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THE FORMATION OF 1,2-DISUBSTITUTED ADAMANTANES VIA THE ACYLATION OF ALKYNES WITH 1-ADAMANTANOYL DERIVATIVES

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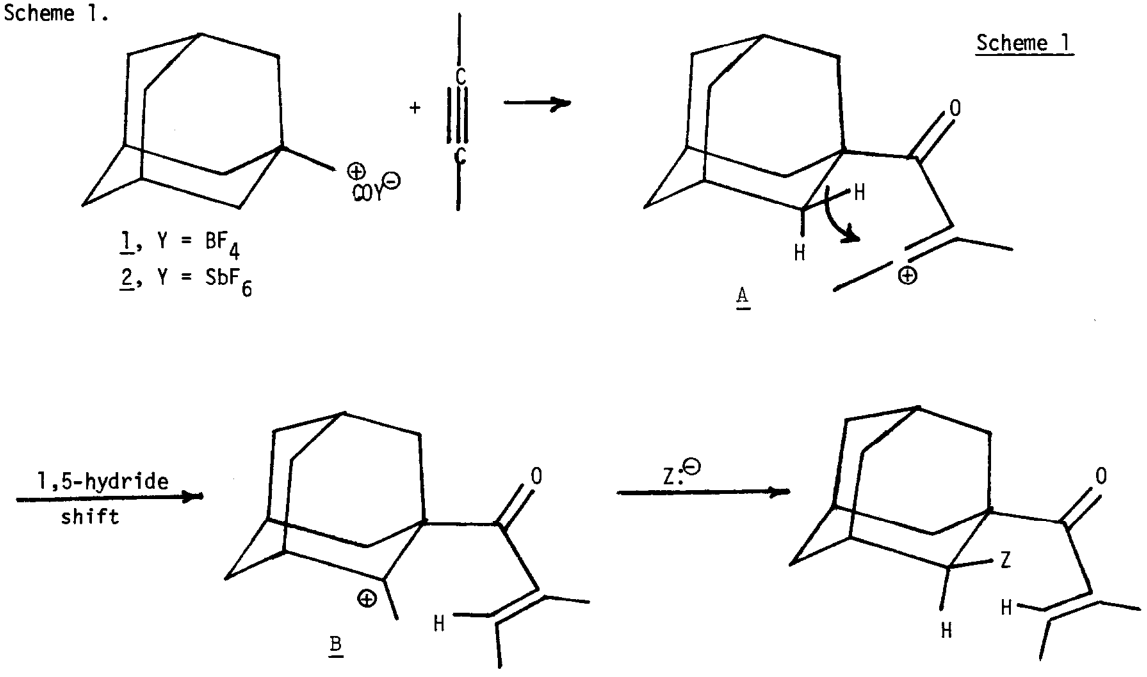
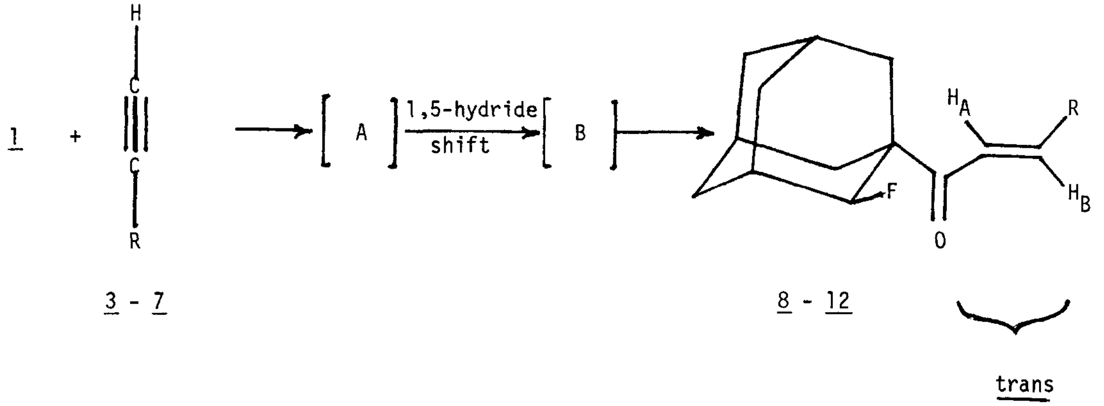
Earlier we demonstrated that a 1,5-hydride shift readily occurs in the vinyl cation intermediate formed in the course of acylation of alkynes with acylium salts.[1] This paper deals with the application of this process for the preparation of a series of 1,2-disubstituted adamantanes.

The interaction of 1-adamantanoyl tetrafluoroborate(1) or hexafluoroantimonate(2)[2] with mono- or disubstituted alkynes proceeds smoothly at -50^0 to -20^0C and affords as the main products 1,2-disubstituted adamantane derivatives according to the general reaction shown in Scheme 1.



Scheme 1

Depending on the nature of acylium salt, and/or the reaction media, different types of products could be prepared. Thus the reaction of the alkynes 3-7 with 1 in CH_2Cl_2-$C_2H_4Cl_2$ yields the 2-fluorinated derivatives 8-12[3], evidently formed by the interaction of intermediate B with the $BF_4^{\ominus}$ counterion, as shown below.



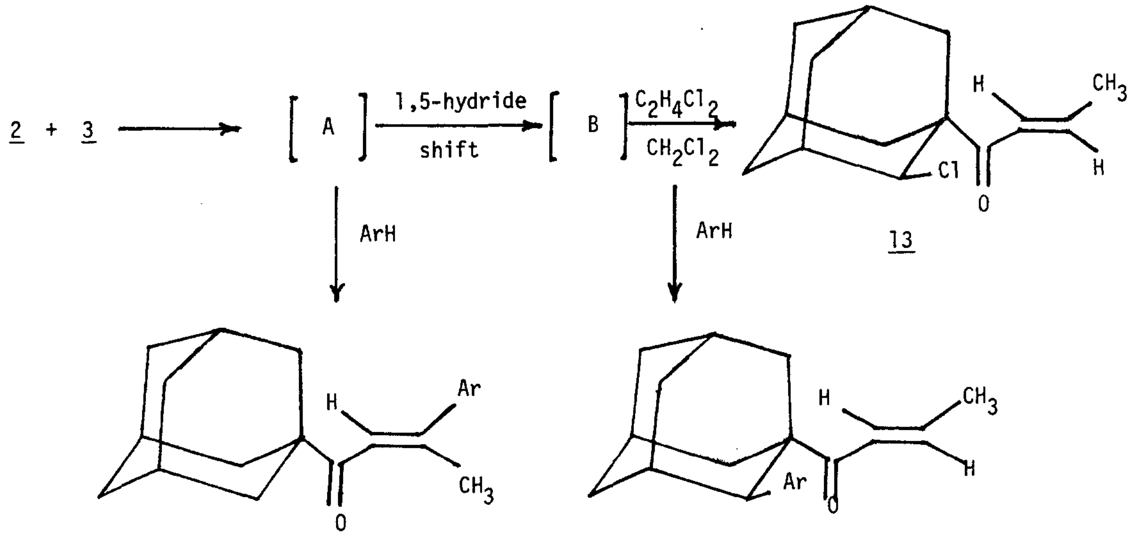
3 - 7

8 - 12

	Yields[4]
3 R = CH_3	8 R = CH_3, 50
4 R = n-C_3H_7	9 R = n-C_3H_7, 60
5 R = $CH_2C(CH_3)_3$	10 R = $CH_2C(CH)_3$, 40
6 R = $C(CH_3)_3$	11 R = $C(CH)_3$, 50
7 R = C_6H_5	12 R = C_6H_5, 60

The typical experimental procedure is as follows: a solution of 1-pentyne(4) (0.1 ml, 1 mmol) and 1-admantanoyl chloride (0.2 g, 1 mmol) in CH_2Cl_2 (5 ml) was added to a solution of $AgBF_4$ (0.3 g, 1 mmol) in CH_2Cl_2-$C_2H_4Cl_2$ (20 ml, 1:1). The mixture was stirred at -60°C for an hour and treated with an aqueous $NaHCO_3$-ether mixture. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and the solvent was removed in vacuo. A preparative tlc separation of the residue (SiO_2, ether-hexane, 1:4, R_f = 0.5) afforded 9, 0.15 g, 60%, as a colorless oil: PMR (Varian DA-60, δ scale, CCl_4), 6.34, d, H_A; 6.81, dt, H_B, J_{AB} = 15.5 cps; 4.8 dd, CH-F, J_{HF} = 49 cps, $J_{H_2H_3}$ = 4 cps MS; 250 (M^+); 153 (AdF^+); 97 ($COCH{=}CHC_3H_7^{\oplus}$). Anal. Calcd. for $C_{16}H_{23}OF$: C, 76.80; H, 9.90. Found: C, 77.34; H, 9.90.

Under essentially the same conditions the reaction of 3 with 2 gives primarily the 2-chloroketone 13, originating from the reaction of the intermediate B (Scheme 1) with the chlorinated solvents.[5] Not surprisingly, the same process carried out in the presence of aromatic solvents results in the formation of 2-arylderivatives 14 and 15[3] along with substantial quantities of 16 and 17 (ratio 14:16 or 15:17 is 1:1; total yield 50-60%).[3] The formation of 16 and 17 correspond to the trapping of the intermediate A with aromatic solvent[6] prior to the 1,5-hydride shift, as shown below.

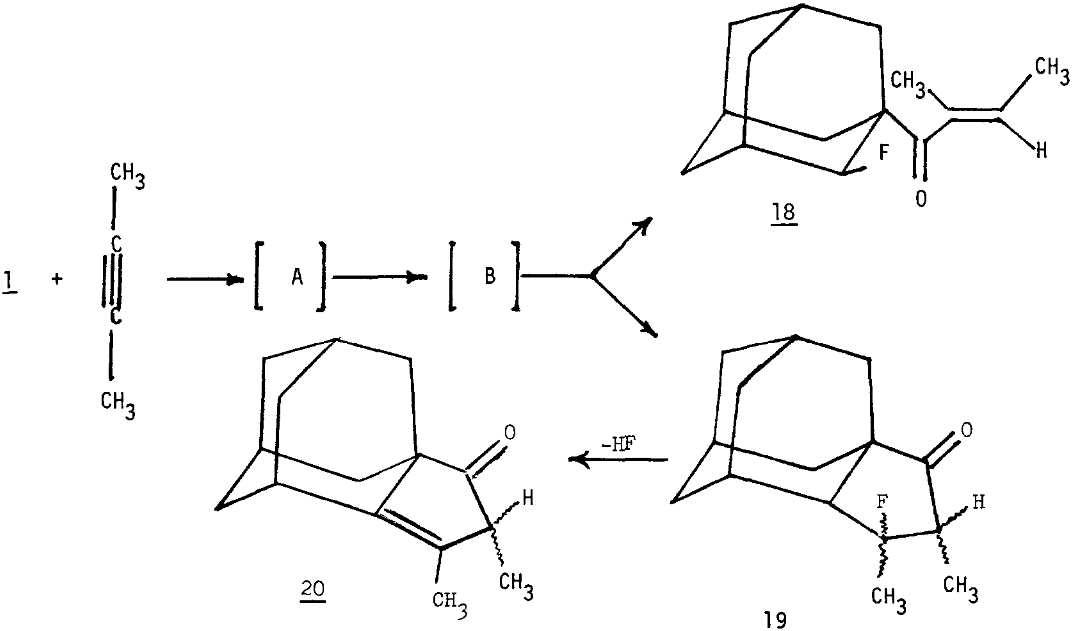


13

16, Ar = C_6H_5
17, Ar = o, m, or p-$CH_3C_6H_4$

14, Ar = C_6H_5
15, Ar = o, m, or p-$CH_3C_6H_4$

Acylation of 2-butyne with 1 proceeds in a more complicated way and results in the formation of mixture of two fluorinated ketones, 18 and 19[3] (ratio 1:1, total yield 60%).[7]



18

20

19

In general the yields of 1,5-hydride shifted products in the adamantane series are higher than those in the cyclohexane series[1,8], evidently owing to the presence of six equivalent β-hydrogens in the adamantane nuclei which are capable of reacting with the vinyl cationic center in intermediate A. The ease of the 1,5-hydride shift is further demonstrated by the essential absence of allenic products (for the acylation of 4 or 5) or rearranged ketones (for the acylation of 6) which could have arisen by alternative pathways of stabilization of the initial vinyl cation intermediates A.

In summary, although the isolated yields of the 1,2-adamantanes synthesized by the described reactions are moderate, the simplicity and versatility of the method make it an attractive alternative to the known procedures for the preparation of 1,2-disubstituted adamantanes.[9] The details and scope of this novel method will be reported in future papers.

References and Notes

1. A. A. Schegolev, W. A. Smit, V. F. Kucherov and R. Caple, J. Amer. Chem. Soc. 97, 6604 (1975)
2. Both salts were generated in situ by the usual exchange reaction: 1-AdCOCl + AgY → $AdCO^+Y^-$ ($Y = BF_4$ or SbF_6).
3. The spectral properties of all products (PMR, CMR, MS, IR-spectra) and elemental analyses are consistent with the structures shown. The details of these analyses will be reported at a later date.
4. All yields in this paper refer to the isolated compounds. Usually the reaction mixtures contain, in addition to the products shown, only oligomeric material and purification of the former could easily be effected by tlc.
5. The abstraction of halogen from the solvent by the secondary carbonium ions is a rather unusual phenomena; for example, see P. J. Kropp, G. S. Poindexter, N. J. Pienta, and D. K. Hamilton, J. Amer. Chem. Soc., 98, 8135 (1976).
6. Several examples of the reactions of vinyl cation derivatives with aromatic nucleophiles were recently reported: P. J. Stang, A. G. Anderson, Tetrahedron Letters, 1485; A. A. Schegolev, W. A. Smit, S. A. Khurshudyan, V. A. Chertkov, V. F. Kucherov, Synthesis, 327 (1977).
7. Ketone 19 is unstable and was identified by its ^1H and ^{19}F-nmr spectra. All attempts at purifying 19 resulted in the elimination of HF and the formation of 20. The PMR, CMR, IR MS and elemental analysis data are consistent with the ascribed structure. The formation of both the 1,5-hydride shifted product 18 and the fused-ring ketone 19 demonstrates the relatedness of these two processes as was suggested earlier: A. A. Schegolev, W. A. Smit, G. V. Roitburd and V. F. Kucherov, Tetrahedron Letters, 3373 (1974). Apparently the fluoroketone 19 arises from the net addition of hydrogen fluoride to the corresponding unsaturated ketone in this instance.
8. M. I. Kanischev, W. A. Smit, A. A. Schegolev, R. Caple, Izvestia Acad. Nauk SSSR, ser. chim. nauk, 1977, N12, in press.
9. R. C. Fort, ed., "Adamantanes: The Chemistry of Diamond Molecules", Studies in Organic Chemistry, vol. 5, Dekker Pub., New York, NY (1976).