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SYNTHESIS OF 7-ALKYL-CYCLOHEPTATRIENES FROM ALLYLIC SILANES AND TROPYLIUM TETRAFLUOROBORATE

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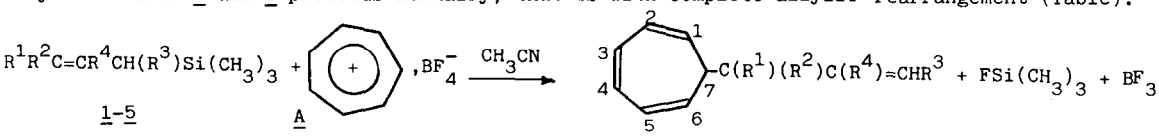
The regiospecific substitution of some allylic silanes using tropylium tetrafluoroborate gives 7-alkyl-cycloheptatrienes.

Allylic silanes are exceptionally versatile compounds with well established utility in organic synthesis (1-4), primarily perhaps because of their regiospecific reactions with different electrophiles. Most of the electrophilic substitutions of allylic silanes have involved the simultaneous use of a Lewis acid ($TiCl_4$ or $AlCl_3$), the role of which is most probably to generate in situ a reactive carbocation (5). As far as we know, only two publications refer to the formation of a new carbon-carbon bond by reacting an allylic organosilane with a stable carbocation, without addition of any Lewis acid: the reaction of allyltrimethylsilane with a range of tricarbonylcyclohexadienyl-iron complexes (6) and the reaction of allylic trimethylsilanes with 1,3-dithienium tetrafluoroborate (7).

Another carbocation seemed most promising: the relatively stable, easily handled, tropylium tetrafluoroborate A. This salt can be readily prepared by hydride abstraction from cycloheptatriene either by trityl-tetrafluoroborate (8-10) or by phosphorous pentachloride and aqueous fluoroboric acid (11-13); it has already been reacted with cyclopropyl-lithium (14) and with the Grignard reagent derived from 2-(2-bromoethyl)-1,3-dioxane (15) to give the corresponding 7-alkyl-cycloheptatrienes (16).

In this Letter, we report that the addition of solid tropylium tetrafluoroborate to a solution of allylic trimethylsilanes 1-5 in acetonitrile gives the expected 7-alkyl-cyclohepatrienes; yields are moderate, except from 3 (15-20%). The reaction from unsymmetrically substituted allylic silanes 4 and 5 proceeds normally, that is with complete allylic rearrangement (Table).



The reaction does not proceed when dichloromethane is used instead of acetonitrile; in neither solvent could any reaction be detected with benzyltrimethylsilane (17).

Experimental procedure: Tropylium tetrafluoroborate (9)(3.55g, 0.02mol) is added from a bent tube, over a 15 min period, to a solution of the allylic silane (0.022mol) in acetonitrile (70ml) at room temperature; the reaction is slightly exothermic (increase in internal temperature 5-10°). Stirring is continued for 20 min at room temperature and the mixture is poured onto a $NaHCO_3$ solution (5%)(50ml) at 0°C. After extraction (ether) and drying (K_2CO_3), the product is distilled.

Table: Reaction of allylic silanes with tropylium tetrafluoroborate

Allylic silanes	R^1	R^2	R^3	R^4	Yield%	b.p. (°C/torr)	^{1}H NMR data, δ (ppm), CCl_4
1	H	H	H	H	45	68/17	6.4-6.65(m,H^3,H^4);4.8-6.4(m,H^1,H^2,H^5,H^6,CH=CH_2);2.4(dd, J=J'=6Hz,CH_2);1.4-1.9(m,H^7).
2(18)	H	H	H	CH_3	58	80/20	6.4-6.65(m, H^3,H^4);5.8-6.2(m,H^2,H^5);4.97(dd,J=6Hz,J'= 10Hz,H^1,H^6);4.65(bs,=CH_2);2.35(d,J=8Hz,CH_2);1.5-2.1(m, H^7,CH_3).
3(19)	H	$(CH_2)_3$		H	15-20	72/0.5	6.4-6.65(m,H^3,H^4);5.75-6.25(m,H^2,H^5);5.65(bs,CH=CH); 5.1(dd,J=6Hz,J'=10Hz,H^1,H^6);1.1-2.6(m,H^7,$(CH_2)_3$CH).
4(20)	CH_3	H	H	H	40	a	6.4-6.65(m,H^3,H^4);4.8-6.4(m,H^1,H^2,H^5,H^6,CH=CH_2);2.1-2.7 (CH_3-CH);1.0-1.6(m,H^7,CH_3).
5(21)	CH_3	CH_3	H	H	40	38/0.5	6.4-6.65(m,H^3,H^4);4.8-6.4(m,H^1,H^2,H^5,H^6,CH=CH_2);1.1-1.5 (m,H^7,$C(CH_3)_2$).

[a]Isolated by bulb to bulb distillation.

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18 Prepared by reacting $(CH_3)_3SiCl$ with $CH_2=C(CH_3)CH_2MgCl$/ether; yield 50%.B.p.(°C/torr): 108-110/760.

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