REACTION OF DIHALOCARBENES WITH ARYL AND CYCLOPROPYL DERIVATIVES OF ETHYLENE*

O. M. Nefedov, R. N. Shafran, and A. I. Ioffe

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The reaction with olefins is one of the main reactions of carbenes [4, 5]. We studied the reaction of dihalocarbenes with series of olefins with different nucleophilic properties in order to determine the nature and the extent of the influence of substituents both in direct conjugation with the carbene double bond under attack and located right at the bond. The following series of olefins were selected for the investigation: p- and α-substituted phenylethylenes (styrenes) and 1-substituted cyclopropylethylenes. The addition of dihalocarbenes to these olefins produces the corresponding dihalocyclopropanes in high yields and is not accompanied by the formation of secondary products, permitting the use of the method of competitive reactions [5] for the determination of the relative activity of the olefins. In addition, since the reactivity of the olefins with respect to dichlorocarbene is practically independent of the method used to generate it and is only weakly dependent on the temperature [6, 7], it is perfectly legitimate to compare the data in Tables 1 through 4, which refer to different reaction conditions.

Tables 1 through 3 present the values obtained for the relative rate constants (k_{rel}) for the addition of dihalocarbenes to the olefins investigated with respect to cyclohexane, which served as the standard. In all cases, as would be expected, the electron-donor substituents increase the reactivity of the double bond, and the electron-acceptor substituents lower it. At the same time, the quantitative aspect of the effect of the substituent is greatly dependent both on the direction of its introduction and on the activity of the reaction series under consideration. For example, an electron-donor methyl group in position 1 increases the activity of cyclohexane, cyclopropylethylene, and styrene by factors of 8.5, 6.7, and 2.2, respectively, while in the para position of styrene it increases the activity by a factor of only 1.5. Therefore, the double bond in styrene is more sensitive to the introduction of the substituent directly to it (into the α position) than to the aromatic nucleus.

In the case of the $p\text{-}RC_6H_4CH{=}CH_2 + CCl_2$ reaction, the log k_{rel} values correlate both with the Braun σ^+ constants and the Hammett σ constants of the substituents according to the equations: $\log k_{rel} = -0.58\sigma^+ - 0.09$ ($r = 0.98$) and $\log k_{rel} = -0.94\sigma + 0.05$ ($r = 0.99$). The following similar equations were obtained in an independent investigation [9] for this reaction series: $\log k_{rel} = -0.62\sigma^+$. These data are consistent with the known electrophilic properties of singlet dihalocarbenes and the asymmetric transition state with partial separation of charges that has been postulated for the reaction under consideration [4. 5]. It should be noted that the introduction of a second CH_3 group to the aromatic nucleus does not result in a further increase in the activity of the double bond of styrene, while the introduction of a third CH_3 group even causes a decrease in activity (especially in the reaction with CBr_2). Such a law is clearly due to the noncoplanar nature of these molecules, which is manifested both by the disruption of the conjugation between the double bond and the aromatic ring and the creation of additional steric hindrances to the attack by carbene, especially in the case of the bulky dibromocarbene.

Another interesting law is the weakening of the effect of the substituents on the reactivity of the double bond in parallel with the increase in their nucleophilic properties in similar reaction series. A systematic treatment of this phenomenon becomes possible, if we compare the parameters of the correlation equations relating log k_{rel} with the Taft σ* constants of the substituents for the reactions we investigated and those described in the literature of 1-substituted olefins with dichlorocarbene (see Table 4).

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*See also [1-3].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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TABLE 1

R in p-$RC_6H_4CH=CH_2$	CX_2	Source of CX_2	T., °C	k^*_{rel}
NO_2	CCl_2	CCl_3COONa	82	0,22
Br	CCl_2	$CHCl_3+t\text{-}C_4H_9OK$	–12	0,56
Cl	CCl_2	CCl_3COONa	82	0,81
H	CCl_2	CCl_3COONa	82	1,00
H	CBr_2	$CHBr_3+t\text{-}C_4H_9OK$	–12	(0,42)
CH_3	CCl_2	$CHCl_3+t\text{-}C_4H_9OK$	–12	1,52
OCH_3	CCl_2	CCl_3COONa	82	2,24
$N(CH_3)_2$	CCl_2	$CHCl_3+t\text{-}C_4H_9OK$	–12	6,80
Vinylxylene	CCl_2	$CHCl_3+t\text{-}C_4H_9OK$	–12	(1,50)
Vinylmesitylene	CCl_2	$CHCl_3+t\text{-}C_4H_9OK$	–12	(1,40)
"	CBr_2	$CHBr_3+t\text{-}C_4H_9OK$	–12	(0,13)

*The k_{rel} values given in parentheses were obtained with an olefin–CX_2-source ratio equal to 2:1. The other values were obtained with a 10:1 ratio.

TABLE 2 *

R in cyclo-$C_3H_5C(R)=CH_2$	k_{rel} with respect to CCl_2
p-BrC_6H_4	0,90
H	1,08
C_6H_5	1,40
Cl	1,41
cyclo-C_3H_5	5,60
CH_3	6,67

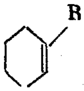
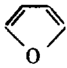
*The CCl_2 source was $CHCl_3$ + t-C_4H_9OK (n-pentane, –12°C). The olefin–CCl_2-source ratio was 10:1.

TABLE 3 *

R in $C_6H_5C(R)=CH_2$	k_{rel} with respect to	
	CCl_2	CBr_2
Cl	0,59	–
H	1,40	0,42
C_6H_5	1,80	1,10
cyclo-C_3H_5	1,80	–
CH_3	2,20	3,30

*The dihalocarbene source was CHX_3 + t-C_4H_9OK (n-pentane, –12°C). The olefin–CX_2-source ratio was 2:1.

TABLE 4

Reaction series	k_{rel} for R=H	ρ	Correlation coefficient, r
$CH_3C(R)=CH_2+CCl_2$ [7]	0,2	–4,30	–
 $+CCl_2$ [2]	1,0	–1,14*	0,94
cyclo-$C_3H_5C(R)=CH_2+CCl_2$	1,1	–1,10	0,95
$C_6H_5C(R)=CH_2+CCl_2$	1,4	–0,46*	0,97
 $—CH=CRR'+CCl_2$ [8]	1,8	–0,27	0,96

*The values of ρ are apparently somewhat underestimated with respect to their absolute values due to the comparatively small molar excess of the olefins, which reduces their apparent reactivity (compare [5]).

The data in Table 4 show that the absolute value of ρ has a clear tendency to decrease with increasing activity of the reaction series, as reflected in the increase in the reactivity of the corresponding unsubstituted olefin. It may be noted that a similar law was reported in [5] for the reaction of alkylethylenes with various carbenes, where the relative selectivity of the carbene (CXY) determined from competitive-addition experiments, which is proportional to ρ_{CXY}/ρ_{CCl_2}, also decreases with increasing electrophilic properties of the

TABLE 5

Dihalocyclopropane	Method of synthesis	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found, %			Empirical formula	Calculated, %		
						C	H	Hal		C	H	Hal
1-Phenyl-1-cyclopropyl-2,2-dichlorocyclopropane	a	48	122–124 (7,5)	1,5520	1,1822	63,39	5,42	31,32	$C_{12}H_{12}Cl_2$	63,45	5,33	31,22
1-Phenyl-1,2,2-trichlorocyclopropane	a	17	mp 53–53,5	–	–	48,15	3,25	48,15	$C_9H_7Cl_3$	48,76	3,18	48,02
1-(p-Bromophenyl)-2,2-dichlorocyclopropane	a	64	mp 44–45 (from hexane)	–	–	40,72	2,58	56,51	$C_9H_7Cl_2Br$	40,63	2,66	56,71
1-(p-Methoxyphenyl)-2,2-dichlorocyclopropane	a	33	129 (6)	1,5558	1,2662	55,41	4,66	32,54	$C_{10}H_{10}Cl_2O$	55,40	4,64	32,60
1-(p-Dimethylaminophenyl)-2,2-dichlorocyclopropane *	a	31	127–129 (3)	1,5878	–	57,37	5,79	30,62	$C_{11}H_{13}Cl_2N$	57,40	5,70	30,80
1-Cyclopropyl-2,2-dichlorocyclopropane	a	45	70 (40)	1,4732	1,1566	47,64	5,48	47,15	$C_6H_8Cl_2$	47,71	5,34	46,95
1-Methyl-1-cyclopropyl-2,2-dichlorocyclopropane	a	43	58 (12)	1,4797	1,1373	51,05	6,08	42,84	$C_7H_{10}Cl_2$	50,93	6,12	42,95
1-Cyclopropyl-1-(p-bromophenyl)-2,2-dichlorocyclopropane	b	18	164 (3,5)	1,5815	1,5037	46,90	3,64	49,33	$C_{12}H_{11}Cl_2Br$	47,10	3,61	49,30
1-Cyclopropyl-1,2,2-trichlorocyclopropane	b	48	66,5–67 (12)	1,5007	1,3261	38,80	4,00	57,07	$C_6H_7Cl_3$	38,85	3,81	57,34

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*Found: N 6.15%. Calculated: N 6.05%; mp 49.5–50.5°C (from alcohol).

carbene. Since in the case of similarly constructed reaction series, the series with the lowest activation energy values (the more active compounds) should be characterized by the lowest absolute values of ρ, our data allow us to conclude that there is a single mechanism for the reaction of dichlorocarbene with the unsaturated compounds studied.

EXPERIMENTAL

The GLC analysis was carried out on LKhM-8MD and Khrom-3 chromatographs with a katharometer. The carrier gas was helium, and the column was 200 × 0.3 cm with 15% Apiezon L on Chromosorb W and P, with 10% Silicon SE-30 or 15% Silicon Siss on Chromosorb W, as well as with 20% Reoplex 400 on Chromosorb P.

The solvents, chloroform, bromoform, cyclohexene, and styrene (commercial reagents), were treated in accordance with accepted laboratory procedures. The synthesis of p-methyl- [1] and p-chlorostyrene [10], 1-methyl-1-phenyl- and 1,1-diphenylethylene [1], 1-cyclopropylethylene [10], and 1,1-dicyclopropylethylene [11] have been described in our earlier reports. The 1-phenyl-1-cyclopropylethylene was obtained by the dehydration of cyclopropylphenylmethylcarbinol [from C_6H_5MgBr and methyl cyclopropyl ketone (MCK)] over $MgSO_4$ [13]. The p-bromostyrene was obtained by the dehydration of p-bromophenylmethylcarbinol (from p-BrC_6H_4MgBr and CH_3CHO) over $KHSO_4$ [14]. The p-methoxystyrene was obtained by the dehydration of β-(p-methoxyphenyl)ethyl alcohol (from p-$CH_3OC_6H_4MgBr$ and ethylene oxide) over KOH in the presence of hydroquinone [15]. The p-nitrostyrene was synthesized by dehydrobrominating β-(p-nitrophenyl)ethyl bromide, which was obtained by nitrating β-phenylethyl bromide (from phenylethyl alcohol and PBr_3), and boiling with triethanolamine and water [16]. The p-dimethylaminostyrene was obtained by the dehydration of p-N,N-dimethylaminophenylmethylcarbinol [from p-$(CH_3)_2NC_6H_4Li$ and CH_3CHO] under rapid vacuum distillation [16]. The isopropenylcyclopropane was obtained by the distillation of cyclopropyldimethylcarbinol (from MCK and CH_3MgCl) over H_2SO_4 [17]. All the olefins just mentioned had a purity (according to the GLC data) of ≥99% and physicochemical characteristics similar to those indicated in the literature.

1-p-Bromophenyl-1-cyclopropylethylene was synthesized with a 65% yield by dehydrating p-bromophenylcyclopropylmethylcarbinol [from p-BrC_6H_4MgBr and MCK, bp 155-160°C (8 mm). Found: C 54.92; H 5.40; Br 32.97%. Calculated for $C_{11}H_{13}BrO$: C 54.74; H 5.42; Br 33.19%] and had bp 120°C (8 mm), n_D^{20} 1.5860. Found C 58.94; H 5.00; Br 35.61%. Calculated for $C_{11}H_{11}Br$: C 59.20; H 4.97; Br 35.83%. 1-Chloro-1-cyclopropylethylene was synthesized with a 75% yield from MCK and PCl_5, bp 94°C, n_D^{20} 1.4560. Found: C 58.84; H 6.88; Cl 34.60%. Calculated from C_5H_7Cl: C 58.55; H 6.88; Cl 34.57%.

Synthesis of Dihalocyclopropanols and Execution of Competitive Reaction

Method a. Alkaline Hydrolysis of Haloforms [18]. A 0.1-mole portion of $CHCl_3$ or $CHBr_3$ was added dropwise over the course of 1 h with stirring and cooling (from −10 to −15°C) to 0.1 mole of the olefin and 0.1 mole of potassium tert-butoxide in 40 ml of n-pentane. The reaction mixture was stirred for an additional 30 min and hydrolyzed by water. The organic layer combined with the pentane extracts from the aqueous layer (two 20-ml portions) was dried over $MgSO_4$, and the respective dihalocyclopropane was isolated after vacuum distillation of the solvent.

Method b. Thermal Dissociation of Sodium Trichloroacetate [18]. A solution of 0.1 mole of CCl_3COONa and 0.1 mole of the olefin in 20 ml of absolute dimethoxyethane was boiled with stirring until the cessation of the evolution of CO_2 (80°C, 5-8 h). The mixture was filtered free from the brown precipitate, which was washed with absolute ether (three 30-ml portions). The corresponding dichlorocyclopropane was isolated by vacuum distillation after the solvent was driven off.

The competitive reactions were carried out according to similar procedures with the mixing of a 2- or 10-fold excess relative to the dihalocarbene source or each of the olefins, which were taken in equimolar amounts. The corresponding reaction mixtures were analyzed by GLC, and the values of the relative rate constants for the addition of the dihalocarbenes were calculated in the usual manner [1, 5, 10].

The yields and properties of the dihalocyclopropanes obtained, with the exception of a number of aryl-gem-dihalocyclopropanes [1, 10, 19] and 1,1-dicyclopropyl-2,2-dichlorocyclopropane [11], which we previously described, are presented in Table 5. The spectral characteristics of the dihalocyclopropanes synthesized have been given in [2], and the PMR spectra of most of the aryldihalocyclopropanes are in [3].

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CONCLUSIONS

The method of competitive reactions has been used to investigate the activity of p- and α-substituted styrenes and 1-substituted cyclopropylethylenes in reactions with dihalocarbenes. The weakening of the influence of the substituents on the activity of the double bond with their increasing nucleophilic properties has been demonstrated, and it has been concluded that there is a single mechanism underlying the reactions of dichlorocarbene with the olefins investigated.

LITERATURE CITED

1. O. M. Nefedov and R. N. Shafran, Zh. Obshch. Khim., 37, 1561 (1967).
2. R. N. Shafran, Dissertation, Moscow (1973).
3. A. K. Mal'tsev, A. Ya. Shteinshneider, A. V. Kessenikh, and O. M. Nefedov, Teor. Eksp. Khim., 8, 265 (1972).
4. O. M. Nefedov and A. I. Ioffe, Zh. Vses. Khim. O-va D. I. Mendeleeva, 19, 305 (1974).
5. M. Jones and R. Moss (editors), Carbenes, Wiley, New York (1972); W. Kirmse, Carbene Chemistry, Academic Press, New York (1971).
6. O. M. Nefedov and R. N. Shafran, Izv. Akad. Nauk SSSR, Ser. Khim., 538 (1965).
7. P. S. Skell and M. S. Cholod, J. Am. Chem. Soc., 91, 7131 (1969).
8. M. I. Kravchenko, Dissertation, Moscow (1973).
9. D. Seyferth, J. Y.-P. Mui, and R. Damrauer, J. Am. Chem. Soc., 90, 6182 (1968).
10. O. M. Nefedov, R. N. Shafran, and N. N. Novitskaya, Zh. Org. Khim., 8, 2075 (1972).
11. O. M. Nefedov, I. E. Dolgii, I. B. Shvedova, and R. N. Shafran, Izv. Akad. Nauk SSSR, Ser. Khim., 1885 (1972).
12. M. A. Behal, Bull. Soc. Chim. France, 50, 632 (1888).
13. N. Kizhner, Zh. Russk. Fiz.-Khim. O-va, 43, 1163 (1911).
14. G. B. Bachman, G. L. Carlson, and M. Robinson, J. Am. Chem. Soc., 73, 1964 (1951).
15. G. S. Kolesnikov and G. M. Pogosyan, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 227 (1958).
16. R. W. Strassburg, R. A. Gregg, and C. Walling, J. Am. Chem. Soc., 69, 2141 (1947).
17. Ya. M. Slobodin, V. I. Grigor'eva, and Ya. É. Shmulyakovskii, Zh. Obshch. Khim., 23, 1873 (1953).
18. W. E. Parham and E. E. Schweizer in: Organic Reactions [Russian translation], Vol. 13, IL (1966), p. 66.
19. O. M. Nefedov and R. N. Shafran, Zh. Org. Khim., 10, 477 (1974).