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Effect of the Catalyst Nature and Quantity on Catalytic Olefination

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Abstract—The study of the catalyst nature effect on the catalytic olefination of 4-chlorobenzaldehyde hydrazone by polyhaloalkanes revealed that the best catalysts for the reaction are copper salts. With polyhaloalkanes more active than CCl_4, like CBr_4 and CCl_3Br, the olefination can proceed without catalyst.

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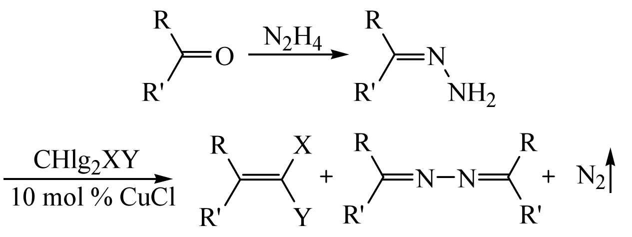
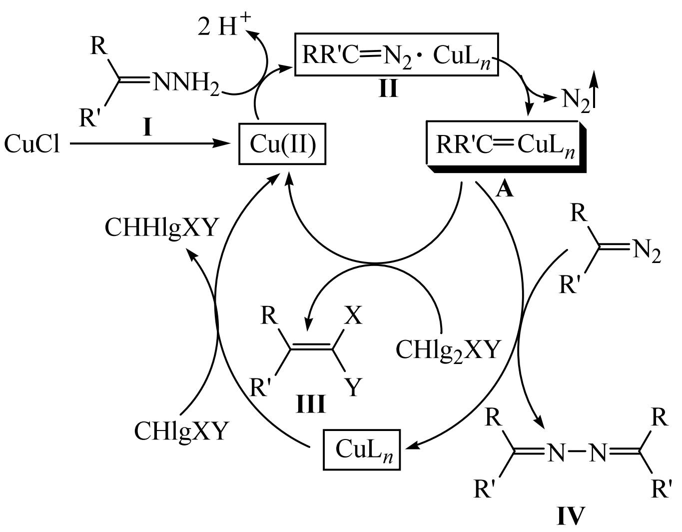
The building of new carbon-carbon bonds is the key problem of the modern chemistry, therefore the search of new reaction of the bonds formation attracts keen attention of organic chemists. The catalytic olefination of carbonyl compounds formerly discovered by our research team aroused a considerable theoretical and practical interest. It was found that the N-unsubstituted hydrazones of carbonyl com-pounds (both of aldehydes and ketones) treated with polyhaloalkanes in the presence of bases and of copper salts in a catalytic amount were converted into olefins furnishing the corresponding azines as side products [1].

The use of the reaction opens a simple and convenient way to a wide range of olefins containing halogens, alkyl and aryl substituents, cyano and ester functions [2]. Based on literature and experimental data we suggested a mechanism of the reaction and a catalytic cycle involving a copper-carbene complex as a key intermediate [2].



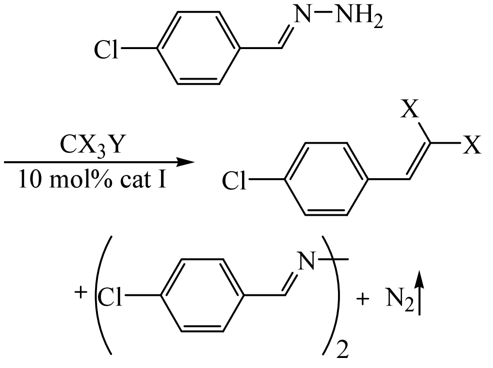
R = Ar, Alk; R' = Alk, H; Hlg = Cl, Br; X = F, Cl, Br, H; Y = F, Cl, Br, CN, CO_2Et.

The copper-carbene complex **A** arises at hydrazone **I** oxidation with the polyhaloalkane in the presence of copper through a stage of diazo compound **II** formation. The yields of the main reaction products depend on relative velocities of two principal processes. The first process consists in the reaction of complex **A** with the polyhaloalkane and affords olefin **III**. The second process involves the reaction of complex **A** with the diazoalkane and furnishes the side product of the reaction, azine **IV**.



L = NH_3, Hlg^-.

The main target of this study was the investigation of the effect of catalyst nature on the catalytic olefination of a model 4-chlorobenzaldehyde hydrazone under the treatment with tetrachloromethane, bromotrichloromethane, and tetrabromomethane in standard olefina-tion conditions in the presence of salts of various transition metals acting as catalysts of carbene transfer (Cu, Co, Pd, Rh, Fe, Ni, Cr) [3], of those whose carbene or diazenido-complexes were described (Cu, Cr, Mn, Fe, Co, Rh, Pd) [4], or of metals used in preparation of diazoalkanes from unsubstituted hydrazones (Hg, Ag, Mn, Ni, Cu) [5]. All the metals used possess several possible oxidation states and therefore they are active in reactions involving electron transfer. The catalytic activity of certain catalyst was evaluated by comparison of the yields of the corresponding olefin and 4-chlorobenzaldehyde azine and also based on the rate of the initial hydrazone consumption monitored by TLC of the reaction mixture and measured by the amount of the liberated nitrogen. The application to the process of polyhaloalkanes of different olifination activity [6] provided the information on the role of polyhaloalkanes activity in the catalysis with various metals. The reactions were carried out in DMSO for 24 h using 10 mol% of the metal salt and 5 equiv of polyhaloalkane. The yields of the main reaction products (alkene and azine) are presented in Table 1.



X = Y = Cl, Br; X = Cl, Y = Br.

The data obtained showed that the nature of the metal essentially affected the ratio of the reaction products, olefin and azine, and the character of this influence depended both on the metal nature and on the activity of the polyhaloalkane. The reaction with tetrachloromethane in the presence of all metals save copper afforded the corresponding azine as the principal product. Qualitatively similar pattern is observed in the reaction with the bromotrichloromethane: the yield of olefins is the highest in the presence of copper salts (apart of manganese chloride), and therewith the yield of dichlorostyrene is considerably higher than in the reaction with tetrachloromethane. At the use of tetrabromomethane the yields of the corresponding dibromoolefins were sufficiently high independent of the metal nature. In many instances the overall yield of the alkene and azine was close to quantitative indicating the absence of other reaction paths.

Under the catalysis by copper salts , except for copper cyanide, the reaction is complete within 3–5 min (TLC data). With the other metals and in the runs carried out without catalysts the reaction mixture was kept for 24 hours till the total conversion of the initial hydrazone. With tetrachloromethane the complete conversion was not attained even within several weeks, and formation of

Table 1. Yields of products of reaction between 4-chlorobenzaldehyde hydrazone and polyhaloalkanes in the presence of various catalysts

Catalyst	CCl_4			$CBrCl_3$			CBr_4		
	Yield of dichloro-styrene, %	Yield of azine, %	Overall yield, %	Yield of dichloro-styrene, %	Yield of azine, %	Overall yield, %	Yield of dibromo-styrene, %	Yield of azine, %	Overall yield, %
CuCl	82	18	100	76	12	88	81	11	92
$CuCl_2$	73	27	100	80	10	90	84	10	94
CuCN	20	65	85	76	6	82	50	22	72
$CuBr_2$	84	11	95	85	6	91	78	14	92
$NiCl_2·6H_2O$	10	62	82	61	6	67	55	44	99
$CoCl_2·6H_2O$	15	62	87	67	9	76	32	53	85
$FeCl_3$	25	58	83	24	57	81	49	27	76
$MnCl_2·4H_2O$	20	73	93	83	17	100	87	13	100
$CrCl_2$	traces	73	73	29	54	83	68	29	97
$HgCl_2$	5	87	92	46	48	94	68	21	89
$RhCl_3·3H_2O$	5	29	34	45	17	62	54	35	89
$AgNO_3$	20	76	96	40	58	98	43	39	82
$PdCl_2$	17	66	83	47	26	73	70	19	89
Blank run	traces	0–10%	0–10%	34	41	75	70	13	83

a small amount of azine might originate from the hydrazone oxidation that was also observed at its storage at room temperature for 24 h. Some metal salts, for instance, those of iron and chromium in reaction with $CBrCl_3$, and those of silver, cobalt, iron, and rhodium in reaction with CBr_4 acted as inhibitors of dihaloolefin formation: In these cases the yield of azine was higher than that of olefin.

It should be stressed that the olefination with bromotrichloromethane and with tetrabromomethane gave rise to high yields of the target alkenes at the use of other metal salts, e.g., those of manganese, and also in the runs carried out in the absence of the metal salts (Table 1).

The generation of the corresponding olefins in the non-catalyzed reactions is not consistent with the previously suggested catalytic cycle involving carbene complex **II** in the key reaction stage. At the same time these results become understandable assuming that the catalysis is performed by the impurity of copper salts in the metals and reagents under investigation. The atomic absorptive analysis of the reagents and some of the metals we used revealed that the copper content in the reaction mixture amounted to thousandths of mol%, and therefore the above conclusion was probable. To reveal the effect of the copper salt amount we carried out a series of reactions of the model 4-chlorobenzaldehyde hydrazone with CCl_4, $CBrCl_3$, and CBr_4 varying the content in the reaction mixture of the copper(I) chloride from 10 to 0.001 mol%. The yields of the reaction products are presented in Table 2 and on Fig. 1.

It turned out that the polyhaloalkanes under study behave different at decreasing catalyst amount. For instance, in reaction with CCl_4 alkene yields sharply decrease to 6% at 0.01 mol% of copper(I) chloride. With bromotrichloromethane the yield of alkene remained high up to 0.2 mol% of the catalyst, and then began to diminish, and at the copper content below 0.01 mol% was still on the level of 33–34% as also in the non-catalyzed reaction. In the olefination with tetrabromomethane the yield of

Table 2. Yields of products of reaction between 4-chlorobenzaldehyde hydrazone and polyhaloalkanes in the presence of various amounts of copper(I) chloride

Amount of catalyst, mol%	CCl_4		$CBrCl_3$		CBr_4	
	Yield of dichloro-styrene, %	Yield of azine, %	Yield of dichloro-styrene, %	Yield of azine, %	Yield of dibromo-styrene, %	Yield of azine, %
10	82	18	76	12	81	11
1	79	20	77	6	79	13
0.5	76	13	74	11	74	13
0.2	56	14	75	14	75	15
0.1	48	22	50	38	74	18
0.01	6	traces	33	54	73	10
0.001	0	0	34	29	76	8
0	0	0	34	41	70	13

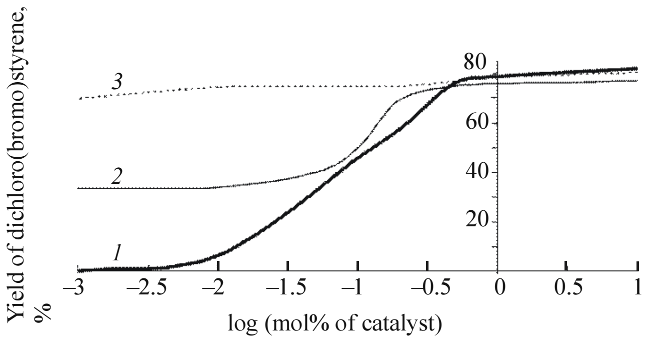


Fig. 1. Yield of alkenes in reaction between 4-chlorobenzaldehyde hydrazone and polyhaloalkanes as a function of the catalyst amount, (*1*) CCl_4; (*2*) $CBrCl_3$: (*3*) CBr_4.

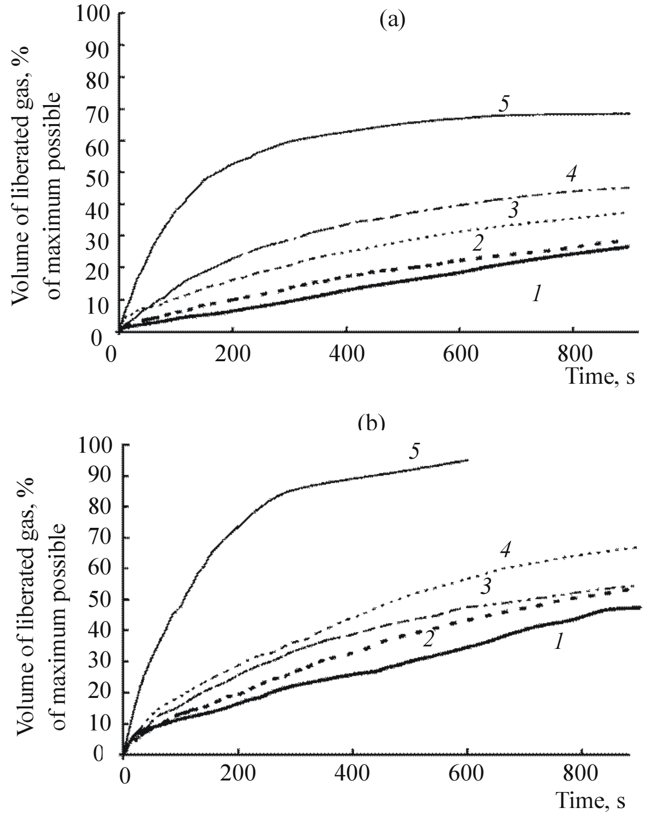


Fig. 2. Gas evolution in reaction between 4-chlorobenzaldehyde hydrazone and CCl_3Br (*a*) and CBr_4 (*b*). (*1*) 0.01, (*2*) 0.1, (*3*) 0.2, (*4*) 0.5, (*5*) 1%.

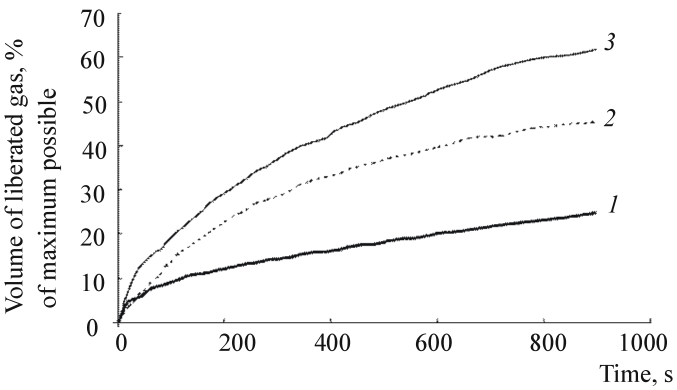


Fig. 3. Dependence of gas evolution rate on the nature of polyhaloalkane, (*1*) CCl_4, (*2*) $CBrCl_3$, (*3*) CBr_4.

the target alkene at decreasing the copper amount in the reaction mixture diminished insignificantly and remained high even at the minimum content of the copper(I) chloride. None the less, a common trend is clearly observed for all reactions: With decreasing amount of the copper catalyst the reaction time grew, and the olefin yield reduced, as seen from the initial parts of the curves of the gas evolution for the reactions with bromotrichloromethane and tetrabromomethane (Fig. 2) and from the data in Table 2.

The results obtained exclude the possibility of catalysis with copper impurities existing in the metals and reagents used, for according to Fig. 1 the presumable concentrations are below the limit where the catalyst no more controls the reaction process, and therewith the products composition is the same as in the non-catalyzed reaction.

Olefins formation in the non-catalyzed reactions with CCl_3Br and CBr_4 also cannot be rationalized within the framework of the previously suggested mechanism and may lead to conclusion that in the reactions with olefinating reagents more active than tetrachloromethane the process can occur along other pathways (Fig. 3).

Table 3. Reaction of 4-chlorobenzaldehyde hydrazone with $CBrCl_3$ and CBr_4 in the presence of TEMPO

Amount of catalyst, mol%	Amount of TEMPO, mol%	Amount of poly-halo-alkane, equiv.	$CBrCl_3$		CBr_4	
			Yield of dichloro-styrene, %	Yield of azine, %	Yield of dibromo-styrene, %	Yield of azine, %
10	10	5	75	9	71	29
1	10	5	75	9	75	11
0.1	10	5	31	52	43	36
0.01	10	5	–	–	37	36
0	10	5	–	–	21	72
10	100	5	15	72		
10	100	1	–			

The bromotrichloromethane and tetrabromomethane are known to be more active than tetrachloromethane in the reactions of radical addition and telomerization [7], and the observed olefination in the absence of metal catalyst may be due to the spontaneous radical addition of trihalomethyl radicals to the double carbon–nitrogen bond initiated by an electron transfer. Such processes are known for addition of various polyhaloalkanes to alkenes, alkynes, and various aromatic compounds in the presence of sodium dithionite or other reductants [8]. Reactions of polyhaloalkanes of radical character are known to occur with phenylhydrazine [9] and amines under catalysis with copper and iron compounds [10]. In all the reactions of this kind the compounds with C–Br bonds are significantly more active than the corresponding chlorides [9].

Therefore it is possible to assume for bromotrichloromethane and tetrabromomethane the occurrence of radical processes in the non-catalyzed olefination of 4-chlorobenzaldehyde hydrazone.

We utilized described in [9] method for recognizing radical nature of the process: The olefination was carried out in the presence of a stable radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) that was often used for inhibiting various radical reactions. We also performed olefination in the light and in the dark.

It was shown that small additives of TEMPO completely inhibited the reaction of bromotrichloromethane with hydrazone in the absence of a catalyst, and in the reaction with tetrabromomethane an induction period was observed whose length was proportional to the amount of the added TEMPO. The consumption of TEMPO was followed by ESR spectra and by TLC. TEMPO addition caused induction periods also in reactions catalyzed by copper chloride, and the length of this period depended both on the amount of the catalyst and TEMPO, and also on the character of the polyhaloalkane used. It was shown that the induction period ended with TEMPO consumption; therewith the disappearance of TEMPO (as shown by ESR and TLC) coincided with the appearance of the reaction product, the corresponding dihalostyrene. We demonstrated also that neither of the reaction components taken alone caused so fast TEMPO consumption as was observed under the reaction conditions in the presence of all components. Thus both in reactions catalyzed by copper chloride and in non-catalyzed reactions the addition of TEMPO led to appearance of the induction period whose end coincided with the start of olefination. These data testify to the radical character of the reaction.

On the other hand the yields of products obtained in the light and in the dark were the same for all examples (Table 4). During the reaction of catalytic olefination performed in the probe of ESR spectrometer no presence of long-lived radicals was detected.

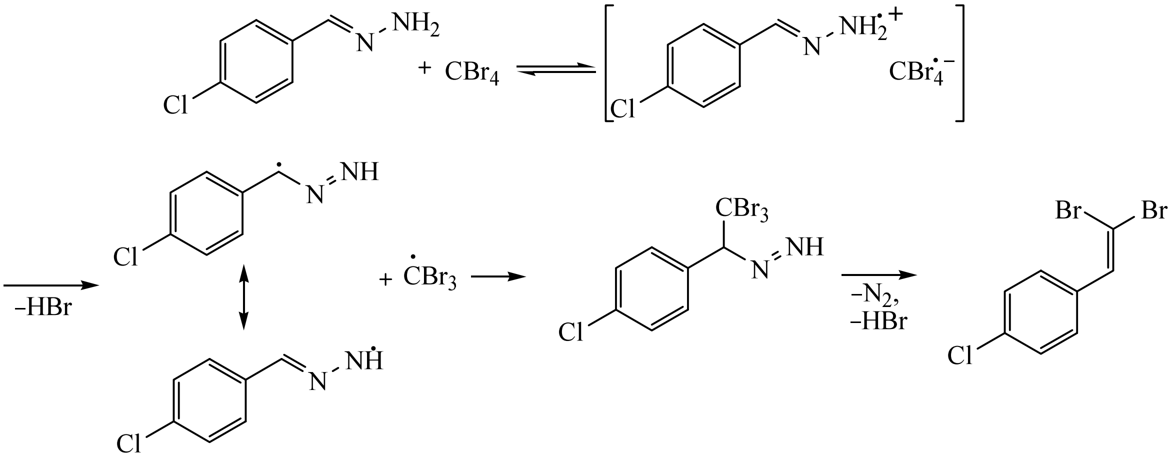
The data obtained, like the existence of non-catalyzed reactions, the appearance of an induction period in the presence of TEMPO, the lack of clear influence of light, the pronounced catalytic effect of the copper salts and the absence thereof for the other tested metals show that the mechanism of catalytic olefination is complicated, and presumable radical alternatives cannot be excluded to the previously suggested mechanism of the catalytic olefination involving copper-carbene complexes. The formerly suggested mechanism and the catalytic cycle although are in agreement with both experimental and published data [11], still can serve only as more or less successful model of the actually occurring processes.

No dependence of the yield of the target olefin on the amount of catalyst in reaction with tetrabromomethane most likely indicates the radical nature of the reaction between polyhaloalkane and hydrazone. Two possible schemes may be assumed [7–9]. The first one involves a generation and further reaction of tribromomethyl and hydrazonyl radicals (the latter is shown as two resonance forms) (Scheme 1).

The second scheme consists in the generation of a tribromomethyl radical and its reaction with hydrazone followed by oxidation with CBr_4. It should be noted however that examples of reactions between electrophilic polyhaloalkyl radicals with the double carbon-nitrogen bonds are hardly known (an exclusion is the reaction of perfluoroalkyl iodide with isonitriles in the presence of copper metal [12]), although the reactions of alkyl, aryl, and acyl radicals with imines, hydrazones, and oximes are sufficiently well documented (Scheme 2) [13–15].

It is presumable that analogous reactions occur also with the bromotrichloromethane, less active than CBr_4 in radical addition reactions, but containing C–Br bond of similar energy[7]. The contribution of radical olefination

Scheme 1.



Scheme 2.

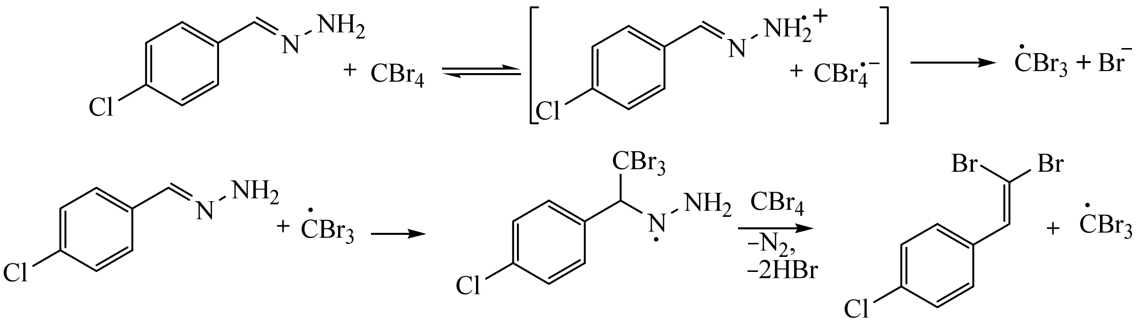


Table 4. Reaction of 4-chlorobenzaldehyde hydrazone with $CBrCl_3$ and CBr_4 in the dark and in the light

Poly-halo-alkane	Amount of catalyst, mol%	Tem-pera-ture, °C	Process time, h	Yield of dichloro-styrene,%		Yield of azine, %	
				in the light	in the dark	in the light	in the dark
$CBrCl_3$	0	30	3.5	43	43	6	9
$CBrCl_3$	0	8	5	44	39	8	10
CCl_4	0	30	5	traces	traces	traces	traces
CCl_4	0.1	30	5	44	42	6	8
CCl_4	0.1	8	5	19	17	10	12

into the reaction with tetrachloromethane is hardly probable for the process in the absence of metal catalysts, but it cannot be completely disregarded in the event of catalyzed reactions.

Thus we studied the effect of the nature and quantity of catalyst on the course of catalytic olefination. It was established that various transition metals could catalyze the reaction, but the copper compounds were the best catalysts. It was shown that the catalytic olefination with active polyhaloalkanes required small amount of catalyst [thousandth parts of copper(I) chloride]. The reaction of bromotrichloromethane and tetrabromomethane with the 4-chlorobenzaldehyde hydrazone was shown to proceed also without catalyst suggesting possible participation of polyhaloalkyl radicals. Based on published data we suggested and discussed presumable schemes of the olefination process.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Varian VXR-400 (operating frequency 400 MHz) from solutions in $CDCl_3$ using TMS as internal reference. ESR spectra were measured on a radiospectrometer RE-1306 in the three-centimetric range. TEMPO concentration in all experiments did not exceed 10^{-3} mol/l.*

TLC was performed on Silufol UV-254 plates, development either by acidified $KMnO_4$ solution in iodine vapor or under UV-irradiation. Preparative chromatography was carried out on columns packed with silica gel (63-200 mesh, Merck). 4-Chlorobenzaldehyde hydrazone was prepared as in [16].

For the experiments without catalysts and with low copper(I) chloride content all the reagents and solvents were additionally purified from the possible copper impurities. DMSO was subjected to distillation, in the synthesis of 4-chlorobenzaldehyde hydrazone the hydrazine hydrate was used after distillation. The water solution of ammonia was prepared by ammonia condensation into distilled water. The glassware for experiments was first treated with hydrofluoric acid, then rinsed in succession with distilled water, EDTA solution, and again with distilled water. Magnetic stirrers for stirring the reaction mixtures were treated in the same fashion.

Reactions of 4-chlorobenzaldehyde hydrazone with CCl_4, $CBrCl_3$, and CBr_4 (general procedure). Into a round-bottom one-neck flask was charged 1 ml of DMSO, 0.38 ml of 25% aqueous ammonia, 0.1 mmol of the appropriate metal salt [in reactions with varied amounts of copper(I) chloride it was added as a solution in 0.38 ml of 25% aqueous ammonia), and 0.155 g (1 mmol) of 4-chlorobenzaldehyde hydrazone. Then from a dropping funnel was quickly added a solution of 5 mmol of polyhaloalkane in 3 ml of DMSO maintaining the room temperature in the flask. After 24 h of the reaction the mixture was poured into 30 ml of 5% water solution of HCl, and the products were extracted into dichloromethane (3 × 25 ml). The combined extract was dried with sodium sulfate, and the solvents were distilled off in a vacuum. The residue was subjected to column chromatography on silica gel. The appropriate mixtures of hexane and dichloromethane were used as eluents. The chromatography yielded two fractions: the corresponding alkene and symmetrical azine [17, 18]. The spectral characteristics of compounds obtained are consistent with the published data [17]. Yields of the products are given in Tables 1–4.

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REFERENCES

1. Shastin, A.V., Korotchenko, V.N., Nenajdenko, V.G., and Balenkova, E.S., *Tetrahedron,* 2000, vol. 56, p. 6557.
2. Nenaidenko, V.G., Korotchenko, V.N., Shastin, A.V., Balenkova, E.S., *Izv. Akad. Nauk, Ser. Khim*., 2003, p. 469.
3. Doyle, M.P., McKervey, M.A., and Ye, T., *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds. From Cyclopropanes to Ylides*, New York:Wiley, 1998, 652 p.

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4. Zollinger, H., *Aliphatic Inorganic and Organometallic Compounds*, Weinheim: VCH, 1995, vol. 2, p. 522.
5. Kitaev, Yu.P. and Buzykin, B.I., *Hydrazoney* (Hydrazones), Moscow: Nauka, 1974.
6. Nenaidenko, V.G, Korotchenko, V.N., Shastin, A.V., Tyurin, D.A., and Balenkova, E.S., *Zh. Org. Khim.*, 2004, vol. 40, p. 1801.
7. Terent'ev, A.B. and Vasil'eva, T.T., *Usp. Khim.,* 1994, vol. 63, p. 280.
8. Amato, C., Naud, C., Calas, P., and Commeyras, A., *J. Fluorine Chem*., 2002, vol. 113, p. 55.
9. Huyser, E.S. and Wang, R.H.S., *J. Org. Chem.,* 1968, vol. 33, p. 3901.
10. Timokhin, B.V., *Usp. Khim.,* 1994, vol. 59, p. 332.
11. Leonel, E., Lejaye, M., Oudeyer, S., Paugam, J.P., and Nedelec, J.-Y., *Tetrahedron Lett.,* 2004, p. 2635.
12. Tordeux, M. and Wakselman, C., *Tetrahedron*, 1981, vol. 37, p. 315.
13. Friestad, G.K., *Tetrahedron*, 2001, vol. 57, p. 5461.
14. Kim, S., *Adv. Synth. Catal.,* 2004, vol. 346, p. 19.
15. Ueda, M., *Yakugaku Zasshi,* 2004, vol. 124, p. 311.
16. Singh, G. and Zimmer, H., *J. Org. Chem.,* 1965, vol. 30, p. 417.
17. Korotchenko, V.N., *Cand. Sci. (Chem.) Dissertation,* Moscow, 2003.
18. Hoggarth, E., *J. Chem. Soc.,* 1949, p. 1918.