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PREPARATION AND ^{1}H-NMR SPECTRA OF SOME ADAMANTANE DERIVATIVES[a,b]

2-FORMYLADAMANTANE, 2-BROMO-3-METHYL-2-HOMOADAMANTENE, 4,4-ADAMANTYLENE-1,3-DIOXANES AND SOME GEMINAL SUBSTITUED ADAMANTANES, INCLUDING 2-ADAMANTYLENECYCLOBUTANONE

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Abstract—A new two-step synthesis for 2-formyladamantane (**3**) from adamantanone is described. The Prins reaction of alkylidene-adamantane affords 4,4-adamantylene-1,3-dioxanes (**9**) and α-2-adamantyl-alkanals (**10**), but no 5,5-adamantylene-1,3-dioxanes. The brominolysis of 2,2-ethyleneadamantane results in 2-bromo-3-methyl-2-homoadamantene (**13**). No 2,2-carbonsubstituted adamantane derivatives were obtained by reaction of organometallic reagents on adamantyleneoxirane. Grignard reagent may easily open the oxirane moiety by action of magnesium iodide, present in the reaction medium. A one-step synthesis of 2-adamantylenecyclobutanone from adamantanone and difenylsulfonium cyclopropylide is described. Some representative 300 MHz ^{1}H-NMR spectra are given and discussed.

Starting from adamantanone, we have tested several roads for the eventual preparation of the 5,5-adamantylene-1,3-dioxane system (**11**) (Scheme 2). The compound (**11**, R = H) has been synthesized recently[1] by Wynberg *et al.* During our unsuccessful attempts however we have obtained some adamantane derivatives, which may present some interest and we want to describe.

2-Formyladamantane (**3**) (Scheme 1). This compound has been prepared by Wynberg *et al.*[2a] and by Farcasiu,[2c] but we found another convenient two-step route with an overall yield[3] of 65·5%, starting from adamantanone. The method followed is depicted in Scheme 1, and the detailed procedures are described in the Experimental. Oxidation of **3** to 2-adamantyl-carboxylic acid is easy.[2a] We have tried to convert the derived α-Br ethyl ester (**5**) into a geminal substituted carbon–carbon adamantane derivative (**6**), but all attempts were unsuccessful.

4,4-Adamantylene-1,3-dioxanes (Scheme 2). Alkylideneadamantanes (**8**) form another interesting series of intermediates. Some of these are known,[4,5] but we have extended the series with R = ϕ, vinyl. Either organolithium, or in the absence of sp^3-β-H-atoms, also Grignard reagents may be used to obtain in good yields the *gem*-hydroxy, alkyl-adamantane derivatives (**7**). Deshydration with sulphuric or phosphoric acid for R = vinyl, leads to polymerization. Allylideneadamantane (**8**; R = $CH_2{=}CH$—) was obtained by treating 2-hydroxy-2-allyladamantane with thionylchloride in pyridine at 0–20°. From the alkylidene derivatives one obtains in almost quantitative yield by treatment with formal and tin(IV)chloride in dichloromethane, a mixture of 4,4-spirodioxanic compounds (**9**) and α(2-adamantyl)aldehydes (**10**) (ratio 4:1) but no 5,5-spirodioxanes (**11**) are formed. This presumably is the result of the relatively easy stabilisation of the 2-adamantyl-cation as the intermediate to **9**.

The formation of the aldehydic compounds (**10**) reflects perhaps also this behaviour, e.g. rationalised by a 1,3-hydride shift at the carbenium intermediate stage, or alternatively by two successive 1,2-hydride shifts.†

2-Bromo-3-methyl-2-homoadamantene (**13**) (see Scheme 3). The homoadamantene derivative (**13**) was obtained in an attempt to open the cyclopropyl-moiety of **12** by brominolysis. It was hoped to prepare a carbon–carbon geminal substituted derivative as depicted by **14**, but GC and NMR analysis of the mixture shows no formation of the desired compound, but that of **13**.

Reaction of adamantyleneoxirane with organometallic compounds (Scheme 4). The opening of the adamantyleneoxirane (**15**) was studied. Grignard derivatives, alkyllithium and aryllithium reag-

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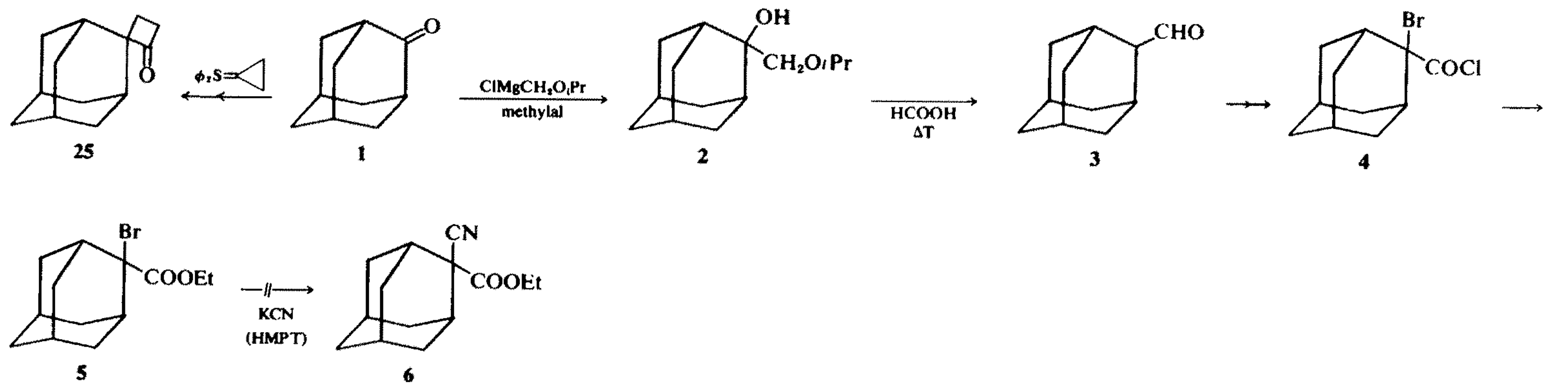
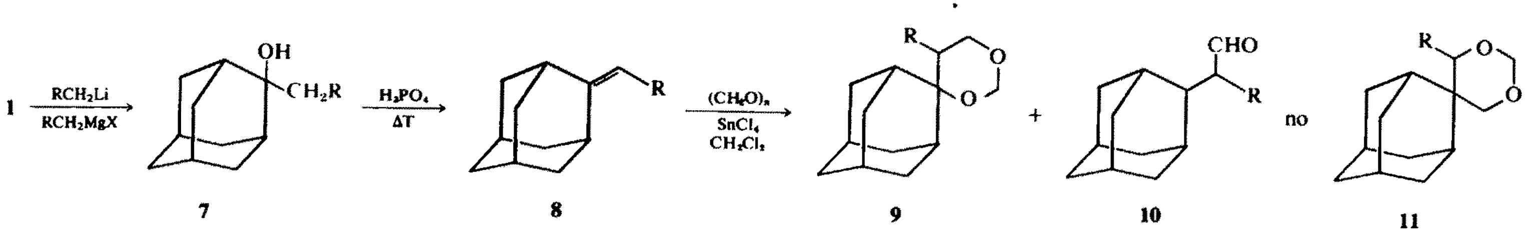
[a] Part of the Ph.D. Thesis of Dr. E. Bernaert.

[b] We dedicate this work to the late Mr Theo Lefèvre, our former Minister for Scientific Programation.

† Attempts to decide between these possibilities by deuteriolabeling (CD_3MgBr) and working up in the usual way were unsuccessful; the only product isolated (NMR) being the undeuterated derivative, seemingly formed by exchange of all of deuterium in the strong acidic medium.



SCHEME 1



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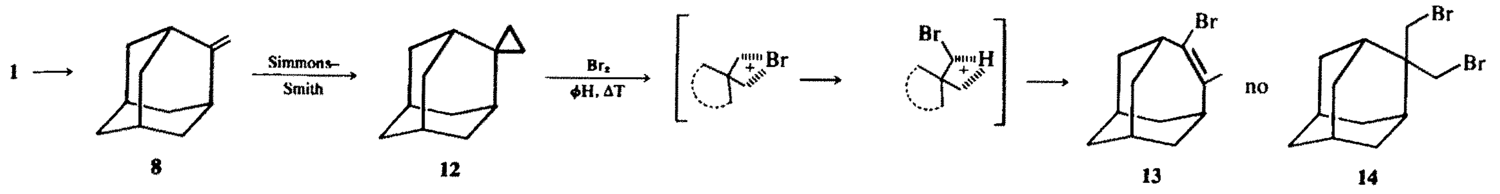
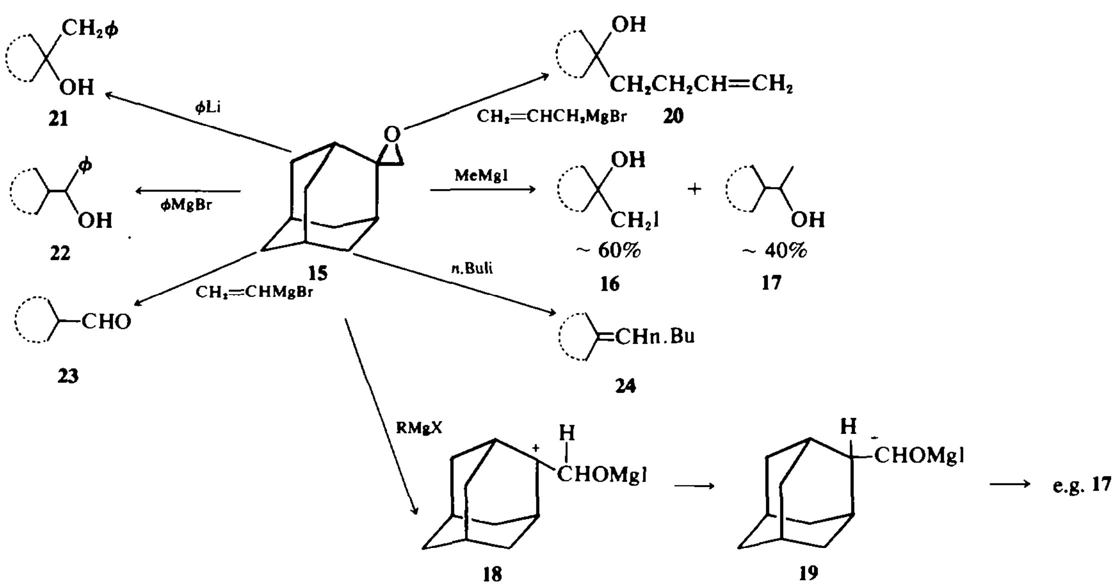


SCHEME 3



SCHEME 4

ents were used. The results are collected in Scheme 4. The opening of the oxirane ring again does not afford the desired geminal carbon–carbon substitution. Either it opens on the wrong side, leading to 2-hydroxy-2-alkyl substituted derivatives, or the original formed cation (**18**) rearranges to 1′-hydroxy derivatives (Scheme 4). As a side product, also 2-hydroxy-2-iodomethyladamantane (**16**) may be formed through an opening with magnesium iodide (Grignard solution).

2-*Adamantylenecyclobutanone* (Scheme 1). Using Trost's procedure,[18] 2-adamantylenecyclobutanone (**25**) could be synthesized in a 95% yield, starting from adamantanone and difenylsulfonium cyclopropylide. This very interesting procedure thus allows the introduction of two carbon moieties starting from carbonyl derivatives. The actual example (adamantanone) shows that even highly substituted ketones may react smoothly.

Work is in progress for the promising preparation of 5,5-adamantylene-1,3-dioxanes, with (**25**) as the precursor.

^{1}*H-NMR spectra*. Some spectral data of adamantane derivatives (i.a. 2-monosubstituted[14] and 2-hydroxy-2-alkyl[15]) can be found in the literature. We refer to Figs 1–5 for some typical representatives obtained now at 300 MHz and which allows a thorough analysis. Peaks belonging to geminal H-atoms are easily detected (AB systems), but this is often difficult for bridge-headed H-atoms.

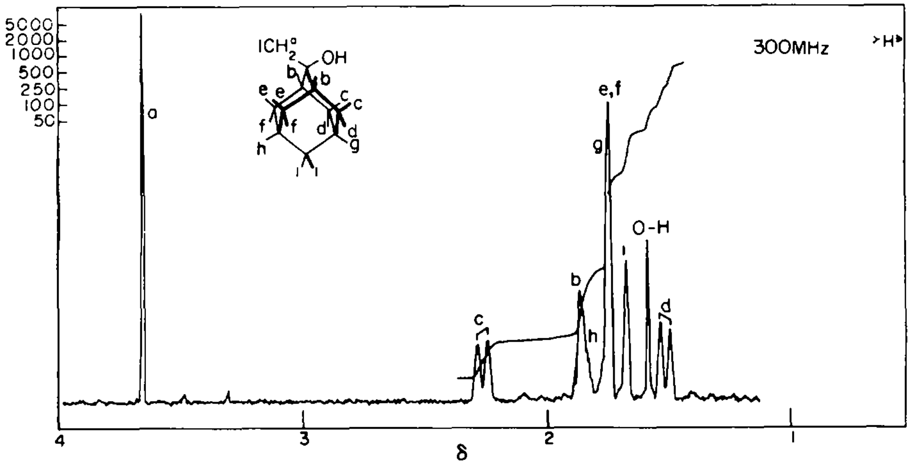


Fig 1. 300 MHz spectrum of 2-hydroxy-2-iodomethyladamantane (**16**) in CCl_4 (TMS internal, 1 vol %, ~ 18°).

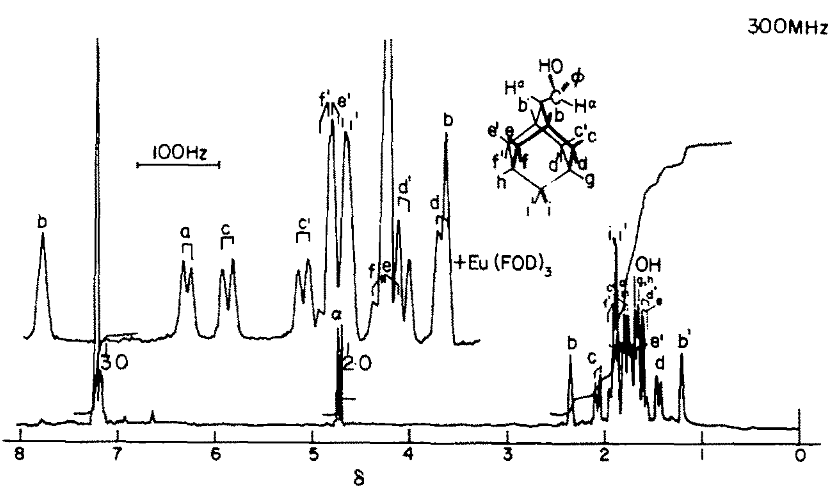


Fig. 2. 300 MHz spectrum of 2-(α-hydroxybenzyl)adamantane (22) in CCl_4 (TMS internal, 1 vol %, ~ 18°). Detail: LIS-spectrum with *ca* 0·5 mole equiv. $Eu(FOD)_3$ added.

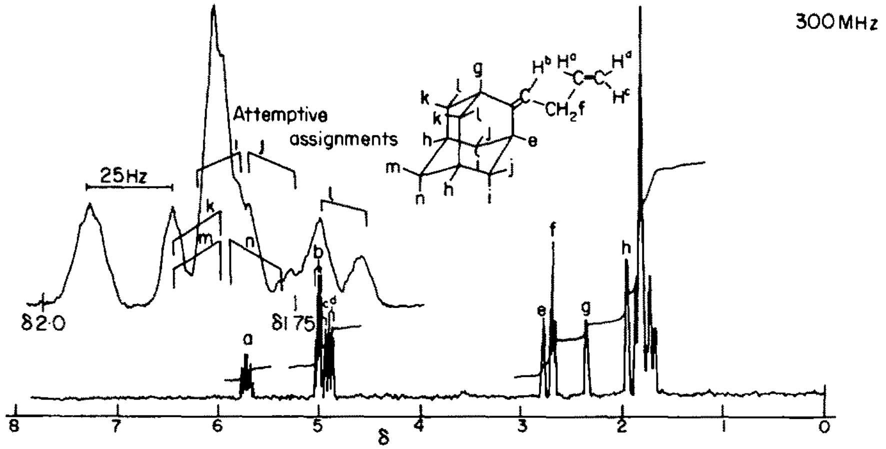


Fig 3. 300 MHz spectrum of 2-(but-3'-enylidene)-adamantane (26) in CCl_4 (TMS internal, 1 vol %, ~ 18°). Detail: protons of the adamantane nucleus.

In contrast to 100 MHz data[15] it is now found possible at 300 MHz and in presence of $Eu(FOD)_3$ (if suitable heteroatoms are present), *to assign all individual atoms* in the ^{1}H-NMR spectra. A linear relationship is obtained for the shifts of the individual signals vs $[Eu(FOD)_3]$, the shift of internal TMS (vs external lock) being used as the parameter for lanthanide concentration. The higher the distance between the H-atom and the site of ligand formation (Dreiding models) the lower the slope. This allowed us to extract all desirable ^{1}H-NMR values, summarized in Table 1. LIS-slope data for 2 - hydroxy - 2 - (but - 3' - anyl) - adamantane (20) and for 2-adamantylenecyclobutanone (25) (Figs 6, 7) are found in Table 1.

Geminal coupling constants in the adamantane nucleus are 12·4–12·6 Hz. F. W. Van Deursen[14] found 11–13 Hz. Coupling constants of H-atoms of the side-chain are found in Table 3. Some δ-values of other derivatives (Fig 1–3) are collected in Table 2.

EXPERIMENTAL

2-Hydroxy-2-isopropoxymethyladamantane (2). Fine Mg turnings (17·5 g, 0·72 mole) in dry methylal (50 ml) and a small amount of iodine were heated under N_2 for 15 min. After cooling to room temp a little mercuric chloride was added. The mixture was stirred for 15 min. From a dropping funnel 1 ml of a soln of freshly distilled chloromethyl isopropylether[7,8] (77·7 g, 0·72 mole) in methylal (100 ml) was added. After the reaction had started (rising temp and gas evolution) the mixture was cooled to − 10°. The rest of the chloromethyl isopropylether was added at such a rate that the temp is kept below − 5°. A soln of adamantanone[6] (20 g, 0·133 mole) in methylal (15·0 ml) was added dropwise during 1 h. Thus a great excess of the Grignard reagent was used. The mixture was poured onto ice (200 g), a saturated ammonium chloride soln (200 ml) was added

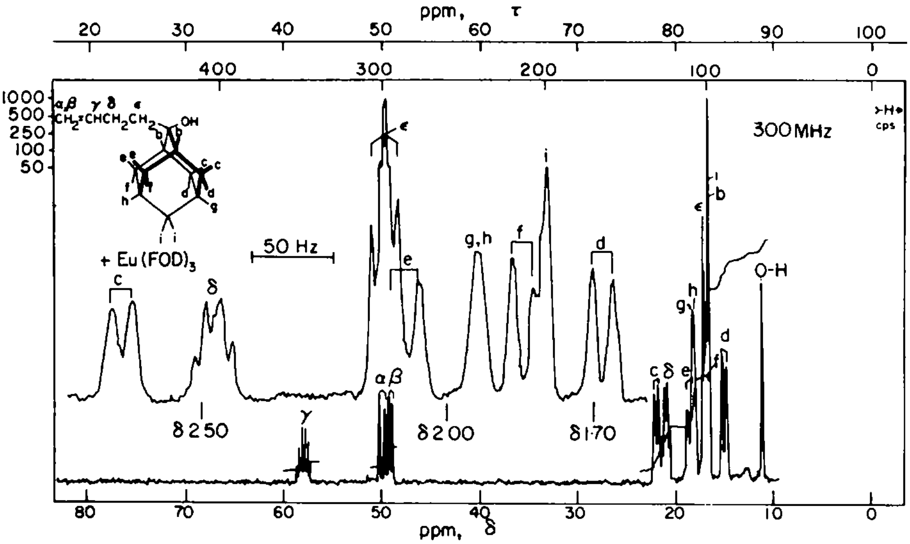


Fig 4. 300 MHz spectrum of 2-hydroxy-2-(but-3′-enyl)-adamantane (20) in CCl_4 (TMS internal, 1 vol %, ~ 18°). Detail: LIS-spectrum with *ca* 0·5 mol equiv. Eu(FOD)$_3$ added.

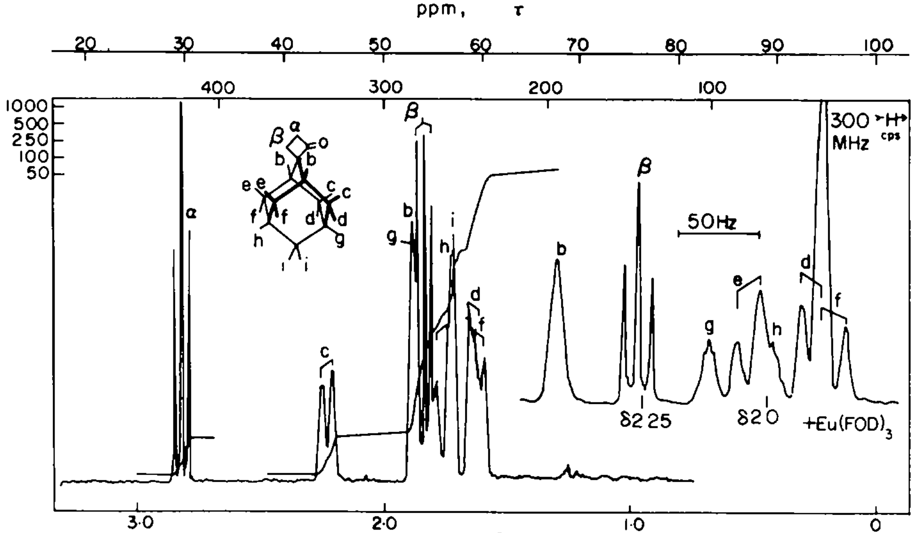


Fig 5. 300 MHz spectrum of 2-adamantylenecyclobutanone (25) in CCl_4 (TMS internal, 1 vol %, ~ 18°). Detail: LIS-spectrum with *ca* 0·5 mol equiv. Eu(FOD)$_3$ added.

and the organic layer separated. After the usual work up the product was distilled (125–128°/15 mm), yield 29·2 g (99%); IR: $\nu(OH) = 3500\ cm^{-1}$; NMR: $\delta|O{-}\underline{H}C(CH_3)_2| = 3{\cdot}52$ multiplet, $\delta|C\underline{H}_2OCH(CH_3)_2| = 3{\cdot}38$ singlet. (Found: C, 75·25; H, 10·18; O, 14·57%. Calc for $C_{14}H_{24}O_2$: C, 74·95; H, 10·78; O, 14·27%).

2-*Formyladamantane* (3). A mixture of 2-hydroxy-2-isopropoxymethyladamantane (28·2 g, 0·127 mole) in formic acid (564 g) was refluxed for 4 h, cooled and poured onto ice (200 g). After extraction with ether (3 × 100 ml), the collected organic layers were washed with water (2 × 200 ml), with 5% NaOH aq (150 ml), again with water (100 ml), and dried over Na_2SO_4. The solvent was evaporated and the residue sublimed *in vacuo*. Yield 13·5 g (65·5% overall yield), m.p. 110–114°; IR: $\nu(C{=}O)$: $1720\ cm^{-1}$; NMR: $\delta(C\underline{H}O) = 9{\cdot}68$ singlet. (Found: C, 80·03; H, 9·95; O, 10·02. Calc for $C_{11}H_{16}O$: C, 80·43; H, 9·82; O, 9·75%). In contrast to literature data,[2a] we found that the compound prepared in the actual way, had no pronounced tendency to polymerize, although after prolonged time an amorphous, insoluble material was formed.

2-*Bromo*-2-*carboethoxy-adamantane* (5). An equivalent amount KOH (0·21 g) was added to 2-bromoadaman-

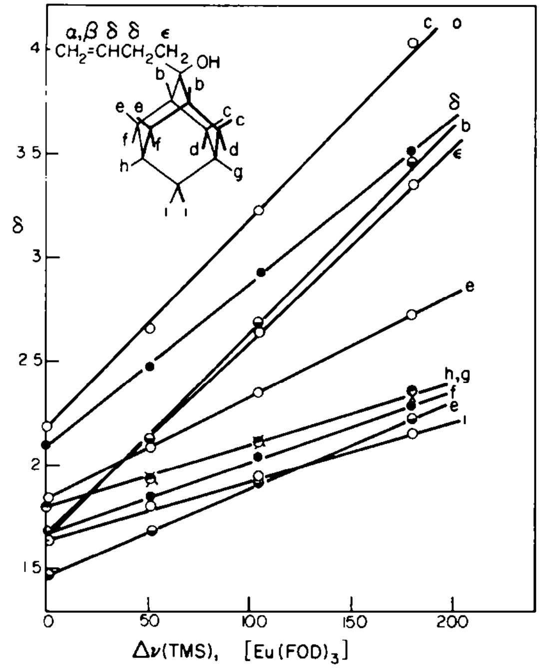


Fig 6. LIS-slopes obtained for 2-hydroxy-2-(but-3′-enyl)-adamantane (**20**). See Table 2 and footnotes.

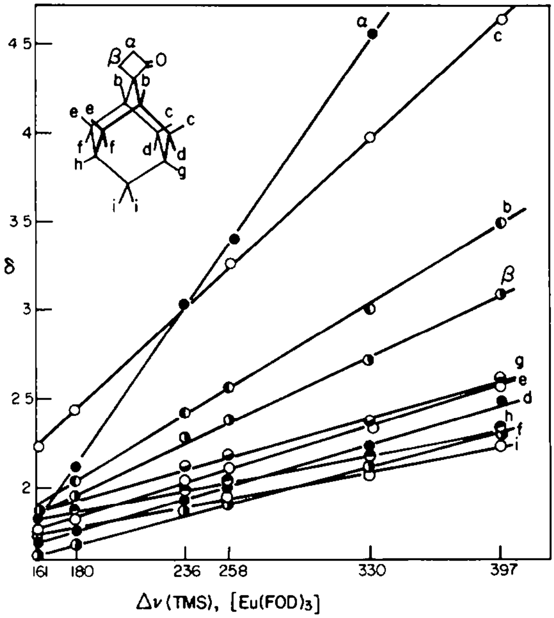


Fig 7. LIS-slopes obtained for 2-adamantylenecyclobutanone (**25**). See Table 2 and footnotes.

Table 1. Euroshift data[e] of 2-hydroxy-2-(but-3′-enyl)-adamantane (**20**) and 2-adamantylenecyclobutanone (**25**) (assignment. *cf* Figs 4, 5)

		i	g	h	f	d	e	b	c	α	β	δ	ε
Slope[a]	(**20**)	0·85	0·90	0·90	1·02	1·25	1·46	2·96	3·00			2·37	2·78
	(**25**)	0·68	0·93	0·83	0·86	1·00	1·02	2·00	3·04		1·55		
δ[b]	(**20**)	1·64	1·80	1·80	1·67	1·47	1·84	1·64	2·18			2·09	1·67
	(**25**)	1·72	1·87	1·73	1·63	1·61	1·76	1·88	2·23	2·82	1·83		
∇(Eu)[c]	(**20**)	0·80	0·90	0·83	1·15	1·40	1·50	3·15	3·65				2·88
	(**25**)	0·57	0·59[d]	0·85	0·88	0·94	1·23	2·31	3·29		1·76		

[a] Slope: $\delta \times 300/\Delta\nu_{TMS}$; $\Delta\nu_{TMS}$ shift difference against external lock.

[b] δ in CCl_4 from TMS internal with $[Eu(FOD)_3] = 0$ (obtained by extrapolation).

[c] Calculated induced Euroshift with the metal location at 3·2 Å away from oxygen along the C—O bond (*cf* Ref 16), and factorised to compare with slope values.

[d] The angle θ for g is almost the magic angle, resulting in a large incertainty for ∇.

[e] Slopes were determined using increasing amounts of $Eu(FOD)_3$ up to about 0·5 mol equiv., see Figs 6 and 7.

Table 2. δ-Values of 2-hydroxy-2-iodomethyladamantane (**16**), 2-(α-hydroxybenzyl)-adamantane (**22**) and 2-(but-3′-enylidene)-adamantane (**26**). (Assignment *cf* Figs 1–3)

Compound	α	a	b	c	d	e	f	g	h	i
16		3·66	2·00	2·19	1·61	1·79	1·79	1·82	1·87	1·71
22	4·71	1·67	2·39	2·05	1·43	1·60	1·73	1·65	1·65	1·85
26						2·78		1·19	2·40	1·81

Compound	j	k	l	m	n	b′	c′	d′	e′	f′	i′
16											
22						1·18	1·80	1·53	1·72	1·92	1·85
26	1·77	1·84	1·69	1·83	1·79						

tane-2-carboxylic acid chloride[2b] (1 g, 37 mmole), dissolved in superdry EtOH (75 ml). The mixture was stirred for 2 h, poured into water (200 ml) and extracted with ether (2 × 100 ml). The ethereal soln was washed with water (100 ml) and dried over Na_2SO_4. The solvent was evaporated. A pure liquid was obtained in quantitative yield, NMR: triplet at 1·30 δ ($—COOCH_2C\underline{H}_3$) and a quadruplet at 4·19 δ ($—COOC\underline{H}_2CH_3$); IR: $\nu(C{=}O)$ 1750 cm^{-1}. (Found: C, 53·85; H, 6·81; O, 10·99; Br, 28·35. Calc for $C_{13}H_{19}BrO_2$: C, 54·40; H, 6·67; O, 11·13; Br, 27·80%).

Alkylideneadamantanes (**8**). Ethylidene-, n.propylidene-, i.propylidene- and n.butylidene-, adamantane were synthesized as described by Landa,[4] methylideneadamantane as described by P. von R. Schleyer.[5]

Benzylideneadamantane. A soln of benzylchloride (10 g, 79 mmole) in ether (50 ml) was added to Mg turnings (1·9 g, 78 mmole) in dry ether (30 ml). The mixture was refluxed for 30 min. A soln of adamantanone[6] (6 g, 40 mmole) in ether (100 ml) was added dropwise. The mixture was heated again for 15 min and worked up in the usual way. The crude carbinol was recrystallized from pentane and sublimed, yield: 9·3 g (96%); m.p. 64°; IR: $\nu(0{—}H) - 3460$ cm^{-1}; NMR: $—C\underline{H}_2OH$: singlet at 2·96 δ. (Found: C, 84·10; H, 9·03; O, 6·87. Calc for $C_{17}H_{22}O$: C, 84·25; H, 9·15; O, 6·60%). The carbinol (9·3 g, 38 mmole) was dissolved in 83% phosphoric acid (100 ml) and heated for 45 min at 200°, cooled and poured onto ice (150 g) and extracted with ether (3 × 100 ml). The ethereal soln was dried over Na_2SO_4 and evaporated. The residue was distilled *in vacuo*, b.p.: 130°/0·5 mm. Overall yield,: 6·0 g (67%); NMR: $\delta(C{=}CH\phi) = 6{\cdot}75$. (Found: C, 90·98; H, 9·02. Calc. for $C_{17}H_{20}$: C, 91·01; H, 8·99%).

Allylideneadamantane. A soln of allylbromide (7·5 g, 62 mmole) in ether (50 ml) was added dropwise followed by a soln of adamantanone[6] (6 g, 40 mmole) in ether (50 ml) to Mg turnings (1·5 g, 62 mmole), covered with ether (50 ml). The mixture was refluxed for 1 h and worked up in the usual way. The carbinol is recrystallized from pentane. Yield: 6·7 g, (95·7%), m.p. 64°. NMR: $—\overset{(a)}{CH_2}\overset{(b)}{CH}{=}\overset{(c,d)}{CH_2}$ δ(Ha) = 2·32; δ(Hb) = 5·78; δ(Hc) = 4·96; δ(Hd) = 5·04; *J*(a,b) = 7·3 Hz; *J*(b,d) = 8·0 Hz; *J*(b,c) = 18·0 Hz. (Found: C, 80·92; H, 10·91; O, 8·17. Calc for $C_{13}H_{20}O$: C, 81·20; H, 10·48; O, 8·32%). Thionylchloride (1·62 g, 14 mmole) is dropped to a cooled soln of 2-hydroxy-2-allyladamantane (2 g, 10 mmole) in pyridine (20 ml) and the temperature is maintained below 20°C. The mixture was allowed to stand over night at 0°, poured into water (100 ml) and extracted with ether (3 × 50 ml). The ethereal layer was washed with water (100 ml), 5% hydrogen chloride (2 × 50 ml), again with water (50 ml) and dried over Na_2SO_4. After evaporation of the solvent, the residue was distilled. B.p. 60·/2 mm. Yield: 1·7 g (95%). NMR: $C{=}\overset{(a)}{CH}{—}\overset{(b)}{CH}{=}\overset{(c,\,d)}{CH_2}$ δ(Ha) = 5·58; δ(Hb) = 6·43; δ(Hc) = 4·92; δ(Hd) = 4·78. *J*(a,b) = 10·5 Hz; *J*(b,c) = 16·5 Hz; *J*(b,d) = 10·0 Hz. (Found: C, 89·82; H, 10·18. Calc for $C_{13}H_{18}$: C, 89·59; H, 10·41%).

4,4-Adamantylene-5-alkyl-1,3-dioxanes (**11**) *general method.* Paraformaldehyde (60 mmole) and tin-(IV)chloride (0·2 ml) were added to a stirred soln of alkylideneadamantane (15 mmole) in methylene chloride (40 ml). The mixture was stirred for 24 h at room temp. The excess of paraformaldehyde was filtered off. The filtrate was poured into a 5% $NaHCO_3$ aq (50 ml) and extracted with methylene chloride (3 × 50 ml), dried over $MgSO_4$ and evaporated. The resiue is distilled *in vacuo*. To separate the 1,3-dioxane (*ca* 80%) from the aldehyde (*ca* 20%) recrystallisation from pentane or gaschromatography (SE 30, 6 m, 225°) was used, yields of **11** (R, m.p.): 75% (H, 24°); 74% (Me, 57°); 44% (Et, 41°); 62% (n.Pr, liquid); 30% (i.Pr, 98°), 27% (ϕ, 148°). R = H: (Found: C, 75·06; H, 9·75; O, 15·19. Calc for $C_{13}H_{20}O_2$: C, 74·96; H, 9·68; O, 15·36%). R = Me: (Found: C, 75·50; H, 9·83; O, 14·66. Calc for $C_{14}H_{22}O_2$: C, 75·63; H, 9·98; O, 14·39%). R = Et: (Found: C, 76·03; H, 10·78; O, 13·19. Calc for $C_{15}H_{24}O_2$: C, 76·23; H, 10·23; O, 13·54%). R = n.Pr: (Found: C, 76·42; H, 10·64; O, 12·94. Calc for $C_{16}H_{26}O_2$: C, 76·75; H, 10·47; O, 12·78%). R = i.Pr: (Found: C, 76·99; H, 10·39; O, 12·62. Calc for $C_{16}H_{26}O_2$: C, 76·75; H, 10·47; O, 12·78%). R = ϕ: (Found: C, 79·98; H, 8·57; O, 11·45. Calc for $C_{19}H_{24}O_2$: C, 80·25; H, 8·50; O, 11·25%). The NMR spectra of these dioxanic derivatives will be discussed in a subsequent paper.

1,1-Adamantylenecyclopropane (**12**).[9] A stirred mixture of Zn dust (4·00 g, 61·5 mmole) cuprous chloride (5·34 g, 54 mmole) and dry ether (15 ml) was refluxed under N_2 for 30 min. Methylideneadamantane[5] (3·2 g, 22 mmole) and methylene iodide (8·04 g, 30 mmole) was added. The stirred mixture was refluxed for 24 h, poured into 5% HCl aq (100 ml) and filtered. The ppt was washed with ether (50 ml). The ethereal soln was washed with water (50 ml), 5% $NaHCO_3$ aq (50 ml) and dried over $MgSO_4$. After evaporation of the solvent, the residue was sublimed, m.p. 116°, yield: 3·15 g (90%). (Found: C, 88·97; H, 11·03. Calc for $C_{12}H_{18}$: C, 88·82; H, 11·18%).

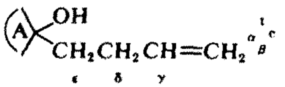
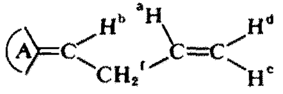
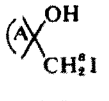
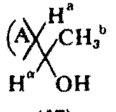
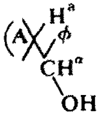
2-Bromo-3-methyl-2-homoadamantene (**13**). Br_2 (3·15 g, 19 mmole) was added dropwise to a soln of 1,1-adamantylenecyclopropane (3·1 g, 19 mmole) in benzene (31 ml). The mixture was refluxed for 24 h. After distillation *in vacuo*, the product was purified by GC (QF_1, 20 m, 190°), yield of 2-bromo-3-methyl-2-homoadamantene 3·5 g (78·5%), m.p. 58°; IR: $\nu(C{=}C) = 1660$ cm^{-1}; MS: M^+: 240 *m/e*; NMR: $\delta(CH_3) = 2{\cdot}25$ (singlet). (Found: C, 59·61; H, 7·46; Br, 32·93. Calc for $C_{12}H_{17}Br$: C, 59·76; H, 7·11; Br, 33·13%).

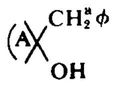
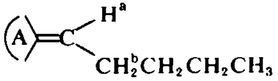
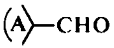
Adamantyleneoxirane[2c,10,11] (**15**). A mixture of trimethyloxosulfonium iodide[12] (14 g, 63 mmole), dimethylsulfoxide (100 ml), sodium hydride (1·60 g, 66 mmole), and adamantanone[6] (4·5 g, 30 mmole) was stirred for 20 h at room temp, and for 1 h at 50°. After cooling the mixture was poured onto ice (100 g) and extracted with ether (200 ml). The ethereal layer was washed with water (3 × 100 ml) and dried over Na_2SO_4. After evaporation of the solvent, the residue was sublimed, yield: 4·7 g (96%), m.p.: 180°; NMR: $\delta(—C\underline{H}_2—O) = 2{\cdot}45$ (CCl_4); MS: M^+: 164 *m/e*. (Found: C, 79·96; H, 10·22, O, 9·82. Calc for $C_{11}H_{16}O$: C, 80·43; H, 9·82; O, 9·75%).

Treatment of adamantyleneoxirane (**15**) *with organometallic derivatives.* For one equiv adamantyleneoxirane, two equivs of organometallic derivatives was used. The reactions were worked up in the usual way. The results are collected in Table 3.

2-Adamantylenecyclobutanone (**25**). To a soln of cyclopropyldiphenylsulfonium fluoroborate[17] (3·92 g, 12·5 mmol) and adamantanone[6] (1·5 g, 10 mmol) in dimethylsulfoxide (30 ml) powdered KOH (1·12 g, 20 mmol) was added under N_2. After stirring the mixture over night at room temp, it was poured into a chilled 1 M soln of tetrafluoroboric acid (25 ml) followed by extraction with ether (2 × 50 ml). The ethereal layer was washed with water (2 × 50 ml) and dried over $MgSO_4$. After evaporation of the ether, the residue was recrystallized from pentane, yield: 1·75 g (92%); m.p. 86°; IR: $\nu(C{=}O) = 1760$ cm^{-1}; M.S.: $M^+ = 190$ *m/e*, 148 *m/e*: base peak

Table 3. Reaction products from adamantyleneoxirane with organometallic reagents (Scheme 4)

Reagent[a]	Reaction time	Yield %	Reaction products	M.p.	NMR (CCl_4)	I.R.	M.S.
$CH_2{=}CHCH_2MgBr$	30 min	94·5	 (**20**) Injection of (**20**) in the gaschromatograph gives 2-but-3'-enylidene-adamantane (**26**)	67°	$J(\beta^c, \gamma) = 10{\cdot}2$ Hz $J(\alpha^t, \gamma) = 17{\cdot}0$ Hz $J(\gamma, \delta) = 6{\cdot}70$ Hz $J(\alpha^t, \delta) = 1{\cdot}75$ Hz $J(\beta^c, \delta) = 1{\cdot}15$ Hz $J(\delta, \epsilon) = 7{\cdot}0$ Hz $\delta(\gamma) = 5{\cdot}80$ $\delta(\alpha^t) = 4{\cdot}98$ $\delta(\beta) = 4{\cdot}89$ $\delta(\epsilon) = 1{\cdot}67$ $\delta(\delta) = 2{\cdot}09$	$\nu(OH) = 3360\ cm^{-1}$ $\nu(C{=}C) = 1650\ cm^{-1}$	
			 (**26**)		$J(a, c^t) = 17{\cdot}1$ Hz $J(a, d^c) = 10{\cdot}0$ Hz $J(a, f) = 6{\cdot}0$ Hz $J(c^t, d^c) = 1{\cdot}8$ Hz $J(c^t, f) = 1{\cdot}7$ Hz $J(d^c, f) = 1{\cdot}7$ Hz $J(b, f) = 7{\cdot}5$ Hz $\delta(a) = 5{\cdot}72$ $\delta(b) = 5{\cdot}00$ $\delta(c) = 4{\cdot}96$ $\delta(d) = 4{\cdot}87$ $\delta(f) = 2{\cdot}69$		
MeMgI[b]	2 h	94	 (60%) (**16**)	63°	$\delta(a) = 3{\cdot}66$ (singlet)	$\nu(OH) = 3400\ cm^{-1}$	$M^+ = 292$ *m/e* peak $272 = M^{+\cdot}\text{-}H_2O$ peak $165 = M^+\text{-}I$ peak $151 = M^+\text{-}CH_2I$
			 (40%) (**17**)	85°	$\delta(\alpha) = 3{\cdot}90$ $(b) = 1{\cdot}23$ $J(\alpha, a) = 10{\cdot}0$ Hz $J(\alpha, b) = 5{\cdot}8$ Hz	$\nu(OH) = 3300\ cm^{-1}$	$M^+ = 180$ *m/e* base peak 162 $(\text{-}H_2O)$ peak 135 (Ad^+)
ϕMgBr	2 h	96	 (**22**)	103°	$\delta(\alpha) = 4{\cdot}71$ $\delta(a) = 1{\cdot}23$ $J(a, \alpha) = 10{\cdot}30$ Hz	$\nu(OH) = 3400\ cm^{-1}$	$M^+ = 242$ *m/e* peak 135 (Ad^+) peak 107 (ϕCH_2O^+)

φLi	3 h	73·5	 **(21)**	64°	$\delta(a) = 2{\cdot}96$	$\nu(\mathrm{OH}) = 3460\ \mathrm{cm}^{-1}$
n.BuLi	30 min	96	 **(24)**	liquid	$\delta(a) = 4{\cdot}93$ $J(a, b) = 7{\cdot}0\ \mathrm{Hz}$	$\nu(\mathrm{C{=}C}) = 1660\ \mathrm{cm}^{-1}$
$CH_2{=}CHMgBr$	1 u	87	 **(23)**	110–114°	$\delta(\mathrm{CHO}) = 9{\cdot}68$ (singlet)	$\nu(\mathrm{C{=}O}) = 1720\ \mathrm{cm}^{-1}$

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[a] The solvent is ether except for vinylmagnesium bromide, where it is THF.

[b] The reaction products are analoguous with those obtained by the reaction of ethylmagnesiumbromide with 1,2-epoxy-2-methylpropane.[13]

(Found: C, 81·59; H, 10·69; O, 7·72. Calc for $C_{14}H_{22}O$ (**20**): C, 81·48, 10·76, O, 7·76%).
(Found: C, 89·59; H, 10·41: Calc for $C_{14}H_{20}$ (**25**): C, 89·29, H, 10·71%).
(Found: C, 45·15; H, 5·62; O, 5·50; I, 43·73. Calc for $C_{11}H_{17}IO$ (**16**): C, 45·22; H, 5·87; O, 5·48; I, 43·43%).
(Found: C, 79·53; H, 11 40; O, 9·07. Calc for $C_{12}H_{20}O$ (**17**): C, 79·95; H, 11·18; O, 8·87%).
(Found: C, 84·61; H, 9·15; O, 6·24. Calc for $C_{17}H_{22}O$ (**22**): C, 84·25; H, 9·15; O, 6·60%).
(Found: C, 84·51; H, 9·45; O, 9·25. Calc for $C_{17}H_{22}O$ (**21**): C, 84·25; H, 9·15; O, 6·60%).
(Found: C, 88·23; H, 11·77. Calc for $C_{15}H_{24}$ (**24**): C, 88·16; H, 11·84%).
(Found: C, 80·03; H, 9·97; O, 10·00. Calc for $C_{11}H_{16}O$ (**23**): C, 80·43; H, 9·82; O, 9·75%).

—($CH_2{=}C{=}O$); NMR (Fig 5 and Table 1) in CCl_4: $—\overset{\alpha}{C}H_2—\overset{\beta}{C}H_2—C{=}O$ $\delta(\alpha) = 2{\cdot}82$, $\delta(\beta) = 1{\cdot}83$, $J(\alpha, \beta) = 8{\cdot}40$ Hz. (Found: C, 85·39; H, 7·68; O, 6·93. Calc for $C_{17}H_{18}O$: C, 85·67; H, 7·61; O, 6·72%).

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