared hydrazone **I** in 2 ml of DMSO, and 10 mmol of the corresponding polyhaloalkane was then added, maintaining the temperature at 20°C. The mixture was stirred for 24 h, poured into 200 ml of water, and extracted with methylene chloride (3× 20 ml). The extracts were combined, dried over sodium sulfate, and evaporated, and the product was isolated by column chromatography. In the reaction of **I** with CBr_4, the latter (3.32 g, 10 mmol) was preliminarily dissolved in 8 ml of DMSO. The physical properties and spectral parameters of the isolated compounds were in agreement with published data [7–10].

Competing reactions with different polyhaloalkanes were carried out in a similar way using a mixture of the corresponding reagents (10 mmol each), and the products were isolated as described above. The resulting mixtures of alkenes were not separated, and their ratio was determined by ^1H NMR spectrscopy.

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