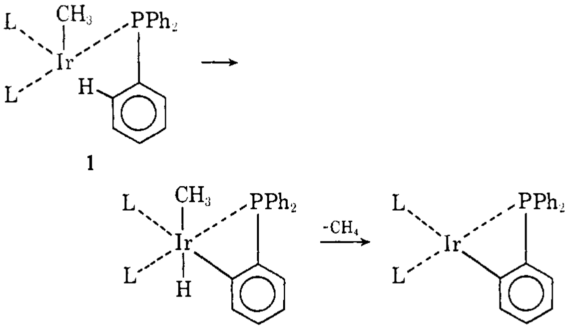
tive of an ortho-disubstituted benzene ring. The spectrum (4000–650 cm^{-1}) is qualitatively identical with that reported[8] for the rhodium analog of **6**. We were unable to satisfactorily purify **6** by recrystallization, and, therefore, reproducible elemental analyses were not obtained. The mass spectrum of **6** was recorded and it substantiates the designated structure for the compound. It shows important peaks (70 eV), consistent with the natural abundance ratio of ^{191}Ir:^{193}Ir of 0.63:1.00, at *m/e* (rel intensity) 978 (53, M$^+$[^{193}Ir], 976 (34, M$^+$[^{191}Ir], 977 (100, M − H), 975 (60, M − H), 715 (30), 714 (81), 713 (43), 712 (60), 711 (23), 637 (27), 636 (80), 635 (27), 634 (63), 633 (23), and 632 (23). The mass spectrum also contains a large peak at *m/e* 262 (PPh$_3$). These observations, and that of the enhanced thermal stability of L_3IrCH_3 imparted by solution in ether, are consistent with a mechanism for thermal decomposition of L_3IrCH_3 which proceeds through the intermediary formation of the hydridoiridium(III) species **5**, as shown in eq 4. Complex **5** is analogous to



1

5 6

(4)

those intermediates in the thermal decomposition process postulated[7,8] for L_3RhCH_3 and isolated[11] for L_3IrCl (see eq 4). It is entirely reasonable that the enhancement of thermal stability observed for L_3IrCH_3 in the presence of ether is due to coordination of a solvent molecule to iridium(I) to yield a coordinatively saturated five-coordinated species which does not readily undergo the intramolecular oxidative addition process to yield **5**. The very great reactivity of L_3IrCH_3 compared to that observed for similar iridium(I),[11] rhodium(I),[7,8] and platinum(II)[4] species is demonstrated in that intramolecular oxidative addition occurs rapidly for L_3IrCH_3 at 0°, whereas this process occurs slowly for L_3IrCl in hot benzene, very slowly for L_3RhCH_3 at 120°, and is not reported to occur for platinum(II) alkyls.

Our studies describing other oxidative addition reactions of L_3IrCH_3, as well as several uses of this complex in organic synthesis, will be reported in the near future.

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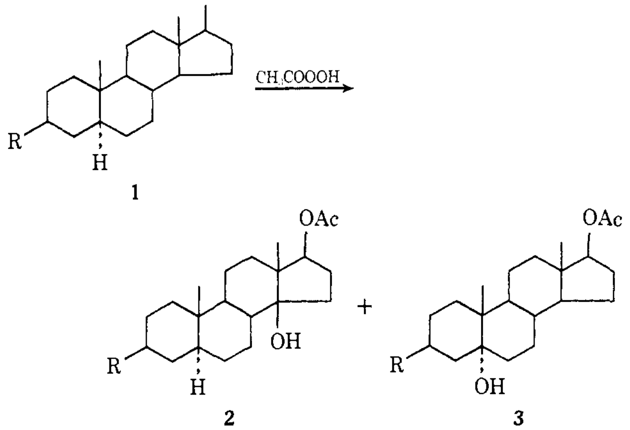
Free-Radical Hydroxylation of Steroids

Sir:

We have previously established[1] the feasibility of an attack on an unactivated tertiary carbon atom in saturated steroids substituted elsewhere by oxygenated functions. It was found that the 14α and 5β hydrogens of **1a** and **1b** were equilibratable with their epimers by bromine atoms generated photochemically *in situ* from mercuric bromide or *N*-bromosuccinimide.

We have now found that hydroxyl substitution at these unactivated centers can be accomplished by irradiation of the substrate with commercial peracetic acid.[2,3]

Thus, a 1.5% solution of androstane-3β,17β-diol diacetate (**1a**) and 8 mol equiv of peracetic acid (15% in acetic acid) in *tert*-butyl alcohol was irradiated with a high-pressure 200-W Hanovia mercury lamp using a Vycor filter. The total product was chromatographed on silica gel resulting in 20% of a 1:1 mixture of the 14β-hydroxy and 5α-hydroxy derivatives **2a** and **3a**, 50% recovered starting material, and a mixture of more polar products. Compound **2a** showed a well-defined nmr doublet for the 17α hydrogen which we have previously found to be characteristic of a 17α hydrogen of 14β steroids.[1a] The structure of **2a** was proven by correlation with a 14β-hydroxylated steroid synthesized from 14β,15β-epoxy-3β-acetoxy-5α-androstan-17-one. Results did not seem to depend strongly on the percentage of peracetic acid or the solvent. The light source could be replaced by lamps emitting at 300 mμ.



1

2 3

a, R = OAc
b, R = H

Similar treatment of 17β-acetoxy-5α-androstane (**1b**) also resulted in a 1:1 mixture of the 14β-hydroxy and 5α-hydroxy derivatives **2b** and **3b** (25% total yield).

We view this reaction as proceeding *via* hydrogen atom abstraction by methyl radicals generated photochemically from peracetic acid according to the scheme of Heywood, *et al.*[3]

It is of great interest to compare these results with those recently published by Breslow, *et al.*,[4] in which

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[1] (a) M. Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.*, **90**, 6540 (1968); (b) M. Gorodetsky, D. Kogan, and Y. Mazur, *ibid.*, **92**, 1094 (1970).

[2] Previous hydroxylation work with peracetic acid was performed only on hydrocarbons (adamantane and decalin) and employed the specially prepared anhydrous 85–100% reagent.[3]

[3] D. L. Heywood, B. Phillips, and H. A. Stansburg, Jr., *J. Org. Chem.*, 26, 281 (1961).

[4] R. Breslow, J. A. Dale, P. Kalicky, S. Y. Liu, and W. N. Washburn, *J. Amer. Chem. Soc.*, **94**, 3276 (1972).

acetoxy steroids were subjected to hydrogen abstraction by photochemically generated CCl_3 and C_6H_5ICl radicals. The products from these reactions were $\Delta^{9(11)}$- and $\Delta^{14(15)}$-olefins reflecting attack at C-9 and C-14 only. Their failure to obtain attack at C-5 was attributed to polar effects. In contrast we obtained attack at C-5 to approximately the same extent in the presence or absence of a 3-acetoxy function. In further contrast we found no evidence for attack at C-9.

The equal reactivity at C-5 and C-14 which we observed in these experiments would not have been predicted from our bromine radical epimerization studies, where reactivity at C-14 was very much greater than at C-5;[1] this may be attributed to the greater selectivity of bromine atom as compared to methyl radical.[5]

We are developing this reaction to provide synthetic access to the difficultly available cardenolides, all of which possess 14β-hydroxy functions.[6]

Acknowledgment. We would like to thank Professor Samuel Levine for helpful discussions during the course of this work.

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(5) William A. Pryor in "Introduction to Free Radical Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1966, p 56.

(6) (a) F. Sondheimer, *Chem. Brit.*, **1**, 454 (1965); (b) R. Deghenghi, *Pure Appl. Chem.*, **21**, 153 (1970).

(7) This work forms part of the Ph.D. Dissertation of A. Rotman to be submitted in partial fulfillment of the requirements of the Feinberg Graduate School, The Weizmann Institute of Science.

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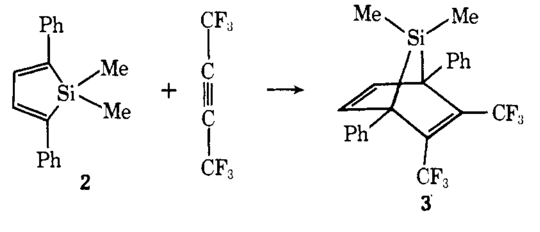
Thermal Decomposition of 1,4-Diphenyl-2,3-bis(trifluoromethyl)-7-dimethylsilabicyclo[2.2.1]heptadiene

Sir:

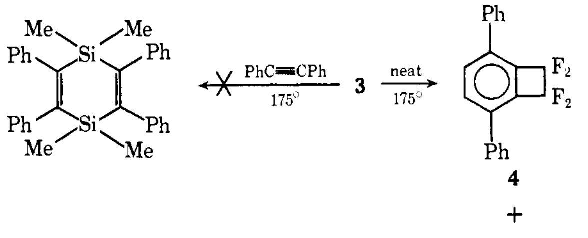
While it is well established that the thermal decomposition of 7-silanorbornadienes cleanly affords silylenes *via* bridge extrusion,[1] this work has been largely limited to those adducts derived from the Diels–Alder reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) and various acetylenes. Recently Maruca has reported that 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**2**) reacts with diphenylacetylene to afford a crystalline material for which the 7-silanorbornadiene structure was suggested.[2] While X-ray diffraction studies have shown that this material is actually a crystal complex,[3] it does appear that at much higher temperatures the adduct is formed and dimethylsilylene is extruded. Even more recently it has been shown that silole **2** reacts with ethynyltrichlorogermane to provide the 4 + 2 adduct which thermally extrudes dimethylsilylene.[4] These reports prompt us to reveal the results of initial studies on the remarkable thermal behavior of the 1,4-diphenyl-2,3-bis(trifluoromethyl)-7-dimethylsilabicyclo[2.2.1]heptadiene (**3**).

The addition of perfluoro-2-butyne to **2** proceeds cleanly at room temperature (4 days, sealed tube, $MeCl_2$) to afford adduct **3**[5] [80%; mp 100–104°; *m/e* 424.110438, calcd *m/e* 424.108085; nmr (CCl_4) δ 0.12 (s, 3 H, $SiCH_3$), 0.64 (s, 3 H, $SiCH_3$), 6.82 (s, 2 H, vinyl), 7.11 (s, 10 H, phenyl)].



Upon heating **3** above 170° in an evacuated, sealed tube dimethyldifluorosilane was evolved as the sole gaseous component and identified by mass spectrometry. This surprising result was precedented by the report of Hota and Willis that the 7-silanorbornadiene derived from tetraphenylsilole (**1**) and perfluoro-2-butyne thermally decomposed to Me_2SiF_2 and polymer.[6] However, we find that from the nonvolatile material from the pyrolysis of **3** can be isolated the benzocyclobutene (**4**)[5] (45%; mp 161.0–162.5°; M^+ *m/e* 328; ^{19}F nmr singlet at 103.2 ppm downfield from $FCCl_3$).

The possibility that **4** results from silylene abstraction of fluorine is made unlikely by the observation that decomposition of **3** in the presence of excess diphenylacetylene yields *no* 1,4-disilacyclohexadiene and essentially a quantitative recovery (>95%) of diphenylacetylene. Diphenylacetylene is known to be an excellent trap for dimethylsilylene generated in this fashion[7] and has been used previously as a negative test for silylene intermediacy.[8]



That decomposition of **3** does not initiate through loss of dimethylsilylene is quite surprising as this is clearly a symmetry-allowed, cheletropic fragmentation which should proceed in a concerted fashion.[9] A possible mechanism would involve initial homolytic cleavage of a Si–C bond to diradical **5** followed by fluorine atom transfer to yield **6**. This is formally a γ-halosilicon elimination and in contrast to the α-halosilicon[10] and β-halosilicon[11] eliminations may well proceed through a free-radical process.[10] Although it is

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(1) For a recent, general review on divalent silicon intermediates, silylenes, see W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(2) R. Maruca, *J. Org. Chem.* **36**, 1626 (1971).

(3) J. C. Clardy and T. J. Barton, *J. Chem. Soc., Chem. Commun.*, 690 (1972).

(4) A. Laporterie, J. Dubac, P. Mazerolles, and M. Lesbre, *Tetrahedron Lett.*, **48**, 4653 (1971).

(5) All new compounds gave satisfactory (±0.3%) elemental analyses.

(6) N. K. Hota and C. J. Willis, *J. Organometal. Chem.*, **15**, 89 (1968).

(7) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

(8) W. H. Atwell and D. R. Weyenberg, *ibid.*, **90**, 3438 (1968).

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinham/Bergstr., Germany, 1970, p 156.

(10) G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Commun.*, 382 (1965).

(11) I. M. T. Davidson, C. Eaborn, and M. N. Lilly, *J. Chem. Soc.*, 2624 (1964).