Diprotonation of 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes

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5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes could potentially be protonated on either or both of two sites, the diene moiety in the five-membered ring or the carbonyl oxygen. The protonation of a series of 5-acylpentamethylcyclopentadienes has been examined and evidence is presented which shows that the former site is essentially completely protonated in FSO_3H and that the carbonyl oxygen is also partially protonated. The extent of diprotonation is shown to be dependent both on the nature of the acyl groups and also the acidity of the medium. At temperatures above 40 °C these protonated species undergo a clean fragmentation to give protonated pentamethylcyclopentadiene from which pentamethylcyclopentadiene can be recovered in good yield on quenching the acid solution.

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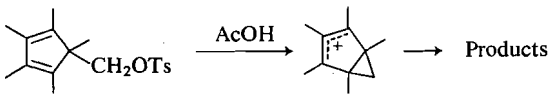
En théorie, les acyl-5 pentaméthyl-1,2,3,4,5 cyclopentadiènes peuvent se protoner sur l'un ou l'autre ou sur deux sites soit la portion diénique du cycle à cinq chainons ou l'oxygène du carbonyle. On a étudié la protonation d'une série d'acyl-5 pentaméthylcyclopentadiènes et on présente des données qui démontrent que le premier site est pratiquement complètement protoné dans le FSO_3H et que l'oxygène du carbonyle est aussi partiellement protoné. On montre que la quantité de diprotonation dépend à la fois de la nature des groupes acyles et aussi de l'acidité du milieu. A des températures supérieures à 40 °C, les espèces protonées subissent une fragmentation propre pour conduire au pentaméthylcyclopentadiène protoné à partir duquel on peut recupérer du pentaméthylcyclopentadiène avec de bons rendements en diluant la solution acide dans de l'eau.

[Traduit par le journal]

Introduction

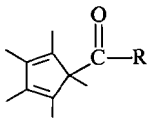
In order to extend our studies on the bicyclo-[3.1.0]hexenyl cations and to explore the importance of the related cyclopentadienylcarbinyl cations in their five-fold degenerate rearrangement (1), it became necessary to prepare examples of these cations with an oxygen substituent at C_6. As it has been previously shown that ionization of the cyclopentadienyl ester **1** takes place with anchimeric assistance to give the bicyclohexenyl cations **2** (2), one obvious synthetic route to these cations would be the reaction of the carbonyl oxygen of a 5-acylcyclopentadiene with a suitable electrophile. When Lewis acids are used as the electrophile this approach works well (3), however the situation is much more complex when a proton is employed. We describe here the results of a study of the protonation of several 5-acylpentamethylcyclopentadienes in FSO_3H and show that protonation of the diene moiety occurs in addition to protonation of the carbonyl oxygen.



1 **2**

Results and Discussion

5-Acetylpentamethylcyclopentadiene, **3**, was protonated by extraction from CH_2Cl_2 into FSO_3H at −78 °C. From the complexity of the low temperature n.m.r. spectrum of the resulting solution, Fig. 1, it was quite clear that protonation was not simply occurring on the carbonyl oxygen. So as to ensure that the n.m.r. spectrum obtained derived simply from products of protonation of **3** and not subsequent rearrangements or fragmentations, the acid solution was quenched in an ether–HCO_3^- suspension to yield **3** in greater than 90% recovery.



3 R = CH_3
4 R = CH_2CH_3
5 R = C_6H_5
6 R = *p*-MeO—C_6H_4

In order to identify the resonance attributable to the C_6 methyl group, the related ketones **4**, **5**, and **6** were protonated with FSO_3H. Examination of the n.m.r. spectra of the solutions so obtained, showed that in each case a similar product to that obtained from **3** was formed. It was apparent that the resonance at 3.07 δ in the

TABLE 1. Proton chemical shifts for protonated ketones and related materials

Compound protonated	Acid medium	Position* C_1/C_3 Me	C_2 Me	C_4 Me	H	C_5 Me	C_6 substituent
3	FSO_3H	3.07 2.90	2.27	1.46d	3.8m	1.89	3.07
		3.08 2.99	2.27	1.63d	3.8m	1.77	2.99
3	FSO_3H–SbF_5	3.08 2.94	2.28	1.48d	3.9m	1.95	3.31
		— —	2.28	1.6d	—	1.83	3.21
4	FSO_3H	3.06 2.93	2.27	1.59d	3.7m	1.75	2.98q 1.32t
		— —	—	1.16d	—	1.85	— —
5	FSO_3H	3.19 2.89	2.42	1.57d	4.3m	2.07	7.79–8.17
		— —	—	1.76d	—	1.92	—
6	FSO_3H	3.12 2.88	2.40	1.68d	4.1m	1.83	4.19, 7.27–7.84
		— —	—	1.45d	—	1.98	—
7	FSO_3H	2.89 2.89	2.22	1.50d	3.56m	1.50	—
		2.89 2.89	2.22	1.43d	3.56m	1.43	—

*In p.p.m. measured from internal CH_2Cl_2 taken as 5.30 δ. All spectra recorded at −25 °C; d, doublet; t, triplet; q, quartet; m, multiplet.

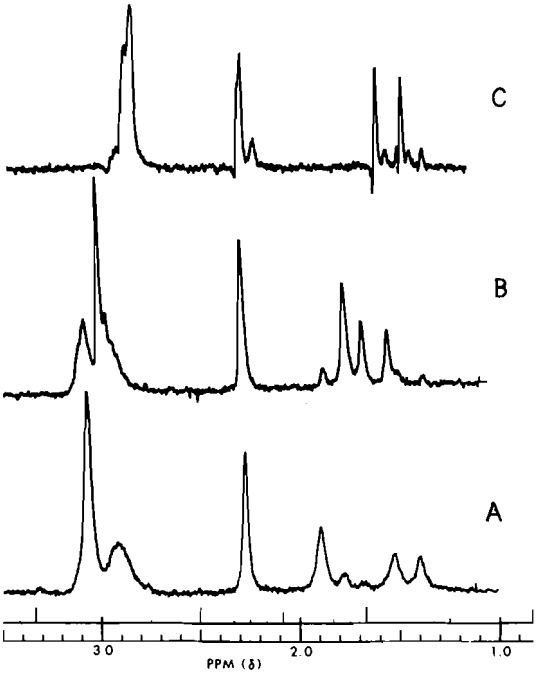


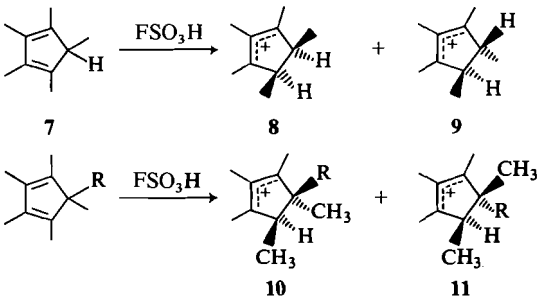
FIG. 1. Protonated 5-acetylpentamethylcyclopentadiene; *A*, initial protonation at −25 °C; *B*, after equilibration at 0 °C; *C*, after thermal fragmentation at 44 °C.

spectrum of protonated **3** was due to the C_6 methyl group and that the rest of the signals must be due to the methyl groups on the five-membered ring.

The high field doublets present in the n.m.r. spectra of these protonated ketones suggested that protonation on the five-membered ring had occurred. Consistent with this is presence of a broad resonance 3.7–4.0 δ, which is in a similar position to that found for a methine proton adjacent to an allylic cation in a five-membered ring (4). Confirmation of this ring protonation was obtained by solution of **6** in FSO_3D when the n.m.r. spectrum so obtained differed from that of **6** in FSO_3H in that the two high field doublets at 1.68 δ and 1.45 δ were now singlets and the resonance at 4.10 δ was absent.

There are two possible structural isomers that could result from protonation of the diene moiety; the proton could be situated either *cis* or *trans* with respect to the acyl group. A similar situation has been found for the protonation of pentamethylcyclopentadiene **7** (5), which gives both **8** and **9** upon solution in super acids. The cations **8** and **9** indeed serve as good models for what would be expected for the positions of the ring methyl resonances of the ketones if protonation of the diene were occurring. Thus while the cations derived from **3**, **4**, **5**, and **6** lack the inherent symmetry of **8** and **9**, it can be seen from Table 1 that the n.m.r. spectra of these two sets of cations are very similar. It would appear clear that protonation of these ketones is taking place on the five-membered ring and that the products can be at least partially represented as being made up of a mixture of **10** and **11**.

While it has not been possible to distinguish between **10** and **11** on the basis of their spectra, it is apparent that they are not produced in



7 8 9

10 11

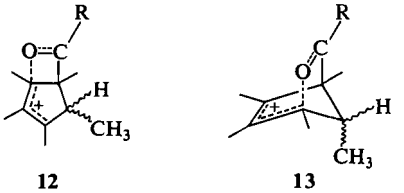
R = Acyl R = Acyl or protonated acyl

equal amounts on protonation of **3** at low temperatures. As is shown in Fig. 1*A*, the two isomers were initially present in a ratio of 80:20. At higher temperatures **10** and **11** interconverted and a thermodynamic product distribution was eventually reached in which the ratio was 15:85, Fig. 1*B*, which was the inverse of the initial kinetic distribution of products. This interconversion of the two isomers was rapid at 0 °C (pseudo first-order rate constant *ca.* 10^{-2} s^{-1}). When **3** was protonated in FSO_3H–SbF_5 (4:1), the same 80:20 kinetic distribution of products was observed, however in this stronger acid medium (6) no interconversion of the isomers **10** and **11** could be detected up to 40 °C, when other rearrangements and a general decomposition occurred. Comparable kinetic and thermodynamic product distributions have been reported with the cations **8** and **9** derived by protonation of **7** (5).

It is not unexpected that protonation of the diene moiety of these ketones is occurring in FSO_3H. 3-Methylene-1,4,4,5,5-pentamethylcyclopent-1-ene is sufficiently basic to be 50% protonated in 33% H_2SO_4 ($pK_a = -1.8$) (7) and other similarly alkylated cyclopentenyl cations are formed in acid of about the same strength. The carbonyl function, however, would be expected to be much less basic than the diene. Pinacolone, which is a reasonable model for **3**, is half protonated in 81% H_2SO_4 ($pK_a = -7.1$) (8). Even the aryl substituted carbonyl groups of **5** and **6**, are expected to be less basic than the diene. Acetophenone is half protonated in 74% H_2SO_4 ($pK_a = -6.15$) and *p*-methoxyacetophenone in 63% H_2SO_4 ($pK_a = -4.71$) (9). Fluorosulfuric acid is a much stronger acid than any of these aqueous sulfuric acid solutions (6) and it is sufficiently acidic to essentially completely protonate either of the two possible sites, the diene or the carbonyl oxygen. From the results presented above it is apparent that protonation of the diene to give a cyclopentenyl cation has taken place. The question arises, however, as to whether the carbonyl oxygen is also protonated in FSO_3H, either in competition with, or in addition to that of the diene.

In the unprotonated ketone **3**, the resonance attributable to the C_6 methyl group occurs at 1.50 δ. When dissolved in FSO_3H, the signal due to this methyl is shifted very considerably further downfield and appears at 3.07 δ. Typically the resonance of a methyl group adjacent to a protonated carbonyl group of an aliphatic ketone occurs at *ca.* 3.0 δ (10), for example, those of acetone and pinacolone occurring at 2.97 δ and 2.90 δ respectively.[1] The large downfield shift of the C_6 methyl group of **3** and the close similarity in its position to other protonated ketones is suggestive that the carbonyl oxygen of **3** is at least partially protonated in FSO_3H. Additional support for this suggestion can be found by examining the changes that occur in the aryl regions of the n.m.r. spectra of **5** and **6** on protonation and comparing them with those observed on protonation of acetophenone and *p*-methoxyacetophenone (11), Table 2.

It is conceivable that instead of protonation on oxygen some interaction of the carbonyl oxygen with the cyclopentenyl cation such as is shown with **12** or **13**, could account for the observed deshielding of the C_6 groups. However, the magnitude of this deshielding and the similarity of the resonance positions of the C_6 substituents with model protonated ketones would render this suggestion unlikely.



12 13

Further, definitive evidence for the protonation of the carbonyl group comes from the observation of an OH resonance in the n.m.r. spectrum of protonated **6**. The spectrum of **6**

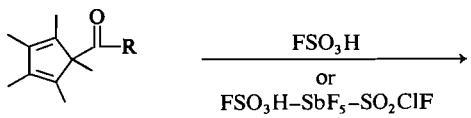
[1]Care has to be taken in simply taking published literature values for the chemical shifts of cations as different standards are used as references. The values quoted in this paper are all based upon internal CH_2Cl_2 taken as 5.30 δ.

TABLE 2. Comparison of proton chemical shifts of some protonated and unprotonated ketones*

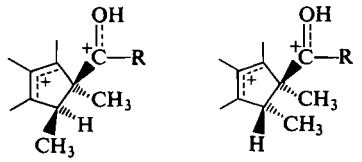
	Position			
	Neutral ($CDCl_3$)		Protonated (FSO_3H)	
Ketone	Aryl H	OCH_3	Aryl H	OCH_3
Acetophenone	7.23–7.80	—	7.71–8.64	—
5	7.14–7.60	—	7.79–8.17	—
p-Methoxyacetophenone	6.79–7.91	3.86	7.18–8.57	4.12
6	6.63–7.74	3.76	7.27–7.84	4.19

*In p.p.m., measured from internal CH_2Cl_2 taken as 5.30 δ for protonated species.

when protonated in a FSO_3H–SbF_5–SO_2ClF (4:1:4) medium was identical to that observed in FSO_3H with the exception that at low temperatures (−70 °C) an additional singlet at 12.70 δ was found. On warming the solution, this peak moved upfield and appeared to average with the solvent peak. The position of this low field resonance is just that expected for the OH signal of a protonated *p*-methoxyphenyl substituted ketone (11, 12). Thus, protonation of **6** would seem to be occurring both on the five-membered ring and also on the carbonyl oxygen. Either this could be taking place at the same time, resulting in the formation of two dications, or there could be an equilibrium between C and O protonated monocations. The latter possibility can be ruled out on several counts. Firstly, as has been previously pointed out, the resonance positions of both the ring methyls and also C_6 substituents are not consistent with a mixture of monoprotonated species being present. More importantly, in FSO_3H–SbF_5–SO_2ClF, observation of both hydroxy proton and methine proton resonances of protonated **6** at the same time shows that if two separate cations were responsible for these resonances, then their rate of interconversion must be slow on the n.m.r. time scale. However as the rest of the spectrum is not compatible with a slow equilibration between O and C monoprotonated cations, it can only be concluded that the hydroxy and methine proton resonances originate from the same species, dications **14** and **15**.[2]



6 R = *p*-$MeOC_6H_4$—



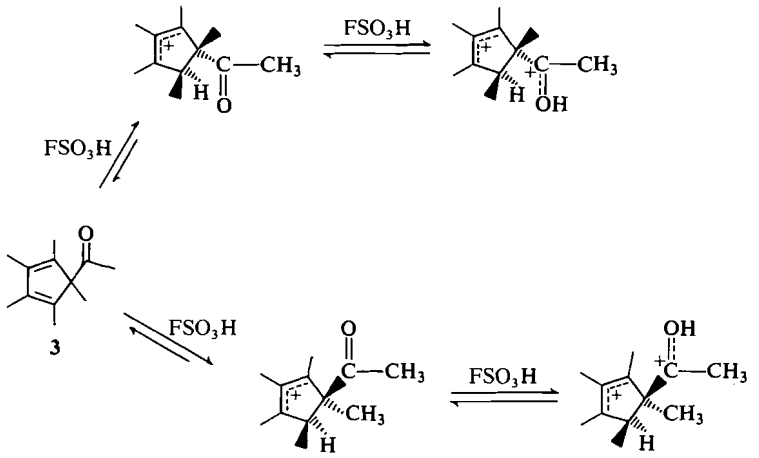
14 R = *p*-$MeOC_6H_4$— **15** R = *p*-$MeOC_6H_4$—

As was pointed out earlier, the n.m.r. spectra of the cations derived by solution of **3** in FSO_3H cannot be simply accounted for on the sole basis of protonation of the five-membered ring. It was not possible however, to detect any —O*H* proton resonance in the low temperature n.m.r. spectra of **3** in FSO_3H–SbF_5 media, although the addition of SbF_5 to the acid did produce an effect on the positions of the methyl resonances. In particular, it will be noted in Table 1 that the resonance attributed to the C_6 methyl moved downfield by 0.24 p.p.m. in going from FSO_3H to a FSO_3H–SbF_5 mixture. This would imply that diprotonation of **3** is not complete in FSO_3H, and that the system exists as a fast equilibrating mixture of mono- and diprotonated species, Scheme 1. As the acidity of the medium is enhanced by the addition of SbF_5, the equilibrium position would be expected to be displaced further in favor of the diprotonated forms, resulting in a downfield shift of the C_6-methyl group.

Thermal Fragmentation

While FSO_3H solutions of ketones **3–6** were stable for long periods of time when kept below

[2]While the two dications **14** and **15** should give rise to two *OH* resonances, only one such signal could be detected. The second *OH* resonance would be expected to be only some 20–25% of the one observed and could be either lost in baseline noise or coincident with the peak at 12.70 δ.



SCHEME 1

room temperature, at higher temperatures they underwent a thermal fragmentation to give protonated pentamethylcyclopentadiene. Thus **3** in FSO_3H reacted at 44 °C (half life 45 min) to give a mixture of **8** and **9**, Fig. 1*C*. Reaction of this acid solution with ether–HCO_3^- at −78 °C gave pentamethylcyclopentadiene **7** in high recovery.

$$\mathbf{3} \xrightarrow[\substack{44\,^\circ C \\ t_{1/2}\ 45\ min}]{FSO_3H} \mathbf{8} + \mathbf{9} \xrightarrow[\substack{ether \\ -78\,^\circ C}]{NaHCO_3} \mathbf{7}$$

The n.m.r. spectrum, Fig. 1*C*, of the products of this fragmentation reaction differed from that of authentic protonated pentamethylcyclopentadiene by the presence of an additional methyl resonance at 2.80 δ. Acyl cations are known to be stable in super acid media such as FSO_3H–SbF_5, and in the case of the fragmentation of protonated **3**, a methyl resonance attributable to the methyloxocarbonium ion at *ca.* 4 δ would be expected (13). The fragmentation of protonated **3** did not take place cleanly in FSO_3H–SbF_5, however the addition of SbF_5 to a FSO_3H solution after fragmentation caused a resonance corresponding to three protons, formally at 2.80 δ, to be shifted to 3.91 δ. It would appear that the acylium cation formed on fragmentation of **3** in FSO_3H must react with a nucleophile present in the acid medium to form a protonated acetic acid derivative, a reaction which is reversed upon the addition of SbF_5.

As pentamethylcyclopentadiene is not a readily available material (14) and acetylpentamethylcyclopentadiene can be obtained in one step from the commercially available hexamethylbicyclo[2.2.0]hex-2,5-diene (15, 16) the scale up of this fragmentation reaction in FSO_3H seemed attractive. However, whereas we have been able to carry out this reaction with up to 200 mg of material at a time, the yields drop as the reaction size is increased and these reactions do not as yet provide a viable alternate synthetic route to **7**.

Experimental

Nuclear magnetic resonance spectra were obtained on Varian HA-100 and A-60 spectrometers fitted with variable temperature probes. Probe temperature was measured with a copper–constantan thermocouple and Leeds and Northrup 8692 temperature potentiometer. The thermocouple was mounted at the appropriate depth in a nonrotating sample tube. Chemical shifts are referred to TMS or in the case of the cations, internal CH_2Cl_2 taken as 5.30 δ. Vapor phase chromatographic analyses were performed on an Aerograph 204B instrument, using 8 ft × $\frac{1}{8}$ in. columns packed with 15% SE-30 on 60–80 Chromosorb W and 20% Carbowax on 60–80 Chromosorb W.

Materials

Pentamethylcyclopentadiene was prepared by the method of de Vries (14). 5-Acylpentamethylcyclopentadienes were obtained by reaction of lithium pentamethylcyclopentadienide (15) with the appropriate acid halide (17). FSO_3H was distilled from a small quantity of NaF and stored in sealed glass ampoules until used. SbF_5 was doubly distilled and stored under nitrogen in a dry box. FSO_3H–SbF_5 solutions were prepared under nitrogen.

Preparation of Cations

Protonations in FSO_3H and FSO_3H–SbF_5 were carried out by slowly adding a CH_2Cl_2 solution (0.2 ml)

of the appropriate compound (20 mg) down the side of an n.m.r. tube which contained FSO_3H at −78 °C. After 15 s the two phases were mixed with a glass rod.

Preparation of Pentamethylcyclopentadiene, 7, from 5-Acetylpentamethylcyclopentadiene, 3

5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene, **3**, (178 mg) in methylene chloride (1 ml) was extracted into $HFSO_3$ (2 ml) kept at −78 °C. The sample was gradually warmed to 40 °C and kept for 3–4 h, complete reaction being checked for by n.m.r.

A suspension of sodium bicarbonate (5 g) in ether (25 ml) was stirred at −78 °C while the acid solution was added dropwise. The resulting mixture was warmed to 0 °C. Ice-water was added to the mixture and the stirring was continued for 15 min. The resulting solution was filtered *in vacuo* and the filtrate extracted with ether (3 × 25 ml). The extract was dried (Na_2CO_3) and evaporation of ether *in vacuo* yielded 148 mg of organic material.

The product was characterized as pentamethylcyclopentadiene by the comparison of its n.m.r. spectrum with that of an authentic sample. No other signal was observed in the n.m.r. spectrum of the product. Only two peaks were observed on the chromatogram when the product was subjected to v.p.c. analysis. The ratio of the amount of the major product to that of the minor was 19:1. The major product was collected and identified as pentamethylcyclopentadiene by the comparison of the n.m.r. spectra with an authentic sample.

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