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Intramolecular Aromatic Cyclizations of Alkenyliodonium Tetrafluoroborates

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1,2-Dihydronaphthalene and 2*H*-chromene derivatives have been synthesized by thermal intramolecular cyclizations of alkenyliodonium tetrafluoroborates under mild reaction conditions.

There have been many reports on coupling reactions of aryl groups with vinyl groups in the presence of transition metal catalysts.[1] Direct vinylation of aromatic compounds by electrophilic aromatic substitution, however, has been shown to be difficult, because of the low reactivity of vinylic compounds such as vinyl halides and esters and the instability of the products under the reaction conditions.[2] Depending on the catalyst and the conditions used, Friedel–Crafts reactions of aromatic compounds using vinyl halides have been reported to give arylalkyl halides or diarylalkanes.[3] α-Phenylvinyl

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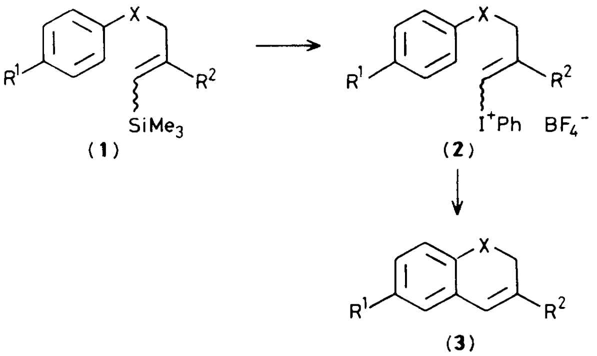


a; $R^1 = R^2 = H, X = CH_2$
b; $R^1 = Cl, R^2 = H, X = CH_2$
c; $R^1 = H, R^2 = Me, X = CH_2$
d; $R^1 = Br, R^2 = H, X = O$

Scheme 1

Table 1. Thermal intramolecular cyclization of alkenyliodonium tetrafluoroborates.

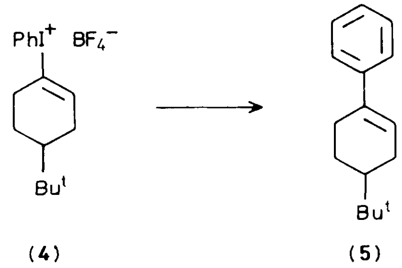
Iodonium salt	Solvent	Conditions: θ/°C, *t*/h	Product	% Yield[a]
(**2a**), *E*	CD_3OD	60, 0.5	(**3a**)	64
(**2a**), *E*	$CHCl_3$	40, 0.5	(**3a**)	65
(**2a**), *E*	$(CD_3)_2CO$	60, 0.5	(**3a**)	53
(**2a**), *E*	CD_3CN	60, 0.5	(**3a**)	52
(**2b**), *E*	$CHCl_3$	60, 0.5	(**3b**)	68
(**2c**), 97:3[b]	CH_2Cl_2[c]	40, 22	(**3c**)	63[d]
(**2c**), 12:88[b]	CH_2Cl_2[c]	40, 22	(**3c**)	7[d]
(**2d**), *E*	CD_3OD	60, 0.5	(**3d**)	71[d]

[a] Yields were determined by g.l.c. unless otherwise noted. [b] *E*:*Z* ratio. [c] The reaction was carried out in the presence of potassium carbonate (5 mol. equiv.). [d] Isolated yield.

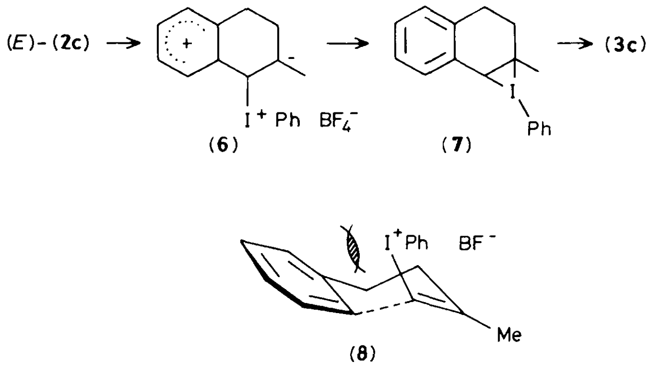
trifluoromethanesulphonates (triflates) have been employed as precursors in an aromatic vinylation, which has been proposed to proceed *via* the intermediacy of vinyl cations.[4]

Previously we demonstrated that vinyliodonium tetrafluoroborates act as highly activated vinyl iodide species in nucleophilic substitutions because of the high leaving ability of the hypervalent iodine(III) substituent, and produce a variety of alkenes including α-cyano and α-nitro derivatives, vinyl sulphides, and α,β-unsaturated esters under mild conditions.[5] From these findings, vinyliodonium salts seem to be much better unsaturated progenitors than vinyl halides for direct vinylation of aromatic compounds. We now report results obtained for thermal reactions of vinyliodonium tetrafluoroborates (**2**).

The required alkenyliodonium salts (**2**) possessing an aromatic group were prepared from alkenylsilanes (**1**) using the procedure developed recently,[5] with slight modifications; the (*E*)-vinylsilane (**1a**), prepared by the coupling reaction of (*E*)-3-chloro-1-trimethylsilylprop-1-ene with benzylmagnesium bromide in tetrahydrofuran in 71% yield, on treatment with iodosylbenzene (3 mol. equiv.) in dichloromethane in the presence of boron trifluoride–diethyl ether (3 mol. equiv.) at 0 °C for 7 h followed by quenching with excess of aqueous sodium tetrafluoroborate, afforded a 77% yield of the (*E*)-vinyliodonium tetrafluoroborate (**2a**) stereoselectively. Similarly, the (*E*)-iodonium salts (**2b**), (**2c**) (*E*:*Z* = 97:3),† and (**2d**) were prepared in 75, 92, and 72% yields, respectively.



Scheme 2



Scheme 3

Intramolecular aromatic vinylation of the iodonium salts (**2**) was found to occur smoothly on gentle heating; when a solution of (*E*)-(**2a**) in CD_3OD was heated at 60 °C (oil bath temp.) for 0.5 h in a sealed tube, the n.m.r. spectrum showed the complete disappearance of (**2a**) and new signals assignable to 1,2-dihydronaphthalene (**3a**) appeared (64% yield). The cyclization also proceeded in chloroform, acetone, or acetonitrile as shown in Table 1, whereas heating in dimethyl sulphoxide resulted in the formation of 4-phenylbutanal as the major product (62% yield) along with a small amount of (**3a**) (10% yield).‡ The reaction was applied to the synthesis of a chromene derivative; the vinyliodonium salt (*E*)-(**2d**), on thermal cyclization, gave 6-bromo-2*H*-chromene (**3d**) (71%).

The success of the intramolecular cyclizations is heavily dependent upon the stereochemistry of the vinyliodonium salts (**2**). In contrast to the ready ring closure of (*E*)-vinyliodonium salts, (*Z*)-isomers do not undergo cyclization. (*E*)-(**2c**) (97% isomeric purity), on heating in dichloromethane in the presence of potassium carbonate (5 mol. equiv.) which was added to neutralize the acid liberated in the cyclization, gave (**3c**) in 63% yield, whereas (*Z*)-(**2c**) (88% isomeric purity)[5] produced only a 7% yield of (**3c**).

Intermolecular vinylation of aromatic compounds also occurs. When 4-t-butylcyclohexenyliodonium tetrafluoroborate (**4**) was heated in excess of benzene at 80 °C for 1 h, the phenyl substituted cyclohexene (**5**) was obtained in 44% yield.

Vinylation of aromatic compounds with vinyl halides or triflates has been shown to proceed *via* the intermediacy of

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† The (*E*)-vinylsilane (**1c**) was synthesized from 4-phenylbut-1-yne in 56% yield according to the procedure developed by Fleming.[6]

‡ Similarly, the iodonium salt (**4**), on heating at 60 °C for 2 h in dimethyl sulphoxide, gave a 62% yield of 4-t-butylcyclohexanone.

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vinyl cations.[2,4] In the intramolecular cyclization of vinyliodonium salts (**2**), participation of vinyl cation intermediates is ruled out for the following reasons. (i) The ionizing power of the solvent has little effect on the cyclization of (**2a**). (ii) The (*Z*)-isomer (**2c**) does not undergo ring closure. (iii) The formation of a cyclohexenyl cation has been shown to be difficult because of the high strain energy involved in the bent vinyl cation.[7]

The precise mechanism for the intramolecular cyclization of vinyliodonium salts is not yet clear, but we propose the addition–elimination sequence as shown in Scheme 3. The failure of the (*Z*)-iodonium salt (**2c**) to cyclize can be explained by the steric repulsion between the aromatic group and the iodine(III) substituent in the transition state (**8**) leading to (**6**). The observed rapid rate of cyclization of (*E*)-(**2a**) compared to that of (*E*)-(**2c**) may reflect the difference in stability of the carbanions generated incipiently at the carbon atom β to the iodine(III) substituent. An alternative to addition–elimination is intramolecular S_N2 displacement at the vinylic centre. The S_N2 route is energetically unlikely on steric grounds[8] but cannot be rigorously ruled out.

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References

1 R. F. Heck, 'Palladium Reagents in Organic Syntheses,' Academic Press, London, 1985, ch. 6; G. H. Posner, in 'Organic Reactions,' ed. W. G. Dauben, Wiley, New York, 1975, vol. 22, ch. 2; P. W. Jolly, in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 8, ch. 56-5.

2 G. A. Olah, 'Friedel–Crafts and Related Reactions,' Wiley, New York, 1964, vol. 2, ch. 15; L. Schmerling, J. P. West, and R. W. Welch, *J. Am. Chem. Soc.*, 1958, **80**, 576; R. M. Roberts and M. B. Abdel-Baset, *J. Org. Chem.*, 1976, **41**, 1698.

3 I. P. Tsukervanik and Kh. Yu. Yuldashev, *Zh. Obshch. Khim.*, 1961, **31**, 858; Kh. Yu. Yuldashev and I. P. Tsukervanik, *Uzb. Khim. Zh.*, 1961, **6**, 40.

4 P. J. Stang and A. G. Anderson, *J. Am. Chem. Soc.*, 1978, **100**, 1520.

5 M. Ochiai, K. Sumi, Y. Nagao, and E. Fujita, *Tetrahedron Lett.*, 1985, **26**, 2351.

6 I. Fleming and T. W. Newton, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1805.

7 Z. Rappoport, in 'Reactive Intermediates,' ed. R. A. Abramovitch, Plenum Press, New York, 1983, vol. 3, p. 427; P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, 'Vinyl Cations,' Academic Press, New York, 1979, ch. 5.

8 D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, 1971, **93**, 1953.