════ REVIEW ════

Reactions of Cyclohexenyliodonium Salts*

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Abstract—The review discusses reaction paths of cyclohexenyliodonium salts in the presence of bases and nucleophiles, in particular those involving formation of cyclohexynes.

I. INTRODUCTION

Iodonium salts possess a two-coordinate positively charged iodine atom which makes these substrates highly reactive [1, 2]. The iodonio group is a strong

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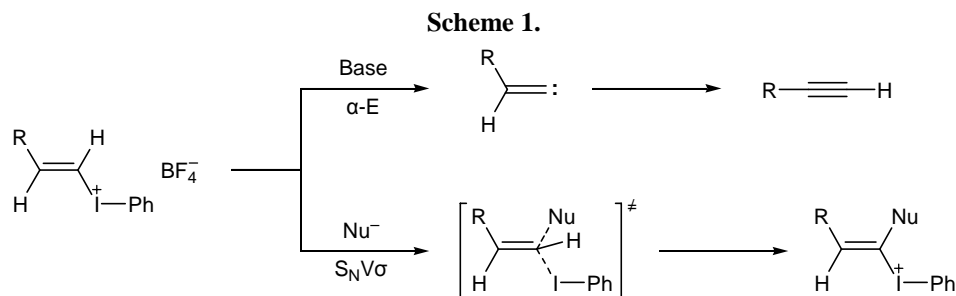
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electron acceptor [3] and an excellent nucleofuge [4]. Under the action of a mild base like carboxylate ions, simple 1-alkenyl(phenyl)iodonium salts undergo very facile α-elimination with formation of alkylidenecarbenes [1, 2, 5, 6] or react according to the S_N2 ($S_N V\sigma$) pattern via "in-plane" attack, leading to inversion of configuration (Scheme 1) [2, 7]. In order to examine other reaction paths, these facile reactions should be inhibited. 1-Alkyl substituent may be used for this purpose. However, the resulting secondary vinyliodonium salt is too unstable to be isolated due to spontaneous heterolysis to give more stable secondary vinyl cation. By contrast, primary vinyl cation cannot be generated under solvolysis conditions, as was demonstrated using a chirality probe [8].

1-Cyclohexenyl(phenyl)iodonium salts **1** are moderately stable; their heterolysis yields a secondary angle-strained vinyl cation, i.e., 1-cyclohexenyl cation **A**. Salt **1** undergoes various reactions, including S_N1-type solvolysis ($S_N V1$), S_N2 reaction via orthogonal attack ($S_N V\sigma$), Michael addition, and β-elimination (Scheme 2), but not $S_N V\sigma$ substitution or α-elimination.

The present review summarizes the above reactions of cyclohexenyliodonium salts with specific attention being focused on β-elimination leading to ring-strained cyclohexynes. Early attempts to generate cyclohexyne were carried out by Favorsky in 1912 g. [9]. Since then, the chemistry of small-ring cycloalkynes has attracted much interest [10, 11]. Although cycloheptyne

Scheme 1.

Base = RO⁻, Et₃N, CN⁻, pyridine, F⁻, RCOO⁻, Cl₂CHCOO⁻ ($pK_{BH^+} > 0$); Nu = Cl, Br, I, MeSO₃, R₂S, R₂Se, ROH ($pK_{BH^+} < 0$).

Scheme 2.
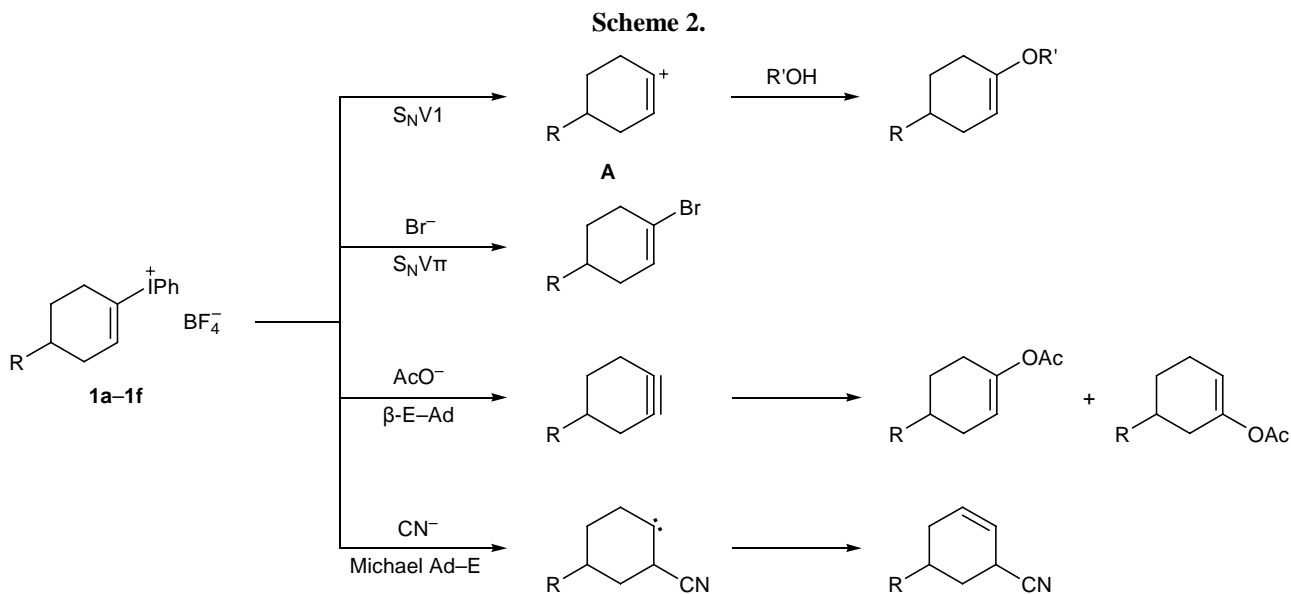
R = H (**a**), Me (**b**), Et (**c**), *t*-Bu (**d**), Ph (**e**), CN (**f**).

is characterized by a short lifetime in solution at –25°C [12], cyclohexyne can be isolated only in matrices at 77 K [13]. They can be generated as transient species by elimination reactions of appropriate precursors; however, these species readily react with nucleophiles or undergo oligomerization [10, 11]. A usual precursor of cyclohexyne is 1-halocyclohexene which is subjected to strongly basic conditions, e.g., to the action of potassium *tert*-butoxide or amide [14, 15]. Such strong bases can induce isomerization of cyclohexyne into 1,2-diene, and formation of an appreciable amount of the latter isomer always accompanies the main product [16]. Thus a mild and general method for selective generation of cyclohexyne is awaited for the study of its reactivity.

II. S_N V1 SOLVOLYSIS

While examining the reactivity of cyclohexenyl-iodonium salts, let us start with solvolysis in aqueous and alcoholic solvents. The solvolysis of 4-*tert*-butyl-1-cyclohexenyl(phenyl)iodonium tetrafluoroborate (**1d**) was carried out in various solvents at 25–70°C [4]. The products were 1-alkoxycyclohexene **2** (and/or cyclohexanone **3**) and cyclohexenyl(iodo)benzenes **4** together with iodobenzene (Scheme 3). Compounds **2** and **3** are expected S_N1 solvolysis products, whereas compounds **4** (mainly *ortho* isomer *o*-**4**, 85%) must be formed via Friedel–Crafts-type recombination (yield 15% in MeOH to 35% in trifluoroethanol). The recombination must occur within the tight ion–molecule pair derived from cyclohexenyl cation **A** and iodobenzene.

Kinetic studies showed that the nucleofugality of the phenyliodonio group is greater by about 6 orders of magnitude than that of trifluoromethylsulfonato group (which is one of the best leaving groups [17]) and by 12 orders of magnitude than that of iodide. The formation of cation **A** was also substantiated by kinetic studies. The rate of solvolysis depends only slightly on the solvent ionizing power Y_{OTs} [18] with a small slope

Scheme 3.

Scheme 4.

Scheme 5.
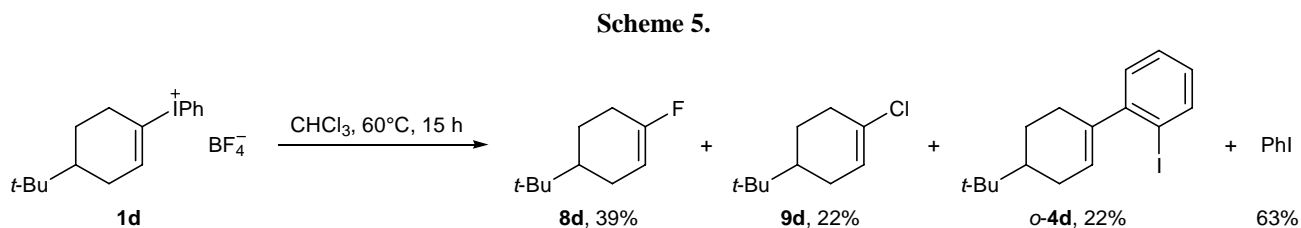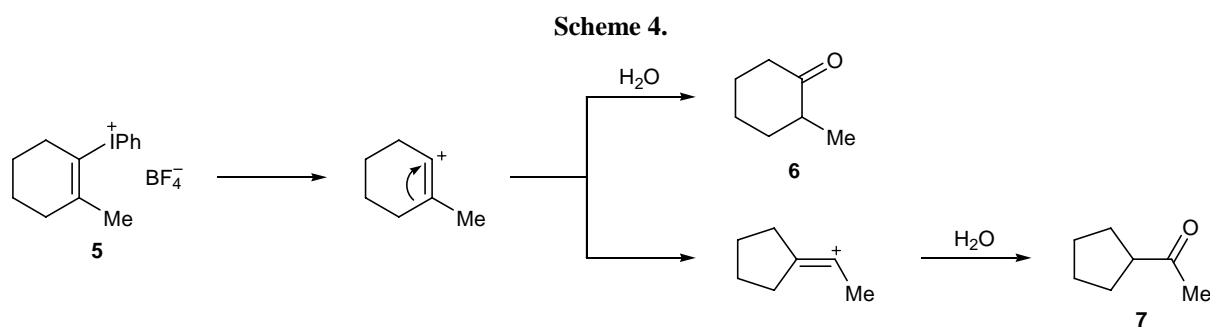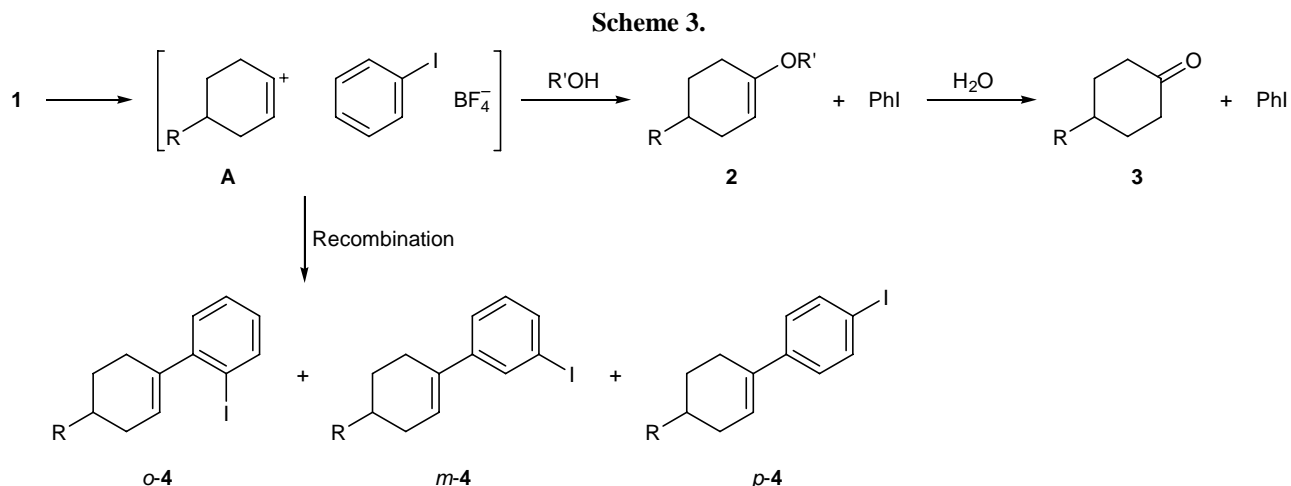
$m = 0.12$. These results conform to a reaction with no charge separation where a ionic substrate produces ionic intermediate. Furthermore, β-methyl substitution strongly (by a factor of ~250) accelerates the solvolysis and leads to 1,2-rearrangement with ring contraction (Scheme 4). Thus the solvolysis of 2-methyl-1-cyclohexenyliodonium salt **5** in aqueous ethanol gives cyclopentyl methyl ketone (**7**), as well as 2-methyl-cyclohexanone (**6**).

Thermolysis of tetrafluoroborate **1d** in chloroform gave 1-fluorocyclohexene (**8d**) and 1-chlorocyclohexene (**9d**) together with the recombination product *o*-**4d** [19] (Scheme 5). The formation of these products strongly suggests intermediacy of vinyl cation **A** which is capable of abstracting chlorine from chloroform and fluorine from tetrafluoroborate ion [20]. Vinyl cation like **A** can be generated even in chloroform under weakly nucleophilic conditions.

III. $S_NV\pi$ REACTIONS

Reactions of **1** in chloroform in the presence of stronger nucleophiles like bromide, azide, and thiolate ions gave exclusively the corresponding 1-substituted products with simultaneous formation of iodobenzene (Scheme 6). These products cannot be formed from intermediate vinylic cation, but they should result from direct nucleophilic substitution. Since the in-plane attack is impossible for steric reasons, the reaction should involve orthogonal attack ($S_NV\pi$). This mode of vinylic S_N2 reaction was theoretically shown to be feasible [21] and was demonstrated by kinetic studies [22] and theoretically to occur in a ligand-coupling manner within a hypervalent adduct, λ^3-iodane [23]. Direct substitution with carbon-centered and other nucleophiles could be achieved with the aid of copper salt [24].

Scheme 6.

$$Nu^- = Br^-, N_3^-, ArS^-.$$
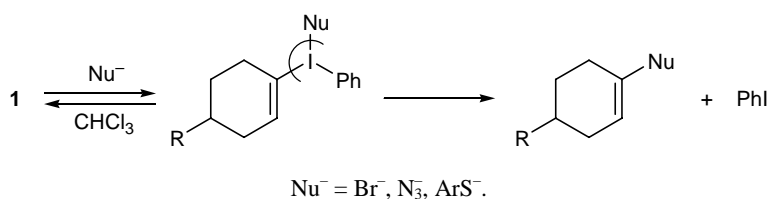
IV. β-ELIMINATION–ADDITION

Nucleophiles can also act as bases, as was revealed in competing S_N2/α-elimination with 1-alkenyliodonium salts [6]. Although azide and thiolate as bases induce α-elimination of 1-alkenyliodonium salts, they act as nucleophiles toward cycloalkenyliodonium salt **1**, giving rise to $S_NV\pi$ reaction. By contrast, acetate and fluoride were found to operate as bases toward **1** in chloroform to induce β-elimination (but α-elimination of 1-alkenyl substrates). When 4-substituted 1-cyclo-hexenyliodonium salts **1** were allowed to react with tetrabutylammonium acetate in chloroform at 60°C, regioisomeric 4- and 5-substituted 1-acetoxycyclo-hexenes **10** and **11** were obtained (Scheme 7) [25] as *ipso* and *cine* substitution products [26]; the isomer ratio **10**/**11** depended on the substituent in the substrate and changed from 28:72 (**1d**, R = *t*-Bu) to 81:19 (**1f**, R = CN) as shown in Table 1. Isomeric 5-substituted iodonium substrates **12** gave the same pair of isomeric products in a ratio similar to that obtained with salt **1**. Furthermore, the olefinic hydrogen atoms in **10** and **11** were replaced by deuterium in the presence of a deuteron source, MeOD. These results are interpreted best in terms of the β-elimination–addition mechanism (E–Ad) involving cyclohexyne intermediate **B**
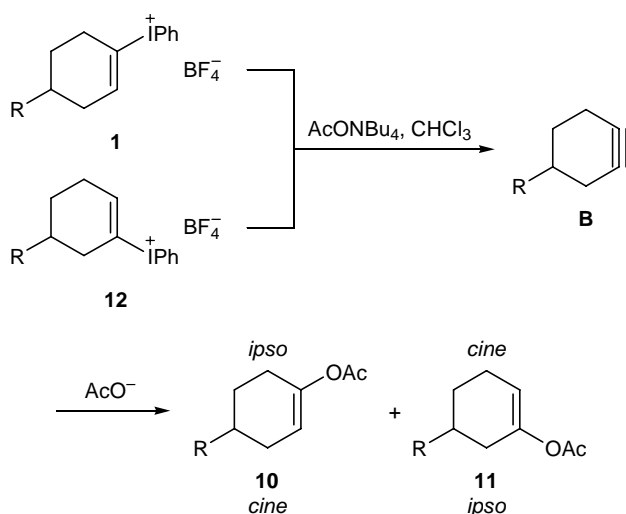
(Scheme 7). The product ratio must reflect the regio-selectivity of nucleophilic addition to cyclohexyne **B**.

In fact, the intermediate cyclohexyne could be trapped effectively with tetraphenylcyclopentadiene (TPCP) to give adduct **13** (Scheme 8). Acetate and fluoride ions as bases generate cyclohexyne inter-mediate almost quantitatively, while amines are poor bases in this reaction (Table 2). Cyclohexyne could also be trapped as platinum complex **14** (Scheme 9).
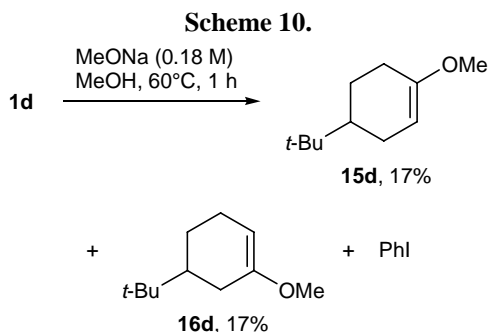
Scheme 8.
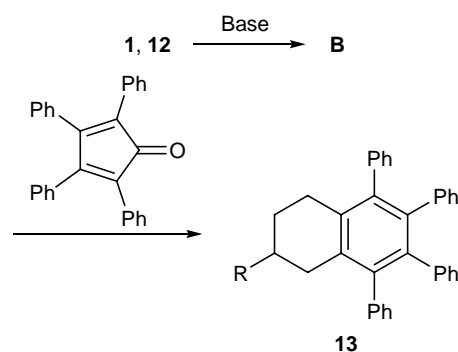
Scheme 9.
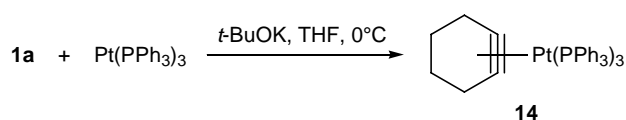
Compound **1d** in methanol in the presence of a weak base like acetate gives only the *ipso* substitution product (compound **15d**). In the presence of sodium methoxide, both *ipso* and *cine* products **15d** and **16d** are formed (Scheme 10). Although acetate base still allow the S_NV1 reaction to occur in methanol, sodium methoxide induces β-elimination to give cyclohexyne **B**, and nucleophilic trapping of the latter affords sub-stitution products **15d** and **16d** (E–Ad mechanism).

As noted above, the reaction of salt **1d** with bromide ion in chloroform yields exclusively the *ipso*-substitution product **17d**; however, both *ipso* and *cine* products **17d** and **18d** were obtained when both bromide and acetate ions were simultaneously present in the reaction mixture. In addition, acetates **10d** and

Scheme 7.

Scheme 10.

15d, 17%

16d, 17%

11d, as well as iodobenzene, were formed. Compounds **17d** and **18d** were formed from intermediate **B** in competition with acetate trapping to give **10d** and **11d**. Scheme 11 shows a typical composition of the reaction mixture.

Scheme 11.

17d, 19%

18d, 29%   7%   12%   80%
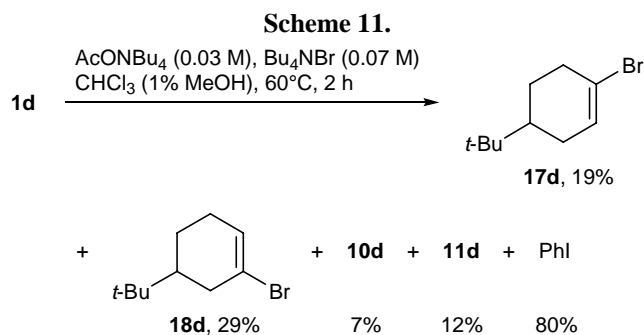
The reaction of salt **1d** with piperidine was examined in chloroform; the major isolated products were two isomeric cyclohexanones **3d** and **19d** (Scheme 12). Compounds **3d** and **19d** resulted from hydrolysis of the *ipso* and *cine* enamines which were formed by nucleophilic addition of the secondary amine to intermediate cyclohexyne **B**. In addition, appreciable amounts of by-products **8d**, **9d**, and *o*-**4d**, which are characteristic of cationic intermediate **A**, were obtained. Such by-products were detected in trapping experiments with TPCP in reactions of **1d** with amines, where the yield of the TPCP adduct with cyclohexyne **13** was not high (Table 2).
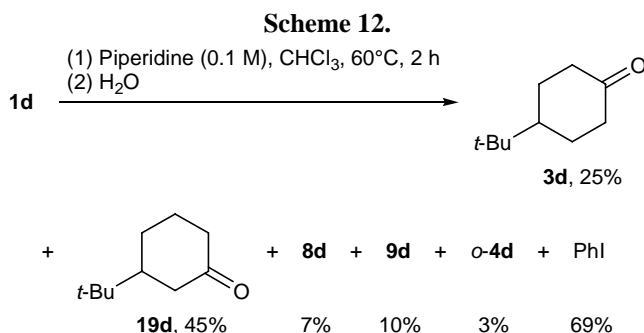
Scheme 12.

3d, 25%

19d, 45%   7%   10%   3%   69%

Table 1. Ratios of products **10** and **11** in the reactions of isomeric iodonium salts **1** and **12** with tetrabutylammonium acetate[a]

Substituent[b]	1	12
Me	46:54	39:61
Et	39:61	
t-Bu	28:72	21:79
Ph	57:43	49:51
CN	81:19[c]	

[a] The reactions were carried out in chloroform at 60°C; $[AcONBu_4] = 0.10$ M.
[b] Substituent R in position *4* or *5* of salt **1** or **12**.
[c] From a mixture of **1f** and **12f** at a ratio of 61:39.

Table 2. Yields (%) of adduct **13** in reactions of salts **1** and **12** in the presence of TPCP[a]

Base (*c*, M)	1a	1b	1c	1d	1e	12d	1f
$AcONBu_4$ (0.01)	90	84	86	98	91	70	64
$FNBu_4$ (0.01)	81	100	95	98	94	63	37
MeONa (0.18)[b]			87	81			
Piperidine (0.10)				52			
Et_3N (0.10)				29			

[a] The reactions were carried out in chloroform, $[1] = [12] = 3$–8 M, $[TPCP] = 10$ mM, 60°C, 1–2 h.
[b] In methanol.

The formation of the above by-products suggests that β-elimination with amines involves cyclohexenyl cation **A** as intermediate, i.e., it follows the E1 mechanism. Correspondingly, no primary isotope effect of β-deuterium was observed with the 2,6,6-trideuterated substrate, **1d**-d_3 ($k_H/k_D \approx 1.1$). By contrast, a primary isotope effect $k_H/k_D = 2.5$ was observed in the reaction with acetate. We can conclude that very efficient elimination with the anionic base occurs according to the E2 mechanism. Acetate ion is more basic than triethylamine in an aprotic solvent [27], and it is reasonable to presume that acetate induces the E2 reaction and that amine gives rise to heterolysis leading to the E1 reaction.

V. REGIOSELECTIVITY OF NUCLEOPHILIC ADDITION TO CYCLOHEXYNES

All the above examples of formation of *ipso* and *cine* substitution products from *tert*-butyl-substituted substrates **1d** and **12d** may be rationalized as the results of nucleophilic addition to intermediate cyclo-
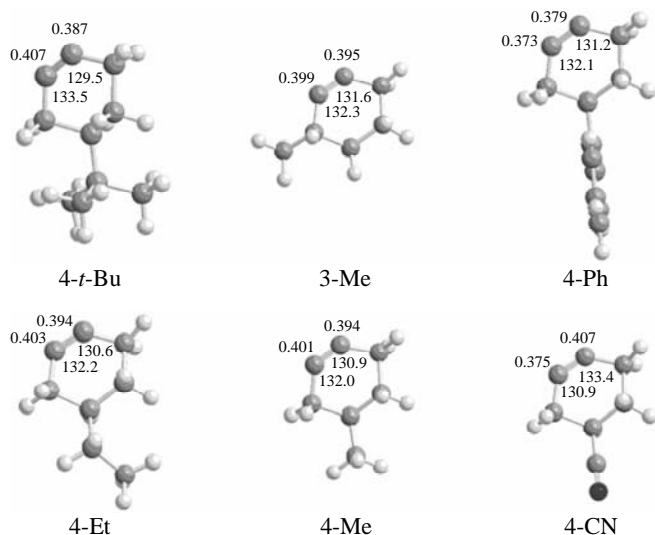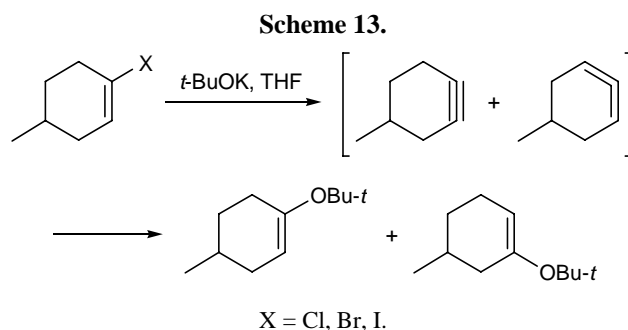
Fig. 1. Bond angles and populations of the lowest unoccupied molecular orbital at the acetylenic carbon atoms in substituted cyclohexynes, calculated at the B3LYP/6-31G(*d*) level.

Scheme 13.

X = Cl, Br, I.

hexyne **B**. The *ipso/cine* isomer ratio reflects primarily the regioselectivity of nucleophilic addition and its weak dependence on the nucleophile nature. Such regioselectivity of addition to cycloalkynes was previously noted in some publications [10, 11], and relatively careful examinations were made for methyl-substituted cyclohexynes generated from 1-halocyclohexenes by the action of a strong base (Scheme 13) [14, 15]. The ratio of the *ipso/cine* substitution prod-

ucts formed under these conditions varied over a wide range, from 98:2 to 56:44, probably due to change in the fraction of intermediate 1,2-cyclohexadiene [16]. For that reason, no reliable data on the regioselectivity were available, and the results obtained in the reaction of acetate ion with various cyclohexenyliodonium salts **1** (Table 1) provide the first data of this kind for nucleophilic addition to substituted cyclohexynes.

A similar regioselectivity was observed for the reaction of dehydrobenzene and was rationalized in terms of inductive polar effects of the substituents [10, 28]. The present results for the 4-cyano and 4-alkyl derivatives seem to conform to the electronic considerations, but those obtained within alkyl derivatives are difficult to be reconciled with electronic inductive effects: the σ_I values for alkyl groups are similar [29], and the position of substitution is separated by two bonds from the reaction site. What is the origin of the regioselectivity of nucleophilic addition?

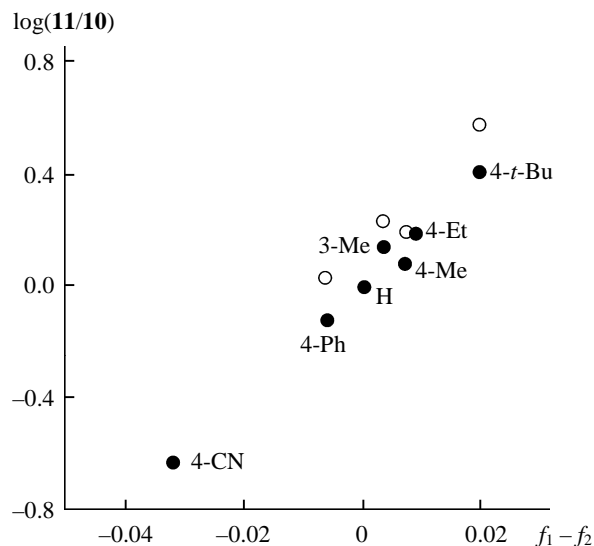**Fig. 2.** Semilog plot of the ratio of acetates **11** and **10** obtained from salts **1** (dark circles) and **12** (light circles) versus the difference in the LUMO populations ($f_2 - f_1$). The data for 3-methylcyclohexyne (3-Me) are also given.
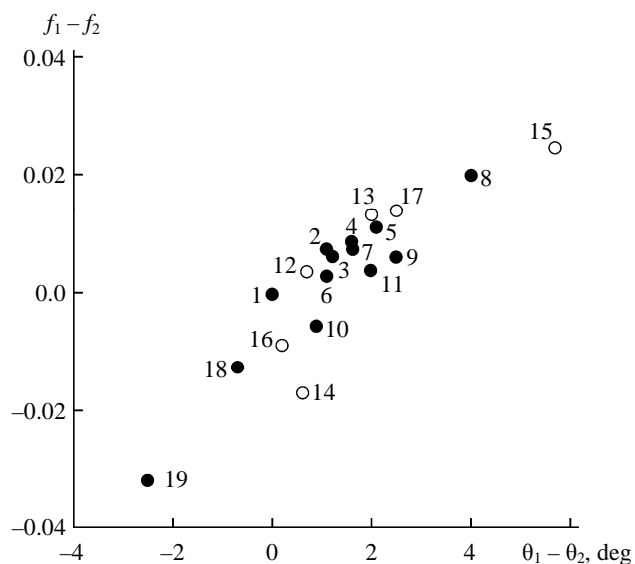

Fig. 3. Plot of the LUMO populations ($f_2 - f_1$) versus bond angles ($\theta_2 - \theta_1$) for 4-substituted (dark circles) and 3-substituted cyclohexynes (light circles).

From the molecular orbital considerations, the lowest unoccupied molecular orbital (LUMO) of cyclohexyne must be important in nucleophilic reaction, and theoretical calculations were performed at the B3LYP/6-31G(d) level. Figure 1 compares the LUMO populations and bond angles at the reaction centers C^1 and C^2. The selectivity values [log($11/10$)] for 4-substituted cyclohexynes **B** and equivalent values for the 3-methyl derivative are plotted against the differences between the LUMO populations at C^2 and C^1 ($f_2 - f_1$) in Fig. 2. A good correlation is observed between the selectivity and LUMO populations, including the 4-phenyl and 4-cyano derivatives.

The bond angles at the acetylenic carbon atoms are about 130°, but they depend on the substituent. The difference in the LUMO populations increases as the difference in the bond angles rises. Figure 3 shows the $f_2 - f_1$ values plotted against the differences in the bond angles at C^2 and C^1 ($\theta_2 - \theta_1$). The acetylenic atom with the larger bond angle, i.e., less deformed carbon atom, has a higher LUMO population and is more electrophilic than the atom deformed to a stronger extent. The selectivity depends on the LUMO population which is controlled by the ring structure determined by the bond angles at the acetylenic carbon atoms.

VI. MICHAEL ADDITION–ELIMINATION

Another possible reaction of nucleophile at the β-position of vinyliodonium ion is Michael addition. This reaction mode was found for the first time in the reaction of cyanide ion with cyclohexenyliodonium salt **1** [30]. The reaction of salt **1d** with tetrabutylammonium cyanide afforded allylic cyanocyclohexene **20d** together with *ipso* and *cine* cyanides **21d** and **22d** (Scheme 14).** 1-Cyanocyclohexene derivatives **21d** and **22d** may be formed via the E–Ad mechanism by nucleophilic trapping of cyclohexyne intermediate **B**.

The formation of a characteristic allylic product **20** may be interpreted in terms of the elimination–addition mechanism (E–Ad) involving 1,2-cyclohexadiene **C** as an extension of the E–Ad mechanism involving cyclohexyne **B** (Scheme 15). Had compound **20** been formed through intermediate **C**, an external proton would add to C^2 in **20**, which could be detected by carrying out the reaction with deuterated substrate


** Appreciable amounts of compound **23** and benzene were formed as a result of cleavage of the C_{arom}–I bond. These compounds were the major products in the homolytic reaction due to electron transfer from cyanide ion to iodonium.

Scheme 14.

Bu$_4$NCN (0.01 M)
CHCl$_3$, 60°C, 1 h

1d

20d, 18%

21d, 5%

22d, 12%

23d, 25%   64%   19%
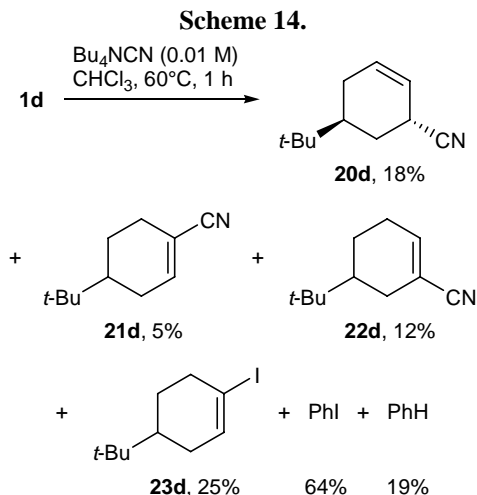
1-d_3. An alternative pathway is Michael addition–elimination (Ad–E) through iodonium ylide **D** and carbene **E**, followed by 1,2-rearrangement of the latter (Scheme 15). In this case, deuterated substrate **1**-d_3 should maintain deuterium at C^2. The reaction of **1**-d_3 containing about 90% of deuterium was examined, and ^{1}H NMR analysis of the products showed that deuterium atoms therein were retained being distributed over C^1, C^2, and C^3 of **20**. This result clearly excludes the first E–Ad mechanism through 1,2-diene **C** but is consistent with the mechanism of Michael Ad–E rearrangement through intermediate ylide **D** and carbene **E**. 1,2-Migration of hydrogen in carbene **E** occurs predominantly from the unsubstituted CH$_2$ carbon atom rather than from the CHCN group. Such selectivity was supported by theoretical calculations [30]. In the transition state for 1,2-migration of hydrogen, the positive charge is partially developed on the carbon of migration origin, and the cyano group has an adverse effect on that transition state. The formation of iodonium ylide, followed by elimination to give carbene has been reported in the Michael reaction of alkyliodonium salts [31].

Alternatively, allylic product **20** could be formed from allylic cation **F**, but the latter cannot arise via 1,2-hydrogen shift from cyclohexenyl cation **A** if it could be generated under these conditions. The cationic path can lead to **20** without loss of deuterium, but this route seems to be improbable. Furthermore, no allylic substitution product was obtained in the solvolysis of salt **1** under basic conditions, although cation **A** was detected as the major intermediate [4]. In conclusion, the formation of allylic substitution product **20** is interpreted best in terms of Michael addition of cyanide ion, followed by elimination to give carbene **E** which rearranges into **20**.

Scheme 15.
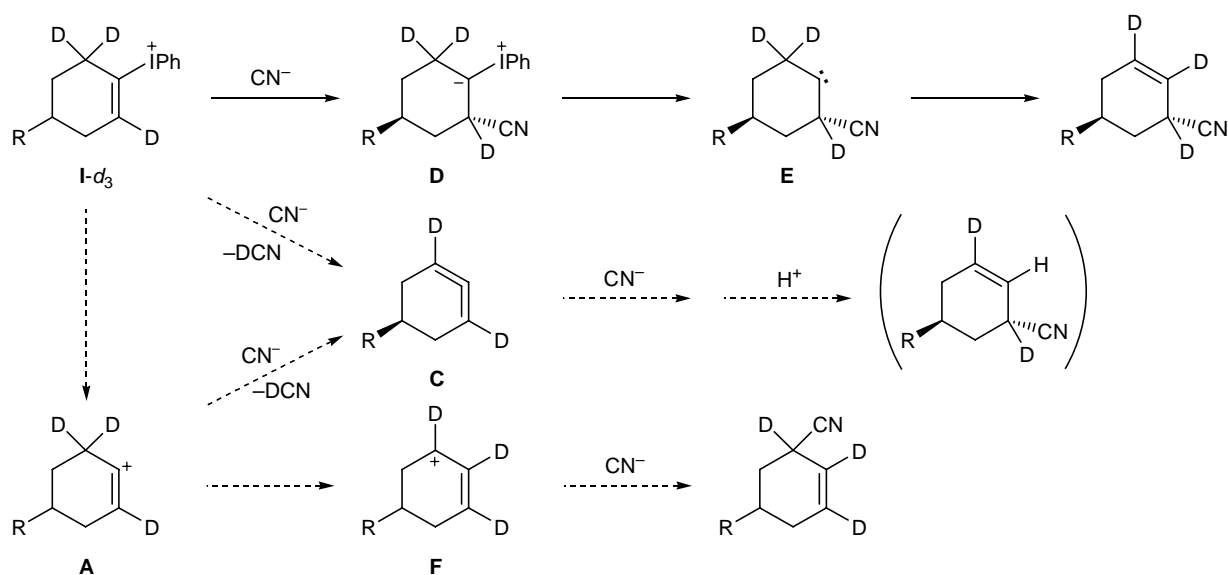
In summary, nucleophilic and basic reactions occur always competitively. Mild bases like acetate and fluoride can induce β-elimination (E2) of cyclohexenyliodonium salts, and the resulting cyclohyxne undergoes nucleophilic addition to give *ipso* and *cine* substitution products. The regioselectivity of nucleophilic addition is controlled by the LUMO population which depends on the angular deformation of the acetylenic carbon atoms. Strong nucleophiles like bromide, azide, and thiolate ions induce $S_NV\pi$ substitution in a ligand-coupling mode, while cyanide ion attacks the β-carbon atom of cyclohexenyliodonium ion, leading to Michael addition–elimination and 1,2-hydrogen shift to give the allylic substitution product. In reactions with poorly reactive, weakly basic, and nucleophilic reagents, cyclohexenyliodonium salts undergo S_NV1 solvolysis (in aqueous or alcoholic media) or E1 elimination (amines in aprotic solvents); here, the intermediate vinylic cation is again the subject of competition between nucleophile and base.

REFERENCES

1. Okuyama, T., *Rev. Heteroatom Chem.*, 1999, vol. 21, p. 257; Ochiai, M., *J. Organomet. Chem.*, 2000, vol. 611, p. 494; Okuyama, T., *Acc. Chem. Res.*, 2002, vol. 35, p. 12; Okuyama, T. and Lodder, G., *Adv. Phys. Org. Chem.*, 2002, vol. 37, p. 1; Ochiai, M., *Hypervalent Iodine Chemistry*, Wirth, T., Ed., Berlin: Springer, 2003, p. 68.

2. Okuyama, T. and Fujita, M., *Proc. Jpn. Acad. B*, 2002, vol. 78, p. 167.

3. Mironova, A.A., Maletina, I.I., Iskhakova, S.V., Orda, V.V., and Yagupol'skii, L.M., *Zh. Org. Khim.*, 1989, vol. 25, p. 306.

4. Okuyama, T., Takino, T., Sueda, T., and Ochiai, M., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 3360.

5. Ochiai, M., Takaoka, Y., and Nagao, Y., *J. Am. Chem. Soc.*, 1988, vol. 110, p. 6565; Ochiai, M., Sueda, K., Uemura, Y., and Masaki, Y., *J. Org. Chem.*, 1995, vol. 60, p. 2624.

6. Okuyama, T., Imamura, S., and Ishida, Y., *Bull. Chem. Soc. Jpn.*, 2001, vol. 74, p. 543.

7. Ochiai, M., Oshima, K., and Masaki, Y., *J. Am. Chem. Soc.*, 1991, vol. 113, p. 7059; Okuyama, T., Takino, T., Sato, K., Oshima, K., Imamura, S., Yamataka, H., Asano, T., and Ochiai, M., *Bull. Chem. Soc. Jpn.*, 1998, vol. 71, p. 243; Okuyama, T., Takino, T., Sato, K., and Ochiai, M., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 2275.

8. Fujita, M., Sakanishi, Y., and Okuyama, T., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 8787; Fujita, M., Sakanishi, Y., Nishii, M., Yamataka, H., and Okuyama, T., *J. Org. Chem.*, 2002, vol. 67, p. 8130.

9. Favorsky, A. and Boshowsky, W., *Justus Liebigs Ann. Chem.*, 1912, vol. 390, p. 122.

10. Hoffmann, R.W., *Dehydrobenzene and Cycloalkynes*, New York: Academic, 1967.

11. Krebs, A. and Wilke, J., *Top. Curr. Chem.*, 1983, vol. 109, p. 189; Gleiter, R. and Merger, R., *Modern Acetylene Chemistry*, Stang, P.J. and Diederich, F., Eds., Weinheim: VCH, 1995, p. 319; Hopf, H., *Classic in Hydrocarbon Chemistry*, Weinheim: Wiley, 2000; Sander, W., *Angew. Chem., Int. Ed. Engl.*, 1994, vol. 33, p. 1455.

12. Wittig, G. and Meske-Schuller, J., *Justus Liebigs Ann. Chem.*, 1968, vol. 711, p. 65.

13. Wentrup, C., Blanch, R., Briehl, H., and Gross, G., *J. Am. Chem. Soc.*, 1988, vol. 110, p. 1874.

14. Brunet, J.J., *Tetrahedron*, 1971, vol. 27, p. 3515; Fixari, B., Brunet, J.J., and Caubere, P., *Tetrahedron*, 1976, vol. 32, p. 927.

15. Bottini, A.T., Corson, F.P., Fitzgerald, R., and Frost, K.A., II, *Tetrahedron*, 1972, vol. 28, p. 4883.

16. Wittig, G. and Fritze, P., *Angew. Chem., Int. Ed. Engl.*, 1966, vol. 5, p. 846; Wittig, G. and Fritze, P., *Justus Liebigs Ann. Chem.*, 1968, vol. 711, p. 82.

17. Stang, P.J., *Acc. Chem. Res.*, 1978, vol. 11, p. 107.

18. Schadt, F.L., Bentley, T.W., and Schleyer, P.v.R., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 7667.

19. Okuyama, T., Fujita, M., Gronheid, R., and Lodder, G., *Tetrahedron Lett.*, 2000, vol. 41, p. 5125.

20. Swain, G. and Rogers, R.J., *J. Am. Chem. Soc.*, 1975, vol. 97, p. 799; Kropp, P.J., McNeely, S.A., and Davis, R.D., *J. Am. Chem. Soc.*, 1983, vol. 105, p. 6907.

21. Glukhovtsev, M.N., Pross, A., and Radom, L., *J. Am. Chem. Soc.*, 1994, vol. 116, p. 5961; Lucchini, V., Modena, G., and Pasquato, L., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 2297; Kim, C.K., Hyun, K.H., Kim, C.K., and Lee, I., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 2294; Bach, R.D., Baboul, A.G., and Schlegel, H.B., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 5787.

22. Okuyama, T., Takino, T., Sato, K., and Ochiai, M., *Chem. Lett.*, 1997, p. 955.

23. Okuyama, T. and Yamataka, H., *Can. J. Chem.*, 1999, vol. 77, p. 577.

24. Ochiai, M., Sumi, K., Takaoka, Y., Kunishima, M., Nagao, Y., Shiro, M., and Fujita, E., *Tetrahedron*, 1988, vol. 44, p. 409; Fujita, M., Sakanishi, Y., Kim, W.H., and Okuyama, T., *Chem. Lett.*, 2002, p. 908.

25. Fujita, M., Kim, W.H., Sakanishi, Y., Fujiwara, K., Hirayama, S., Okuyama, T., Ohki, Y., Tatsumi, K., and Yoshioka, Y., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 7548.

26. Gold, V., *Pure Appl. Chem.*, 1983, vol. 55, p. 1281.

27. Maskill, H., *The Physical Bases of Organic Chemistry*, Oxford: Oxford Univ., 1985, p. 185.

28. Hart, H., *The Chemistry of Functional Groups, Supplement C2*, Patai, S., Ed., Chichester: Wiley, 1994, p. 1017; Kessar, S.V., *Comprehensive Organic Synthesis*, Trost, B.M. and Fleming, I., Eds., Oxford: Pergamon, 1991, vol. 4, p. 483.

29. Hine, J.S., *Structural Effects on Equilibria in Organic Chemistry*, New York: Wiley, 1975, chap. 3.

30. Fujita, M., Kim, W.H., and Okuyama, T., *Chem. Lett.*, 2003, vol. 32, p. 382; Fujita, M., Kim, W.H., Fujiwara, K., and Okuyama, T., *J. Org. Chem.*, 2005, vol. 70, p. 480.

31. Stang, P.J., *Modern Acetylene Chemistry*, Stang, P.J. and Diederich, F., Eds., Weinheim: VCH, 1995, p. 67.