THE EFFECT OF SOLVENTS ON THE SELECTIVITY OF ELECTROPHILIC REAGENTS. III.*

THE ADDITION OF DICHLOROCARBENES TO OLEFINS

J. DOLANSKÝ**,† V. BAŽANT and V. CHVALOVSKÝ

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol

Received November 29th, 1972

A study was made of the effect of aromatic (benzene, toluene, and *p*-xylene) and ethereal (di-n-propyl ether, di-isopropyl ether, di-n-butyl ether, and tetrahydrofuran) solvents and n-heptane on the selectivity of the addition of dichlorocarbene, generated both by thermal decomposition of phenyl(bromodichloromethyl)mercury (*A*) at 80°C, and by thermal decomposition of trichloromethyltrichlorosilane (*B*) at 200°C, to a series of olefins. It was found that with sterically less hindered olefins the selectivity of the dichlorocarbene generated by method *B* decreases in n-heptane as solvent and increases with increasing proton-donor ability of other solvents. In the case of sterically hindered olefins also greater steric demands of the solvated reagent play a role. Contrarily, changes in the selectivity of the dichlorocarbene generated by method *A* along the series of the solvents studied do not exceed experimental errors.

So far, we have investigated the effect of solvents on the selectivity of electrophilic reagents in several radical reactions: radical halogenation of substituted toluenes[1] and radical addition of CF_3J, CCl_3Br, and HBr to olefins of vinylic type[2]. The observed increase in the selectivity of reagents in solvents which act as σ-electron donors (ethers) or π-electron donors (aromatic solvents) led us to a working hypothesis that in these systems the attacking radical forms a complex with π-electron system of aromatic solvents, or by interaction with unshaired electron pair of ethereal solvents, and that this complex is less electrophilic and more sterically demanding. From a comparatively good correlation of relative rate constants of the radical reactions with the basicity of solvents it was concluded that the ease with which the complex is formed increases with the basicity of solvent. The same effect was also observed on decreasing reaction temperature and increasing solvent concentration.

This work deals with the effect of the basicity of solvents on the selectivity of the electrophilic reaction with ionic mechanism, the addition of dichlorocarbene to olefins. Of a variety of the methods for generating dichlorocarbene, we have chosen Haszeldine's method of decomposition of trichloromethyltrichlorosilane[3] at 200 to 250°C and Seyferth's method of decomposition of phenyl(trihalogenomethyl)mer-

* Part II: This Journal *33*, 2886 (1968).

** Present address: Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague - Řež.

cury[4] at 80°C. The electrophilic character of the dichlorocarbene generated by Haszeldine's method was already evidenced[5]. The measurements of relative rate of the addition of the so generated dichlorocarbene to the couple of the olefins, vinyltrichlorosilane-cyclohexene, in tetrachloromethane, n-heptane, *p*-xylene, and di-n-butyl ether have indicated that the selectivity of the addition might be increased by using the solvents which are σ or π-donors[6]. The electrophilic character of the dichlorocarbene generated by Seyferth's method has also been established[7,8]. The effect of solvents on the initial rate of the reaction of $C_6H_5HgCBrCl_2$ with 2,3-dimethyl-2-pentene[8] as well as on the selectivity of the addition of the so generated dichlorocarbene[9] has been found to be relatively small.

An association of the reagent with solvent may be inferred from the measurements of the rates of the additions of other electrophilic reagents proceeding likely *via* similar mechanism as the addition of dichlorocarbene. Thus, the rate of the addition of hydrogen chloride and hydrogen bromide to cyclohexene and 3-hexene has been reported[10] to be fast in the solvents which are not, or are only weak, electron donors (*e.g.* heptane, xylene) and slow in the solvents which act as strong electron donors (ether, dioxane). The reactivity is not thus essentially dependent upon their dielectric constants. Similar solvent effects were also observed in the study of the addition of hydrogen bromide and hydrogen chloride to α-pinene[11]. The rate of the epoxidation of cyclohexene by perbenzoic acid has been found[12] to be slowest in ethereal solvents. The rate of iodination of olefins[13,14] seems to be strongly influenced by formation of a complex by interaction of iodine with solvent. Apart from kinetic data, a number of physical data prove the formation of charge-transfer complexes of ethers[15] and aromatic hydrocarbons[16,17] with electrophiles (halogens, proton, BF_3, *etc.*).

EXPERIMENTAL

Solvents were dried in the usual way and distilled prior to using. Their purity was checked by g.l.c. and by refractive index and density determinations.

1-*Heptene* (I) was prepared by pyrolysis of heptyl acetate[18] and cyclohexene (*II*) was obtained by dehydration of cyclohexanol[19]. Both hydrocarbons were subjected to fractionation and dried over Calsit 4A molecular sieve prior to use. 2-*Ethyl*-1-*butene* (*purum*, Fluka) was rectified, 2,3-*dimethyl*-2-*butene* (IV) and 3,3-*dimethyl*-1-*butene* (V) (*puriss.*, Fluka) were used without further purification.

Phenyl(bromodichloromethyl)mercury was prepared by the reaction of 117 g of phenylmercury chloride with 116 g of bromodichloromethane and 40 g of potassium tert-butylate[20]. The reaction afforded 25 g (18%) of needle-crystals melting 109–110°C (dec.). *Trichloromethyltrichlorosilane* was obtained in 63% yield by UV-induced chlorination of chloromethyltrichlorosilane. The product was purified by distillation at 155°C under nitrogen atmosphere.

7,7-*Dichloronorcarane*. A mixture of 26·4 g (0·06 mol) of phenyl(bromodichloromethyl)mercury, 14·8 g (0·18 mol) of cycloxenene, and 100 ml of dry benzene was refluxed for 6 h. A total of 21 g (98%) of phenylmercury bromide, m.p. 284–286°C, was collected by filtration. The solvent and the excess olefin were removed by distillation at 25°C/5 Torr. The residue was trap-to-trap distilled (*in vacuo*, the condenser was cooled to −78°C). 7,7-Dichloronorcarane was distilled through a short column filled with metallic spirals, b.p. 78–79°C/15 Torr (lit.[3] 79–90°C/15 Torr) n_D^{20} 1·5023 (lit.[21] 1·5022). The same procedure was used to prepare 1-*pentyl*-2,2-*dichlorocyclo-*

propane, b.p. 82—83°C/15 Torr (lit.[21] 73—75°C/110 Torr), n_D^{20} 1·4539 (lit.[21] 1·4495), 1,1-*diethyl*-2,2-*dichlorocyclopropane*, b.p. 56—56·5°C/16 Torr (lit.[22] 51·5—52·5°C/14 Torr), n_D^{20} 1·4608 (lit.[22] 1·4608), 1-*tert-butyl*-2,2-*dichlorocyclopropane*, b.p. 33—34°C/15 Torr, n_D^{20} 1·4518; for $C_7H_{13}Cl_2$ (168·3) calculated: 50·30% C, 7·24% H; found: 50·26% C, 7·23% H, and 1,1,2,2-*tetramethyl*-3,3-*dichlorocyclopropane*, m.p. 50—51°C (lit.[23] 49·8—50·5°C).

Competition addition of Seyferth reagent. To a 6—8 ml glass ampoule, phenyl(bromodichloromethyl)mercury and both olefins were successively weighed, the appropriate amount of the solvent was pipetted and the ampoule was sealed. The weighed amounts of the olefins were in reciprocal ratio to their reactivities (determined by preliminary experiments). Phenyl(bromodichloromethyl)mercury was used in the amounts which ensured that the conversion of olefins did not exceed 5 per cent. The sealed ampoule was fastened to a vibratior, placed in a temperature-controlled bath (80°C ± 0·05°C) and shaken for 3 h. After cooling, the solid phenylmercury bromide was removed by filtration. As even a small amount of phenylmercury bromide would interfere with chromatographic analysis, the reaction mixture was cooled in the distillation flask to −78°C, distilled under reduced pressure (0·1 Torr), while gradually increasing its temperature to +80°C, and collected in the flask cooled to −78°C.

Competition additions of Haszeldine reagent to the olefins were performed in the same way, except that the temperature of Wood metal bath was kept at 200°C and the reaction mixture was analysed by g.l.c.

Analysis of reaction mixtures. The reaction mixture from the additions of Seyferth reagent were analysed on Griffin D6 chromatograph (Griffin and George, London). Except the addition in *p*-xylene, the analysis was made on a column (0·4 cm i.d., 200 cm long), filled with 10% poly(ethylene glycol) 1 000 (Carlo Erba) on Chromosorb. The analysis of the reaction mixture from the addition in *p*-xylene was carried out on a column (0·4 cm i.d., 300 cm long) filled with 15% silicone elastomer E 301 on Chromosorb. The reaction mixtures from the additions of Haszeldine reagent were analysed on a chromatograph produced by Vývojové dílny ČSAV, Prague, and equipped with thermal-conductivity detector. In the measurements of relative reactivities of the couples heptene–cyclohexene, heptene–2-ethyl-2-butene, and heptene–3,3-dimethyl-1-butene, in all the solvents but *p*-xylene, the reaction products were separated on a column (0·6 cm i.d., 200 cm long) filled with 6% poly(ethylene glycol) 1 000 (Carlo Erba) on Chromosorb. The reaction mixture from the addition carried out in *p*-xylene was analyzed with the use of a column (0·4 i.d., 300 cm long) filled with 3% Silicone Elastomer E 301 on Chromosorb. The same column was used to analyze the mixtures from the additions of Haszeldine reagent to the couple cyclohexene-2,3-dimethyl-2-butene in all the solvents.

Relative rate constants of the addition of dichlorocarbene to olefins were calculated in the usual manner[24,25]. The weight ratios of the addition products were obtained from the ratios of corresponding peak areas by means of calibration graphs. Each competition addition was repeated 3—6 times. Each sample was chromatographed thrice and relative rate constant k_{rel} was taken as the average value of the three measurements. Standard deviation σ was estimated from the coefficient of variation according to Dean and Dixon[26].

RESULTS AND DISCUSSION

Relative rate constants of the addition of the dichlorocarbene generated by Seyferth's method to olefins are summarized in Table I. As follows from Student test, the differences between individual average values of k_{rel} in different solvents may be

explained by accidental experimental errors. In order to shift an equilibrium of formation of a weak complex between dichlorocarbene and a solvent in favour of its formation, we made several measurements using higher concentration of the solvent. From Table I it becomes immediately clear that the increase of solvent concentration from 60 to 90 v.% does not practically affect relative rate constants of the addition of Seyferth reagent to 1-heptene (*I*) and cyclohexene (*II*). From the above results it may be concluded that the selectivity of the dichlorocarbene generated by the above method is practically the same in all the solvents studied. It seems likely

TABLE I

Relative Rate Constants of the Addition of Dichlorocarbene Generated from $C_6H_5HgCCl_2Br$ to Olefins

Solvent	k_{II}/k_I [a]	2σ	k_{II}/k_I [b]	2σ	k_{III}/k_I [a]	2σ
n-Heptane	4·55	0·44	4·54	0·22	10·63	0·34
Benzene	4·37	0·30	4·49	0·24	10·35	0·63
Toluene	4·66	0·12	—	—	10·88	0·58
p-Xylene	4·75	0·22	—	—	10·80	0·51
Di-n-propyl ether	4·69	0·18	—	—	10·77	0·38
Di-iso-propyl ether	4·60	0·32	—	—	11·01	0·33
Di-n-butyl ether	4·76	0·38	4·71	0·33	10·86	0·50
Tetrahydrofuran	4·81	0·35	4·63	0·49	10·70	0·36

Solvent[a] 60% v., [b] 90% v.

TABLE II

Relative Rate Constants of the Addition of Dichlorocarbene Generated from Cl_3SiCCl_3 to Olefins

Solvent	k_{II}/k_I	2σ	k_{III}/k_I	2σ	k_{IV}/k_{II}	2σ	k_V/k_I	$2\sigma \cdot 10^3$
n-Heptane	2·76	0·15	5·01	0·11	18·89	1·06	0·1204	0·64
Benzene	2·77	0·12	4·82	0·20	18·04	1·08	0·1169	0·40
Toluene	2·89	0·18	5·47	0·18	20·78	1·30	0·1019	0·46
p-Xylene	3·43	0·18	5·78	0·47	23·02	1·06	—	—
Di-n-propyl ether	2·91	0·15	5·80	0·18	22·96	1·23	0·0987	0·62
Di-iso-propyl ether	3·34	0·22	6·88	0·12	25·89	1·19	—	—
Di-n-butyl ether	3·39	0·20	6·89	0·47	23·89	1·54	0·0977	0·92
Tetrahydrofuran	3·03	0·25	5·85	0·38	21·25	0·59	0·0916	0·78

that under these conditions dichlorocarbene is not solvated by (coordinated to) solvents that are σ or π-electron donors.

Relative rate constants of the addition of the dichlorocarbene generated by Haszeldine method to olefins are summarized in Table II. The results indicate that the so generated dichlorocarbene is electrophilic reagent, since the rate of the addition increases with the number of alkyl groups, *i.e.* with increasing electron density at the double bond. The selectivity is almost two times decreased, compared with the selectivity of Seyferth[27] reagent. This is not surprising in view of the known temperature dependence of the selectivity[5]. Of the olefins, the least reactive is 3,3-dimethyl-1-butene (*V*), likely due to a great steric hindrance towards attack of the double bond by the reagent, caused by bulky tert-butyl group.

Contrarily to Seyferth reagent, the selectivity of dichlorocarbene generated from Haszeldine reagent depends upon electron-donor properties of solvents. With all the couples of olefins studied the selectivity was found to be highest in ethereal solvents. The selectivity of the addition in benzene is nearly the same as in n-heptane; on going to the stronger electron donors, toluene and *p*-xylene, the selectivity increases, being highest in *p*-xylene, the strongest π-electron donor. Over-all change of the selectivity along the series of the solvents investigated is small; however, discussed differences in the selectivity quite unambiguously exceed experimental errors. In contrast to the aromatic solvents, with clean-cut dependence, the selectivity in the series of ethereal solvents cannot be correlated with any "basicity scale of ethers" (for "basicity scales" see *e.g.* ref.[15]). The position of individual ethers in these basicity scales strongly depends upon the type of the interaction measured as well as upon the sort of the quantity used to express the above mentioned interaction. It is very difficult to decide which of the above processes is most alike to the interactions assumed by us to occur during the addition.

The increased selectivity observed in the addition of Haszeldine reagent may be ascribed to a coordination of a solvent with the reagent, which both affects the electronic structure of the reagent (which would manifest itself in decrease of its selectivity) and increases its effective size. The second factor would play an important role especially in reactions with sterically hindered olefins. On going from the solvent not able of such an interaction to the solvent with strong coordinative ability, the reactivity of either olefin of the couple (or its conversion after the same time) decreases. This decrease, caused by changed electronic effects, is however greater with the olefin which has lower total +I effect of alkyl groups. Steric effects act in opposite way: reactivity decrease due to changed steric conditions is greater in the addition to more sterically hindered olefins, *i.e.* those with the greater total +I effect of alkyl groups, relative to 1-heptene. Relative importance of steric and electronic effects varies with different olefins. 1-Heptene (*I*) is least sterically hindered and has the lowest total +I effect. Both effects gradually increase along the series: cyclohexene (*II*) < 2-ethyl-1-butene (*III*) < 2,3-dimethyl-2-butene (*IV*). Although the electron density at the

double bond in 3,3-dimethyl-1-butene (*V*) is higher than in 1-heptene, the steric effect of the bulky tert-butyl group obviously prevails over electronic effects[2]. That is why on going from the solvent not able to coordinate with the reagent to the solvent with strong coordination ability, the reactivity of the former hydrocarbon decreases more than the reactivity of 1-heptene. The opposite role of electronic and steric effects may also be the reason why the differences between individual k_{rel}'s are so small.

On the other hand, the increase in the selectivity might also be explained by solvation of the transition state. This solvation could, under certain assumptions, exert the same effect on reaction rate and selectivity as does the solvation of the reagent. The solvation of the transition state would result in stabilization of the positive charge at the olefinic carbon and in decrease of the free energy of the transition state. This would lead to rate increase, if were the decrease of entropy, caused by solvation, not operated. Rate decrease would be observed only if the decrease in the entropy of the transition state were more important than the decrease in the free energy. On these quantities no data are available at the moment. The only fact which is known with certainty is that reaction rate decreases in electron-donor solvents (the conversion attained under identical conditions is lower than in n-heptane). In the case of the reaction under study it may be assumed that relative decrease of the electron density at the olefinic carbon in the transition state will be small, and so also the solvation of the transition state.

Comparison of the results of the measurements of selectivities of both reagents leads to surprising finding. On the one hand, nucleophilic solvents affect the selectivity of the addition of the less selective reagent, formed at the higher temperature, on the other hand, they do not exert any effect on the selectivity of Seyferth reagent which is twice as selective as Haszeldine reagent. The "indifference" of Seyferth reagent towards nucleophilic solvents may be explained by interaction of the so generated dichlorocarbene with another nucleophilic component of the reaction system; this interaction would prevail over the interaction with the solvent, so that it would not be influenced by the change of the solvent. The only component with such properties present in the reaction system is C_6H_5HgBr.

REFERENCES

1. Hradil J., Chvalovský V.: This Journal *33*, 2029 (1968).
2. Čapka M., Bažant V., Chvalovský V.: This Journal *33*, 2886 (1968).
3. Bewan W. J., Haszeldine R. N., Young J. C.: Chem. Ind. (London) *1961*, 789.
4. Seyferth D., Burlitch J. N., Heeren J. K.: J. Org. Chem. *27*, 1491 (1962).
5. Koutková J., Chvalovský V.: This Journal *37*, 2100 (1972).
6. Koutková J.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1966.
7. Seyferth D., Burlitch J. H.: J. Am. Chem. Soc. *86*, 2730 (1964).
8. Seyferth D., Yich-Pui Mni J., Burlitch J. M.: J. Am. Chem. Soc. *89*, 4953 (1967).
9. Gordon M. E.: *Thesis*. Massachusetts Institute of Technology, 1968.

10. O'Connor S. F., Baldinger L. H., Vogt R. R., Hennion G. F.: J. Am. Chem. Soc. *61*, 1954 (1939).
11. Hennion G. F., Irwin C. F.: J. Am. Chem. Soc. *63*, 860 (1941).
12. Renolen O., Ugelstad J.: J. Chim. Phys., Phys.-Chim. Biol. *57*, 634 (1960).
13. Robertson P. W., Butchers J. B., Durham R. A., Healy J. K., Heyes J. K., Johanneson J. K., Tait D. A.: J. Chem. Soc. *1950*, 2191.
14. Sergučev J. A., Šilov E. A.: Ukr. Chim. Ž. *1968*, 1025.
15. Searles S. J., Tamres M.: in the book: *The Chemistry of the Ether Linkage* (S. Patai, Ed.), p. 243. Interscience, New York 1967.
16. Brandon S. M., Tamres M., Searles S. J.: J. Am. Chem. Soc. *82*, 2129 (1960).
17. Keefer R. M., Andrews L. J.: J. Am. Chem. Soc. *77*, 2164 (1955).
18. Goldof H. A., Vibaut J. P.: Rec. Trav. Chim. *67*, 105 (1948).
19. Coleman G. H., Johnstone H. F.: Org. Syn., Coll. Vol. *1*, 183, (1941).
20. Seyferth D., Burlitch J. M.: J. Organometal. Chem. *4*, 127 (1965).
21. Seyferth D.: J. Am. Chem. Soc. *87*, 4259 (1965).
22. Weyerstall P., Klamann D., Finger C., Werden F., Buddrus J.: Chem. Ber. *100*, (6), 1858 (1967).
23. Doering W. V. E., Henderson W. A.: J. Am. Chem. Soc. *80*, 5274 (1958).
24. Ingold C. K., Shaw F. R.: J. Chem. Soc. *1927*, 2918.
25. Closs C. L., Schwartz C. M.: J. Am. Chem. Soc. *82*, 5729 (1960).
26. Dean R. B., Dixon W. J.: Anal. Chem. *23*, 636 (1951).
27. Seyferth D., Derteuzos H.: J. Organometal. Chem. *11*, 263 (1968).

Translated by J. Hetflejš.