Synthesis of Tricyclic Ketones Containing an Angular Methyl Group in 'Superacid' Media

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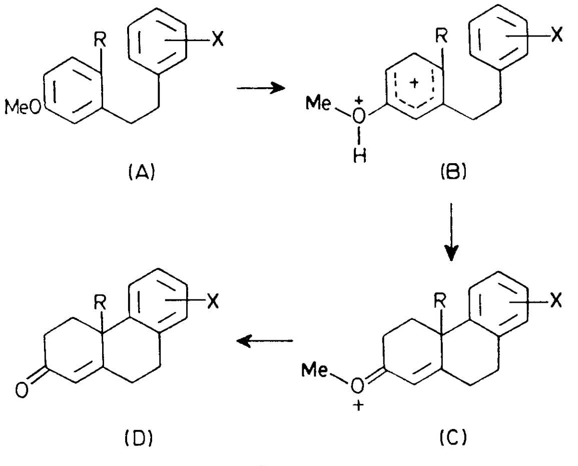
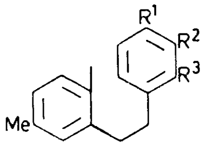
Summary In the 'superacid' SbF_5–HF, substituted 1,2-diphenylethanes undergo cyclisation *via* diprotonated species to afford in good yield tricyclic ketones containing an angular methyl group as primary products; isomerisation of these products occurs with longer reaction times.

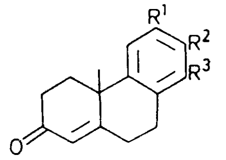
The reactivity of some phenols (and ethers) in 'superacids', especially in SbF_5–HF, has been explained by a double protonation process: first on oxygen and then on the *meta*-carbon atom. The transient diprotonated species obtained can either rearrange to more stable ions, precursors of dienones[1] or react with suitable nucleophiles.[2] We report here a novel example of such reactions leading to the synthesis of tricyclic ketones possessing an angular alkyl group. Diprotonation of the starting material (A), a substituted 1,2-diphenylethane, gives the dication (B) which can react intramolecularly to afford (C) (see Scheme).



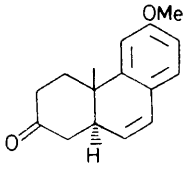
Scheme

Preliminary results in the Table show the reactivity of molecules of type (A) with R = Me and X = H or OMe. Compounds (**1**)—(**4**) can be prepared easily from 5-methoxy 2-methylbenzaldehyde[3] by Grignard condensation or Wittig–Horner reaction followed by reduction, in an overall





(1)	$R^1 = R^2 = R^3 = H$	(5)
(2)	$R^1 = R^2 = H$, $R^3 = OMe$	(6)
(3)	$R^1 = OMe$, $R^2 = R^3 = H$,	(7)
(4)	$R^1 = R^3 = H$, $R^2 = OMe$	(11)



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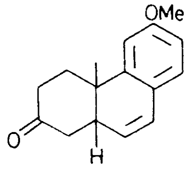

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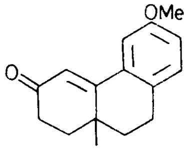

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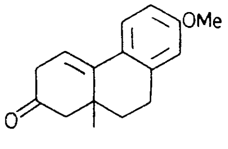

(12)

yield of 70—90%. The new compounds (**1**)—(**4**) were characterized by elemental analysis and n.m.r. spectroscopy.†

TABLE[a]

Sub-strate	[SbF_5–HF]/M	Time	Products (% yield)[b]
(**1**)	3·5	40 min	(**5**) (70)
(**2**)	2·3	6 h	(**6**) (71)
(**3**)	3·5	5 min	(**7**) (78) and (**8**) (3)
(**3**)	4·6	80 min	(**7**) (3·5), (**8**) (4), (**9**) (22), and (**10**) (7·5)[c]
(**4**)	2·3	4·5 h	(**11**) (45) and (**12**) (22)

[a] Reactions were performed at 0 °C as previously described (ref. 1). [b] Yields are for isolated products after purification by column chromatography over SiO_2. [c] Also isolated are 20—30% of phenols arising from dealkylation of the ethers (**8**) and (**9**) in the 'superacid' media.

In all cases yields of the ketones (**5**), (**6**), (**7**) and (**11**) are good, even though reaction conditions have not yet been optimized. The enone (**5**) was identical with an authentic sample and all enones have physical constants and u.v., i.r., and n.m.r. spectra identical to those reported.[4] These primary products can rearrange further in SbF_5–HF by diprotonation of the enone system.[5]

The enone (**7**) thus affords three new products: the *trans*-fused ketone (**8**) which is kinetically favoured by the easier 10α-H migration, the thermodynamically more stable *cis*-fused ketone (**9**), and the enone (**10**) which is formed *via* a spiro-intermediate as previously observed in polyphosphoric acid for closely related molecules.[6]‡ Hydrogenation (low pressure) over Pd–C of (**8**) and (**9**) gives *trans* and *cis*-fused hexahydrophenanthrenones, respectively, which were also obtained from the enone (**7**) by known methods.[4] The ketone (**10**) was also unambiguously prepared in 30% yield by condensation of methyl vinyl ketone with the known 3,4-dihydro-7-methoxy-2-methylnaphthalen-1(2*H*)-one[7] using NaH-Me_2SO. Under the same conditions the enone (**11**) rearranges by methyl migration to (**12**), an oil, whose structure was established from spectral data: ν_{max} ($CHCl_3$) 1715, 1605, and 1500 cm^{-1}; λ_{max} (EtOH) 265 nm, log ϵ 4·12; δ (CCl_4) 0·99 (3H, s, Me), 3·71 (3H, s, OMe), 6·02 (1H, t, *J* 4 Hz, vinylic-H), 6·3—7·2 (2H, ArH), and 7·30 (1H, d, *J* 8 Hz, ArH) (only characteristic signals are given).

These preliminary results show the possibility of using such cyclisation processes to prepare complex polycyclic ketones from readily available substrates.

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† *E.g.*, for (**2**): δ (CCl_4) 2·26 (3H, s, Me), 2·73 (4H, s, CH_2CH_2), 3·64 (3H, s, OMe), 3·72 (3H, s, OMe), and 6·3—7·2 (7H, ArH).

‡ (**8**), m.p. 113 °C, δ (CCl_4) 1·16 (3H, s), 3·75 (3H, s), 5·40 (1H, d, *J* 10 Hz), 6·45 (1H, d, *J* 10 Hz), and 6·7—7·1 (3H, ArH); (**9**) oil, δ (CCl_4) 1·18 (3H, s), 3·73 (3H, s), 5·71 (1H, dd, *J* 10 and 6 Hz), 6·34 (1H, d, *J* 10 Hz), and 6·6—7·0 (3H, ArH); (**10**) m.p. 81 °C, δ ($CDCl_3$) 1·20 (3H, s), 3·77 (3H, s), 6·43 (1H, s), 6·85 (1H, dd, *J* 2 and 8 Hz), 7·07 (1H, d, *J* 8 Hz), and 7·13 (1H, d, *J* 2 Hz) (only characteristic signals are given).

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