New Reactions of Triplet Oxygen which avoid the Spin Barrier

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The cation triphenylmethylium and the cation radical tris-(*p*-bromophenyl)ammoniumyl are effective catalysts for oxygenation of ergosteryl acetate (1; R = Ac) to the peroxide (2; R = Ac): the triphenylmethylium-catalysed reaction is a photo-oxygenation, whereas the cation radical reaction is thermal. Several other 'forbidden' additions of triplet oxygen to cisoid dienes have been demonstrated. A number of cation radicals have been examined for catalytic oxygenation ability. Ergosteryl acetate can also be converted into its peroxide by triplet oxygen in the presence of various Lewis acids.

Two mechanisms for overcoming the spin barrier for triplet oxygen addition have been defined by experimental work. A mechanistic interpretation of the facts is proposed.

DURING studies related to the use of trityl cation for the deprotection of masked steroidal alcohols,[1] we treated ergosterol 3β-methoxymethyl ether (1; R = $MeO{\cdot}CH_2$) with trityl tetrafluoroborate (0.3 equiv.) in dichloromethane without precautions to exclude oxygen. At −78 °C the peroxide (2; R = $MeO{\cdot}CH_2$) was formed in high yield. Ergosterol 3β-acetate (1; R = Ac) similarly afforded the 5α,8α-peroxide (2; R = Ac).[2] Further investigation showed that the acetate (1; R = Ac) in dry dichloromethane containing a *catalytic* amount of trityl tetrafluoroborate at −78 °C, on exposure to air and laboratory lighting, gave the peroxide (2; R = Ac) quantitatively in 2.75 h. In the dark there was no reaction. Irradiation of this system with a tungsten lamp (500 W) gave the peroxide (2; R = Ac) in 30 min. Under an atmosphere of pure oxygen, peroxide (2; R = Ac) formation was complete (1.03 mol. equiv. uptake) in 10 min at −78 °C even on a preparative scale (>1 g). The trityl cation was isolated as triphenylmethanol (86%) from aqueous work-up. Photo-oxygenation at −15 °C, 0 °C, or room temperature did not give clean reactions. Only at less than −15 °C was the peroxide (2; R = Ac) formed in good yield.

When trityl cation in dichloromethane at −78 °C, in the presence of oxygen, was irradiated in the absence of ergosteryl acetate, no oxygen was consumed (*cf.* ref. 3).

To compare conventional singlet oxygen photo-oxygenation [4] and the trityl cation system the experiments summarised in Table 1 were carried out. The rate ratio k(1; R = Ac)/k(3; R = Ac) was *ca.* 6 000 for the trityl system whereas the ratio for the eosin system was *ca.* 3.3. In our opinion this dramatic difference in reactivity discounts the trityl cation acting merely as a triplet-to-singlet oxygen sensitiser. Azotriphenylmethane (5) in dichloromethane at −78 °C with ergosteryl acetate (1; R = Ac) was oxygenated under irradiation. Warming the mixture to −15 °C gave no peroxide (2; R = Ac), only triphenylmethyl peroxide.[5] Trityl radicals are not, therefore, the catalytic oxygenation species. Trityl hexachloroantimonate,[6] perchlorate, and hexafluorophosphate [7] were all effective oxygenation catalysts, and a comparative study indicated no appreciable difference in the rate of formation of the peroxide (2; R = Ac) with each catalyst.

Ergosteryl acetate in dichloromethane (−78 °C) containing trityl tetrafluoroborate was oxygenated in light

TABLE 1

Comparative photo-oxygenations with the trityl cation and with eosin

Substrate	Conditions	Time of oxygenation	Product (% yield)
(1; R = Ac)	Substrate (100 mg), $Ph_3C^+BF_4^-$ (10 mg), CH_2Cl_2; −78°; O_2	2 min	(2; R = Ac) (100)
(3; R = Ac)	Substrate (100 mg), $Ph_3C^+BF_4^-$ (10 mg), CH_2Cl_2; −78°; O_2	10 h	5% Conversion into (4; R = Ac)
(1; R = Ac)	Substrate (50 mg), eosin (10.5 mg), PhCN–CH_2Cl_2 (2 : 1); −15°; O_2	30 min	(2; R = Ac) (>95%)
(3; R = Ac)	Substrate (50 mg), eosin (10.5 mg), PhCN–CH_2Cl_2 (2 : 1); −15° O_2	100 min	(4; R = Ac) (>95%)

[1] (*a*) D. H. R. Barton, P. D. Magnus, G. Smith, and D. Zurr, *Chem. Comm.*, 1971, 861; (*b*) D. H. R. Barton, P. D. Magnus, G. Streckert and D. Zurr, *ibid.*, p. 1109; (*c*) D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert, and D. Zurr, *J.C.S. Perkin I*, 1972, 542; (*d*) D. H. R. Barton, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J.C.S. Chem. Comm.*, 1972, 447 (preliminary account of this work).

[2] V. Prelog and P. Wieland, *Helv. Chim. Acta*, 1947, **30**, 1028.

[3] E. E. van Tamelen and T. M. Cole, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 6158; D. M. Allen and E. D. Owen, *Chem. Comm.*, 1971, 848.

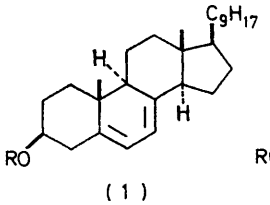
[4] K. Gollnick and G. O. Schenk, 'Oxygen as a Dienophile in 1,4-Cycloaddition Reactions: The Diels–Alder Reaction in Heterocyclic Syntheses,' ed. J. Hamer, Academic Press, New York, 1967, p. 255; C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104; D. R. Kearns, *Chem. Rev.*, 1971, **71**, 395; K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

[5] M. Gomberg, *Ber.*, 1900, **33**, 3150; *Chem. Rev.*, 1924, **1**, 91.

[6] J. Holmes and R. Pettit, *J. Org. Chem.*, 1963, **28**, 1695.

[7] G. A. Olah, J. J. Svoboda, and J. A. Olah, *Synthesis*, 1972, **101**, 544.

(tungsten lamp). The formation of the peroxide (2; R = Ac) terminated at once in darkness but resumed on irradiation. This appears to invalidate a photochemically initiated radical-chain mechanism. Oxygenation of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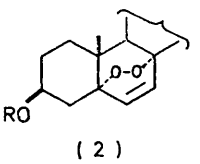
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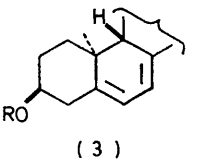
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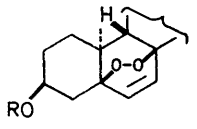
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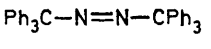
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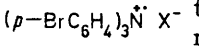
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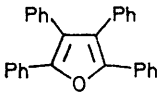
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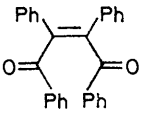
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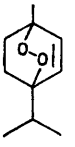
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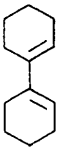
(1; R = Ac) with trityl tetrafluoroborate *in the dark* proceeded if diphenylpicrylhydrazyl was present in slightly greater amounts than trityl tetrafluoroborate and gave the peroxide (2; R = Ac) quantitatively. Oxygenation of (1; R = Ac) with diphenypicrylhydrazyl alone in the dark gave *no* peroxide (2; R = Ac).

Triarylamines can be oxidised to give relatively stable crystalline amine radical cation salts. Electron-donating substituents stabilise the radical cations, whereas electron-withdrawing groups can destabilise the salts to such an extent as to make isolation impossible.[8] Tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate[9] (6; X = $SbCl_6$) catalysed the formation of ergosterol acetate peroxide (2; R = Ac) *in the dark* at −78 °C. Indeed, tris-(*p*-bromophenyl)ammoniumyl fluoroborate (6; X = BF_4) (10 mg) in dichloromethane catalysed the oxygenation of ergosteryl acetate (1; R = Ac) (100 mg) in a *dark* reaction to give quantitatively the peroxide (2; R = Ac) (5 min). Use of higher temperatures did not give clean products. Lumisteryl acetate (3; R = Ac) did not react under these conditions either at −78 °C or at room temperature.

Tetraphenylfuran (7) was oxygenated smoothly with trityl cation as catalyst at −78 °C to give *cis*-dibenzoylstilbene (8) in 67% yield.[10] The ammoniumyl fluoroborate and hexachloroantimonate salts (6; X = BF_4 or $SbCl_6$) were less effective, yielding 30 and 10% of the stilbene (8) respectively.

The photo-oxygenation of *p*-mentha-1,3-diene (9) with trityl cation catalysis gave 1,4-epidioxy-*p*-menth-2-ene (10)[11] (90%). Again the amine cation radicals (6; X = BF_4 or $SbCl_6$) gave 55 and 16% yields of (10), respectively. If these reactions are proceeding *via* a peroxyl radical intermediate, then 1,1'-bicyclohexenyl (11)[12] should afford a mixture of *cis*- and *trans-endo*-peroxides.[13] In the event oxygenation of 1,1'-bicyclohexenyl (11) in the presence of trityl cation (*hν*) or the amine cation radical (dark) (6; X = BF_4) gave only the *cis*-peroxide (12) in 64 and 74% yield, respectively. The peroxide was hydrogenated to the *cis*-diol (13) to provide proof of configuration.

1,3-Diphenylisobenzofuran (14)[14] is a highly reactive singlet oxygen acceptor and can even react slowly with triplet oxygen to give *o*-dibenzoylbenzene (15).[15] Its reactions with trityl cation and the amine cation radical (6; X = $SbCl_6$) proved to require molar amounts of these species rather than catalytic. The reagents were consumed immediately on mixing to give *o*-dibenzoylbenzene (15) in high yield. 9-Phenylanthracene and 9,10-diphenylanthracene, both of which react rapidly with singlet oxygen, remain substantially unaffected by our oxygenation conditions. 9,11-Didehydroergosteryl acetate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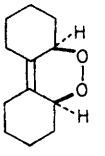
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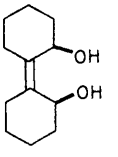
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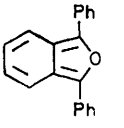
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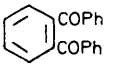
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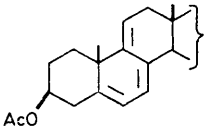
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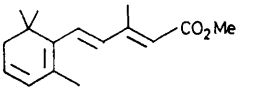
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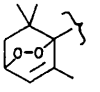
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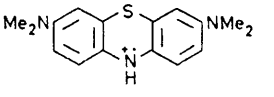
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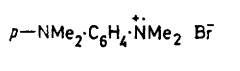
(20)

(16) is stable to these oxygenation conditions, although it reacts readily with singlet oxygen.[16] Tetraphenylcyclopentadienone and 4-methyl-2,5-diphenyloxazole[17] are both reactive towards singlet oxygen but are unaffected by the trityl cation or amine radical cation oxygen-

[8] R. I. Walter, *J. Amer. Chem. Soc.*, 1966, **88**, 1923.
[9] F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc.* (*C*), 1969, 2719.
[10] G. O. Schenk, *Z. Electrochem.*, 1960, **64**, 997.
[11] G. O. Schenk and K. Ziegler, *Naturwiss.*, 1944, **32**, 157.
[12] E. E. Gruber and R. Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 2555.
[13] K. H. Schulte-Elte, Dissertation, Göttingen, 1961.
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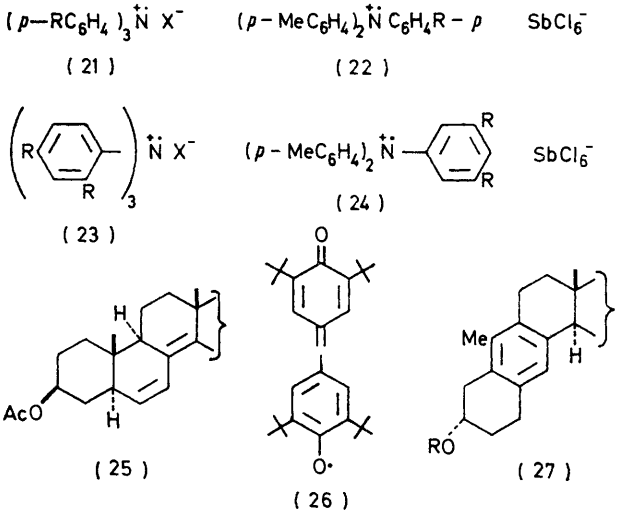
[15] A. LeBerre and R. Ratsimbazafy, *Bull. Soc. chim. France*, 1963, 229.
[16] P. Bladon, R. B. Clayton, W. Greenhalgh, H. B. Henbest, E. R. H. Jones, B. J. Lovell, G. Silverstone, G. W. Wood, and G. F. Woods, *J. Chem. Soc.*, 1952, 4882.
[17] G. H. Cleland and C. Niemann, *J. Amer. Chem. Soc.*, 1949, **71**, 841.

ation conditions. Allylic hydroperoxide formation was not observed with isolated double bonds: cholesteryl acetate did not react. Similarly, there was no analogy with the reactions of singlet oxygen with electron-rich olefins utilising the mesomeric effect of nitrogen or oxygen.[18] This was illustrated by the lack of reactivity of the pyrrolidine enamine[19] and ethyl enol ether[20] of cholest-4-enone. 'Skipped' dienes such as cyclohexa-1,4-diene, norbornadiene, and linoleic acid were not oxygenated by any of the above reagents. The diene precursor (17) to *trans*-abscisic acid gave a multi-component mixture on treatment (−78 °C) with trityl cation or amine cation radical in oxygen, none of the products being the peroxide (18).[21]

In view of the preparative limitation, an attempt was made to find other reagents to catalyse the oxygenation of dienes.

Onium salts[22] were ineffective, as were a range of free radicals: bisnitrophenyl nitroxide,[23] bismethoxyphenyl nitroxide,[24] galvinoxyl,[25] 1,3,5-triphenylverdazyl,[26] and 1,3-diphenyl-1,2,4-benzotriazinyl.[27] These radicals did not oxygenate even when mixed with the trityl cation in the *dark*. The ammoniumyl salt from Methylene Blue (19)[28] and Würster's Blue (20)[29] were also ineffective oxygenating catalysts.

In view of the specific requirements of the catalyst a study of triarylammoniumyl salts was made. The counterion X^- in (6) does not appear to alter the reactivity, since (6; X = $SbCl_6$, BF_4, or PF_6) were all equally effective in the conversion of (1; R = Ac) into (2; R = Ac). A series of triarylamines were prepared and oxidised to the corresponding radical cations. The tritolyl (21, R = Me) and tris-*p*-methoxyphenyl (21; R = OMe) radical cations were not effective as catalysts for the conversion of (1; R = Ac) into (2; R = Ac). The trichloro- (21; R = Cl) and tri-iodo- (21; R = I) radical cations were excellent catalysts. The ditolylamine radical cations (22; R = Br, Cl, or I) were synthesised and proved not to be oxygenation catalysts. In contrast (22; R = CN) was highly effective. Similarly, incorporation of other electronegative groups (22; R = NO_2 or CO_2Me) gave useful catalysts. Tris-(*p*-methoxycarbonylphenyl)ammoniumyl hexachloroantimonate (21; R = CO_2Me) was an extremely active catalyst. Tris-(2,4-dibromophenyl)- and tris-(2,4-dichlorophenyl)-ammoniumyl hexachloroantimonates (23; R = Br or Cl) were good low-temperature catalysts. The 3,5-bismethoxycarbonyl radical cation (24; R = CO_2Me) was an active oxygenating catalyst, whereas the 3,5-dimethoxy-radical-cation (24; R = OMe) was inactive. A series of cobalt complexes, and porphin–metal complexe were without any catalytic activity.



It was suggested by one of us (R.K.H.) that since cationic complexing of the diene appeared important, simple Lewis acids might also be effective catalysts for the oxygenation of *cis*-dienes to *endo*-peroxides.[30] Table 2 indicates Lewis acids that convert

TABLE 2

Lewis acids effecting conversion (⩾98% as estimated spectrophotometrically) of ergosteryl acetate (1; R = Ac) [1.14 × 10^{-4}M in CH_2Cl_2 (25 ml)] at −78°C under irradiation into (2; R = Ac)

Lewis acid (equiv.)	Time (min)
BF_3 (0.1) *	8—12
$SnCl_4$ (0.2) *	2—10
$SnCl_4$ (1.0)	⩽2
$SnBr_4$ (0.2)	8—15
$SnBr_4$ (1.0)	⩽6
SbF_5 (0.05)	8—15
$SnCl_5$ (0.1)	*ca.* 15
WF_6 (0.1)	10
I_2 (0.2 or 1.0) *	*ca.* 15

* No significant peroxide formation (<3%) in the dark during 30 min.

ergosteryl acetate (1; R = Ac) into the *endo*-peroxide (2; R = Ac) in at least 98% yield and require irradiation. The Lewis acids listed in Table 3 produced coloured reaction mixtures with ergosteryl acetate (1; R = Ac) (unlike those in Table 2) and were less effective in catalysing the formation of the *endo*-peroxide (2; R = Ac). Aluminium trichloride also caused isomerisation of (1;

[18] C. S. Foote and J. Wei-Ping-Liu, *Tetrahedron Letters*, 1968, 3267.
[19] F. W. Heyl and M. E. Herr, *J. Amer. Chem. Soc.*, 1953, **75**, 1918.
[20] P. L. Julian, E. W. Meyer, W. J. Karpel, and W. Cole, *J. Amer. Chem. Soc.*, 1951, **73**, 1982.
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[22] K. Fukui, K. Ohkubo, and T. Yamabe, *Bull. Chem. Soc. Japan*, 1969, **42**, 312.
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[24] K. H. Meyer and H. G. Billroth, *Ber.*, 1919, **52**, 1476; K. H. Meyer and W. Reppe, *Ber.*, 1921, **54**, 327.
[25] P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, 1962, **84**, 2596; G. M. Coppinger, *ibid.*, 1957, **79**, 501.
[26] R. Kuhn and H. Trischmann, *Monatsh.*, 1964, **95**, 457; R. Kuhn and H. Trischmann, *Angew. Chem. Internat. Edn.*, 1963, **2**, 155.
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[29] C. Würster and R. Sendtner, *Ber.*, 1879, **12**, 1803.
[30] D. H. R. Barton, R. K. Haynes, P. D. Magnus, and I. D. Menzies, *J.C.S. Chem. Comm.*, 1974, 511.

R = Ac) into the 6,8(14),22-triene (25) in competition with the formation of the *endo*-peroxide (2; R = Ac). The Lewis acids listed in Table 4 gave quantitative yields of the *endo*-peroxide (2; R = Ac) in the *dark*. For the experiments in Table 5 the initial reaction was carried out in the dark. When the formation of peroxide (2; R = Ac) became slow or ceased (within the given times) subsequent irradiation generally converted unchanged ergosteryl acetate (1; R = Ac) into the peroxide (2; R = Ac). Since diphenylpicrylhydrazyl induced a thermal reaction with trityl cation, additives were used with certain Lewis acids that were ineffective in the dark. The results are given in Table 6. When the aromatic hydrocarbons were used as co-catalysts the order of addition of the reactants was important. Addition of the aromatic hydrocarbon to a mixture of ergosteryl acetate (1; R = Ac) and antimony pentachloride did *not* produce significant quantities of the *endo*-peroxide (2; R = Ac) in the dark during 30 min.

Oxygenation reactions run at 0 °C gave deeply coloured mixtures and the formation of (2; R = Ac), whilst initially rapid, ceased at the indicated times (Table 7).

TABLE 3

Lewis acids effecting lower conversions of ergosteryl acetate (1; R = Ac) (conditions as for Table 2) into (2; R = Ac) under irradiation

Lewis acid (equiv.)		Conversion (%)	Time (min)
BCl_3	(0.2)	90 [traces of (25)]	160
BBr_3	(0.2)	46 [44% of (25)]	160
$AlCl_3$	(1.0)	93	160
$AlCl_3$, $MeNO_2$	(1.0)	50—93 [traces of (25)]	80—160
$AlCl_3$, excess $MeNO_2$	(1.0)	89—93	20—40
$AlCl_3$, excess $MeNO_2$	(1.0) [a]	83	30
$AlCl_3$, excess $MeNO_2$	(1.0) [b]	88	12
$AlBr_3$, $MeNO_2$	(1.0)	20 [33% of (25)]	10
TiF_4	(1.0)	89	180
$TiCl_4$	(0.2)	80	360
$SbCl_3$	(3.0)	94	60
$PtCl_4$	(0.2)	80	60
FSO_3H	(0.2)	10	40
$ClSO_3H$	(0.2)	30	40

[a] 2.28×10^{-4}M in chlorobenzene at −40 °C. [b] 2.28×10^{-4}M in toluene at −80 °C.

TABLE 4

Lewis acids effecting quantitative (≥98% as estimated spectrophotometrically) conversion of ergosteryl acetate (1; R = Ac) [1.14×10^{-4}M in CH_2Cl_2 (25 ml)] at −78 °C in the dark

Lewis acid (equiv.)		Time (min)
$VOCl_3$	(0.05)	≤0.5
$FeCl_3$ (solid)	(1.0)	240
$FeCl_3$, Et_2O	(0.2)	60
$FeCl_3$, Et_2O	(1.0)	≤0.5
$FeCl_3$, Me_2CO	(0.2—1.0)	≤0.5
$FeCl_3$, $POCl_3$	(1.0)	≤0.5
$FeBr_3$	(1.0)	60
$FeBr_3$, Et_2O	(1.0)	≤0.5
$MoCl_5$	(0.2)	25
WCl_6	(0.01 and 0.02)	≤0.5

TABLE 5

Lewis acids effecting conversion of (1; R = Ac) into (2; R = Ac) (conditions as for Table 4) at first in the dark, then under irradiation

Lewis acid (equiv.)		Conversion (%)	Time (min)	Total conversion on subsequent irradiation
$SnCl_4$	(1.0)	73	120	Quantitative
$SnBr_4$	(1.0)	5	120	Quantitative
SbF_5	(0.05)	5	60	Quantitative
$SbCl_5$	(0.1)	5	60	Quantitative
$FeCl_3$, Et_2O	(0.05)	9	60	Quantitative
$FeCl_3$, Et_2O	(0.1)	60	60	Quantitative
$FeCl_3$, $POCl_3$	(0.2)	85	60	Quantitative
$FeBr_3$	(0.2)	27	60	Quantitative
$FeBr_3$	(0.2)	27	60	83%
$MoCl_5$	(0.1)	62	60	90%
$MoCl_5$, $POCl_3$	(0.2)	64	60	Quantitative
WCl_6	(2×10^{-3})	30	60	30%
WCl_6	(5×10^{-3})	96	60	96%
$(p\text{-}BrC_6H_4)_3\overset{+}{N}\cdot Sb\text{-}Cl_6$	(5×10^{-3})	36	30	40%

TABLE 6

Lewis acids effecting conversion of (1; R = Ac) into (2; R = Ac) (conditions as for Table 4) in the dark

Lewis acid (equiv.)	Co-catalyst (equiv.)	(2; (R = Ac) (%)	Time (min)
$AlCl_3$, excess $MeNO_3$ (1.0)	$CuCl_2$ (—)	77	120
$AlCl_3$, excess $MeNO_2$ (1.0)	DPPH (0.2)	100	8—10
$SbCl_5$ (0.2)	*o*-Chloranil (0.2)	30	60
$SbCl_5$ (0.2)	TCNE * (0.2)	20	1
$SbCl_5$ (1.0)	TCNE (1.0)	90	1
$SbCl_5$ (0.2)	Anthracene (0.2)	100	1
$SbCl_5$ (0.2)	9,10-Diphenylanthracene (0.2)	100	1
$SbCl_5$ (0.2)	Pyrene (0.2)	100	1
$SbCl_5$ (0.2)	Phenanthrene (0.2)	15	30
$SbCl_5$ (0.2)	$(p\text{-}BrC_6H_4)_3\overset{+}{N}SbCl_6^-$ (0.2)	59	30

* Tetracyanoethylene.

TABLE 7

Lewis acid catalysed oxygenation of ergosteryl acetate (1; R = Ac) (1.14×10^{-4}M in CH_2Cl_2 at 0 °C)*

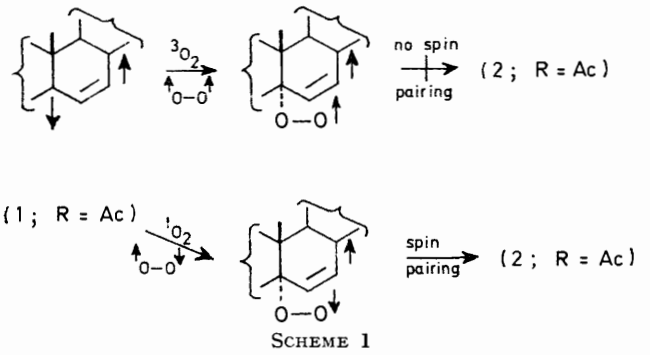
Lewis acid (equiv.)	Conversion (%)	Other products	Time (min)
Under irradiation			
BF_3	93	(25) (*ca.* 5%)	60
$AlCl_3$, $MeNO_2$ (0.1)	71		60
$AlCl_3$, $MeNO_2$ (1.0)	60	(25) (34%)	60
$AlCl_3$, excess $MeNO_2$ (0.2)	80	(25) (10%)	60
$SnCl_4$ (0.2)	78	(25) (trace)	5
In the dark			
$Ph_3C^+BF_4^-$ (0.1)	80	(25) (trace)	45
$FeCl_3$, EtO (0.1—1.0)	50—70		0.5
$FeCl_3$, Me_2CO (0.1)	50—70		0.5
WCl_6 (0.01)	30		0.5
WCl_6 (0.1)	85		0.5
WCl_6 (0.2)	100		0.5

* The following systems produced *no* peroxide (2; R = Ac) from (1; R = Ac): $AgBF_4$, $COCl_2$, VCl_3, PCl_5, $ReCl_3$, $FeCl_3$, $6H_2O$, $COBr_2$, $RuCl_3$, $RhCl_3$, $RhCl(PPh_3)_3$, $IrCl_3$. Some of these results are due to the insolubility of the potential catalyst.

The aluminium trichloride–nitromethane reagent appeared more efficient at 0 °C than at −80 °C, although at room temperature (*ca.* 20 °C) no peroxide (2; R = Ac) formation occurred.

Treatment of ergosteryl acetate (1; R = Ac) with the radical cation (6; X = $SbCl_6$) under nitrogen at room temperature afforded the anthrasteroid (27; R = Ac) (50%); an authentic specimen of the corresponding benzoate was kindly provided by Professor W. B. Whalley.[31] The formation of this compound must involve two one-electron transfers from (1; R = Ac) and loss of H^+.

The work described above provides for the first time many different catalysts for the addition of triplet



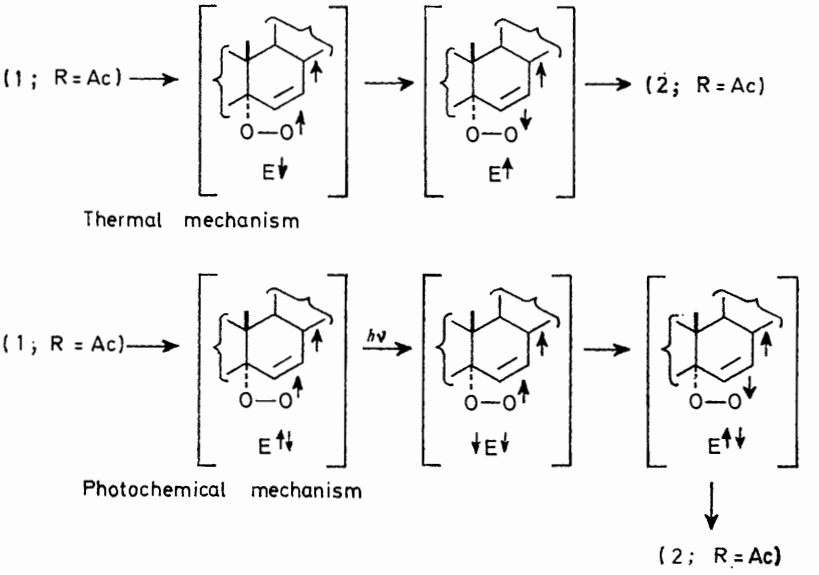
SCHEME 1

oxygen to cisoid dienes. The fact that, for example, ergosteryl acetate peroxide is not formed spontaneously from ergosteryl acetate and triplet oxygen, but is so chemical. The data of Table 5 are particularly pertinent in showing the existence of the two mechanisms. Although it is premature to consider any mechanism as established, the data can most simply be understood in terms of the complexes of Scheme 2. We discuss now the evidence in favour of this Scheme and the data which, at first sight, appear exceptional.

All catalysts for the thermal reaction are electrophilic in nature and contain an unpaired electron spin. Table 4 contains two diamagnetic compounds, $VOCl_3$ and WCl_6. Both are good oxidising agents and their reduced valency states would be paramagnetic. We therefore ascribe their catalytic activity to this reduction. Tungsten hexachloride is a particularly good dark catalyst. Tungsten hexafluoride, which is less easily reduced, is only active on irradiation (Table 2).

Not all amine radical cations are active catalysts. As already indicated above such radical cations are only active if sufficiently electrophilic to complex with ergosterol acetate.

There is no neutral radical which is catalytically active. We explain this by considering that none of these radicals is sufficiently electrophilic to form a complex. However, one of these radicals, diphenylpicrylhydrazyl, is active in the presence of a suitable electrophilic species. Here we assume that the electrophilic species complexes with



SCHEME 2 E = electrophilic species; [ ] = complex

formed with singlet oxygen is *a priori* explainable either on thermodynamic or on kinetic grounds. The results in this paper show that the latter explanation is correct, not the former.

The kinetic barrier to the addition of triplet oxygen to ergosterol acetate is accepted to be a problem of spin pairing, illustrated in a formal manner in Scheme 1. It is clear that the catalysts that we have discovered provide a mechanism for overcoming the spin barrier.

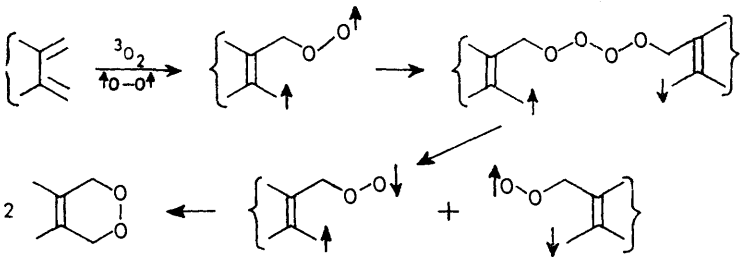
The experimental facts above show that there must be two mechanisms available, one thermal and one photo- both the ergosterol acetate and the radical so that, after oxygen insertion, spin exchange can take place. Other examples of radical cations which are catalytically active and produced by electron transfer are shown in Table 6. It is to be noted that no spin-paired cationic species of the many (ammonium, sulphonium, oxonium) that we have examined shows any catalytic effect in the dark reaction.

All catalysts for the photochemical reaction are also

[31] N. Bosworth, J. M. Midgley, C. J. Moore, W. B. Whalley, G. Ferguson, and W. C. Marsh, *J.C.S. Chem. Comm.*, 1974, 719.

electrophilic in nature and may be supposed to form complexes with ergosteryl acetate. Irradiation then converts the singlet complex into a triplet complex and permits, after oxygen insertion, the spin exchange that allows the formation of peroxide (2; R = Ac). Whether oxygen is inserted before (Scheme 2) or after singlet-to triplet conversion is not defined by our theory.

In our first communication [1e] we suggested that the triplet state of the trityl cation could act as an oxygen-transfer reagent with spin exchange to give singlet cation and spin-paired peroxide. This mechanism would not explain why all catalysts are strongly electrophilic and it is hardly conceivable that the triplet states of boron trifluoride or tin tetrachloride should act as oxygen transfer reagents.



SCHEME 3

Some of the results in Table 5 are a proof of the existence of two mechanisms. The results with iron(III) chloride are especially interesting. We consider that with small amounts of iron(III) chloride the catalyst is destroyed competitively with the desired oxygenation process to give spin-paired products. Irradiation then affords triplet states by which the alternative mechanism can then operate.

It was mentioned above that 9,11-didehydroergosterol acetate (16) and 9-phenyl- and 9,10-diphenylanthracene,[32] compounds which are efficiently converted into peroxide with singlet oxygen, do not react with triplet oxygen under our catalytic conditions. We regard these reactions as failing for thermodynamic reasons, there being no free energy decrease available with triplet oxygen.

In contrast, there are a limited number of *cis,cis*-dienes reported to form *endo*-peroxides spontaneously by reaction with triplet oxygen.[33] The compounds involved are all destabilised by strain or resonance with respect to the peroxide. We consider that this allows a radical addition of triplet oxygen followed by spin inversion by exchange (Scheme 3). It is known that the equilibrium between peroxide radicals and tetraoxides is faster than the decomposition of the latter into singlet oxygen and alkoxyl radicals.[34]

Our additions of triplet oxygen to cisoid dienes may also have relevance to biochemical processes. Certainly, at least one of the reactions hitherto considered in biological systems to be characteristic of singlet oxygen, namely *endo*-peroxide formation, is not.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured for solutions in chloroform unless otherwise stated. N.m.r. spectra were measured for solutions in [^{2}H]chloroform with tetramethylsilane as internal standard. All solvents were purified and dried by standard techniques before use. Light petroleum refers to the fraction of b.p. 60—80° unless otherwise stated. $[\alpha]_D$ Values were obtained for solutions in chloroform. The u.v. spectra of all cations were taken for solutions in dry dichloromethane. All other u.v. spectra were recorded for solutions in ethanol.

Triphenylmethylium Tetrafluoroborate.—Triphenylmethanol in propionic anhydride was treated with aqueous fluoroboric acid, according to the method of Dauben,[35] to give trityl fluoroborate (95%), m.p. 195—202° (decomp) [lit.,[35] 200° (decomp)].

Ergosterol 3β-Methoxymethyl Ether (1; R = CH_2·OMe).—Ergosterol (1 g) in ether (20 ml) was stirred with sodium hydride (350 mg) under N_2 for 1 h. To this mixture was added a solution of methoxymethyl tosylate (1.55 g) in ether (4 ml). After 10 min ethanol (2 ml) was added, the solution evaporated, and the residue dissolved in benzene (25 ml). This solution was washed with water, dried (Na_2SO_4), and evaporated to give the *methoxymethyl ether* (1; R = CH_2·OMe) (85%), m.p. 108—109° (from ethanol), $[\alpha]_D^{23}$ −66°, $\nu_{max.}$ 1 255, 1 115, 1 055, and 980 cm^{-1}, $\lambda_{max.}$ 261.5, 271.5, 282, and 293.5 nm (ε 7 500, 9 400, 11 700, and 6 550), τ 9.36 (3 H, s), 9.22 (3 H, s), 6.58 (3 H, s), 5.26 (2 H, s), 4.75 (2 H, m), and 4.48 (2 H, d, *J* 7 Hz) (Found: C, 82.0; H, 11.0. $C_{30}H_{48}O_2$ requirs C, 81.8; H, 11.0%).

Ergosterol 3β-Methoxymethyl Ether 5α,8α-Peroxide (2; R = CH_2·OMe).—Trityl tetrafluoroborate (10 mg) in dry dichloromethane (2 ml) was added to ergosterol 3β-methoxymethyl ether (1; R = CH_2·OMe) (44 mg) in dichloromethane (2 ml) at −78 °C. After 2 h (exposure to atmosphere) the reaction was quenched at 0 °C with saturated aqueous sodium carbonate (0.2 ml). Extraction with dichloromethane (10 ml), drying (Na_2SO_4), and evaporation gave the *peroxide* (2; R = CH_2·OMe) (38 mg, 80%), m.p. 157—159° (from methanol), $[\alpha]_D^{23}$ −25° (in $CHCl_3$), $\nu_{max.}$ (Nujol) 1 470, 1 380, 1 145, 1 115, 1 040, 1 000, 975, 945, and 925 cm^{-1}, τ (CCl_4) 3.9 (2 H, q, *J* 9 Hz), 4.9 (2 H, m), 8.01 (3 H, s), and 7.63 (2 H, s)(Found: C, 76.1; H, 10.1. $C_{30}H_{48}O_4$ requires C, 76.2; H, 10.2%).

[32] J. Rigaudy, *Pure Appl. Chem.*, 1968, **16**, 169.

[33] R. Criegee, *Angew. Chem. Internat. Edn.*, 1962, **1**, 519; C. M. Bowes, D. F. Montecalvo, and F. Sondheimer, *Tetrahedron Letters*, 1973, 3181; P. J. Machin, A. E. A. Porter, and P. G. Sammes, *J.C.S. Perkin I*, 1973, 404.

[34] V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 3949; K. U. Ingold, *Accounts Chem. Res.*, 1969, **2**, 1.

[35] H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.

Ergosteryl Acetate 5α,8α-Peroxide (2; R = Ac).—Trityl tetrafluoroborate (10 mg) in dichloromethane (1 ml) was added to ergosteryl acetate (100 mg) in dichloromethane (10 ml) at −78 °C. Dry oxygen was passed through the irradiated solution (laboratory lighting). After 2 min saturated aqueous sodium carbonate (1 ml) was added to the mixture, which was allowed to warm to 0 °C. The dichloromethane layer was dried (Na_2SO_4) and evaporated. Plate layer chromatography (p.l.c.) gave ergosteryl acetate 5α,8α-peroxide (2; R = Ac) (105 mg, 98%), m.p. and mixed m.p. 201—204° (from light petroleum) (lit.,[2] 201—204°) and triphenylmethanol (6.7 mg, 86%), m.p. 160—164° (lit.,[35] 162.5°)

Control Experiments for the Reaction of Ergosteryl Acetate (1; R = Ac) *with Trityl Tetrafluoroborate.*—(*a*) Ergosteryl acetate (1; R = Ac) (100 mg) was dissolved in dichloromethane (10 ml) in the *dark* at −78 °C and trityl tetrafluoroborate (10 mg) in dichloromethane (1 ml) was added. No peroxide (2; R = Ac) was detectable (t.l.c.) after 2.75 h. The mixture was then exposed to room lighting and oxygenation proceeded to completion in 3.25 h.

(*b*) Ergosteryl acetate (1; R = Ac) (100 mg) in dichloromethane (14 ml) at −78 °C was treated with trityl tetrafluoroborate (20 mg) in dichloromethane (1 ml). Air was bubbled through the solution in room light. After 10 min *ca.* 20% reaction had occurred (t.l.c.). Exclusion of light from the reaction mixture stopped peroxide formation. Reintroduction of light caused peroxide formation to continue.

(*c*) Trityl tetrafluoroborate (5 mg) in dichloromethane (0.5 ml) was added to 1; R = Ac) (50 mg) in dichloromethane at 78 °C. Oxygen was bubbled through the illuminated solution. Reaction was complete in 10 min (t.l.c.). Work-up and p.l.c. gave the peroxide (2; R = Ac) (93%).

(*d*) This experiment was performed as for (*c*) but at 0 °C or room temperature. The solutions turned green-black. No peroxide had been formed after 1 h.

Rate Comparison of Oxygenation with Trityl Tetrafluoroborate and Eosin.—(*a*) Lumisteryl acetate (3; R = Ac) (100 mg) in dichloromethane (14 ml) at −78 °C was treated with trityl tetrafluoroborate (10 mg) in dichloromethane (1 ml), oxygen being bubbled through the illuminated solution. After 10 h, the mixture was worked up in the usual way with saturated aqueous sodium hydrogen carbonate (1 ml). P.l.c. gave lumisteryl peroxide (4; R = Ac) (5%), m.p. 157—159° (lit.,[36] 156—157°).

(*b*) Ergosteryl acetate (1; R = Ac) (50 mg) in benzonitrile (10 ml) and dichloromethane (5 ml) at −15 °C containing eosin (10.5 mg) was irradiated (tungsten lamp) while oxygen was bubbled through the solution. After 30 min the mixture was filtered through alumina (20 g). P.l.c. of the evaporated eluate gave the peroxide (2; R = Ac) (98%), m.p. 201—204°.

(*c*) Lumisteryl acetate (3; R = Ac) (50 mg) in benzonitrile (10 ml) and dichloromethane (5 ml) at −15 °C, containing eosin (10.8 mg), was irradiated (tungsten lamp) while oxygen was bubbled through the solution. After 100 min work-up gave (4; R = Ac) (93%), m.p. 156—159° (lit.,[36] 155—157°).

Reaction of Ergosteryl Acetate (1; *R = Ac*) *with Trityl Radicals.*—Hydrazotriphenylmethane[37] (105 mg) in dichloromethane (10 ml) at −78 °C was treated with bromine (25 mg) in dichloromethane (1 ml). After all the hydrogen bromide had been liberated, ergosteryl acetate(1; R = Ac) (100 mg) in dichloromethane (5 ml) was added and the solution allowed to warm to −15 °C while oxygen was passed through. At −15 °C nitrogen was evolved and triphenylmethyl radicals produced. No peroxide (2; R = Ac) was detectable (t.l.c.). Triphenylmethyl peroxide was isolated (83 mg, 78%), m.p. 182—185° (lit.,[15] 185—186°).

Trityl Hexafluorophosphate.—Trityl chloride (560 mg) in dichloromethane (10 ml) was treated with silver hexafluorophosphate (500 mg). The precipitated silver chloride was filtered off and the filtrate poured into light petroleum. Trityl hexafluorophosphate (670 mg, 87%) was filtered off and dried *in vacuo*; m.p. 143—146° (decomp.) [lit.,[7] 145° (decomp.)]. Trityl perchlorate[35] and hexachloroantimonate [6] were prepared as described in the literature.

Comparison of Oxygenation Rates with Trityl Salts.—All reactions were conducted with dichloromethane (10 ml) as solvent at −78 °C. Dry oxygen was passed through solutions of ergosteryl acetate (1; R = Ac) irradiated with a tungsten lamp (500 W). The usual work-up gave the peroxide (2; R = Ac) in over 98% yield, in all cases (Table 8).

TABLE 8

(1; R = Ac) (mg)	Trityl salt (mg)	Oxygenation time (min)
94.2	$Ph_3C^+BF_4^-$ (16.5)	25
102.3	$Ph_3C^+ClO_4^-$ (17.0)	25
103.7	$Ph_3C^+PF_6^-$ (19.5)	25
100.0	$Ph_3C^+SbCl_6^-$ (24.0)	20

Oxygenation of Ergosteryl Acetate (1; R = Ac) *with Diphenylpicrylhydrazyl (DPPH) and Trityl Tetrafluoroborate Mixtures.*—(*a*) Ergosteryl acetate (1; R = Ac) (50 mg) in dichloromethane (10 ml) at −78°, with oxygen bubbling through in the dark was treated with trityl tetrafluoroborate (10 mg) in dichloromethane (1 ml) and DPPH (10 mg) in dichloromethane (1 ml). After 25 min more DPPH (20 mg) in dichloromethane (0.5 ml) was added. The reaction was completed in 1.5 h. Work-up in the usual way gave ergosteryl acetate peroxide (2; R = Ac) (41 mg, 78%).

(*b*) DPPH (5 mg) and trityl tetrafluoroborate (10 mg) were dissolved in dichloromethane (10 ml) at −78 °C under argon. After 3 h oxygen was bubbled through the solution and the acetate (1; R = Ac) (50 mg) added. Work-up in the usual way after 1 h gave the peroxide (2; R = Ac) (43 mg, 84%).

Tris-(p-bromophenyl)ammoniumyl Hexachloroantimonate (6; X = $SbCl_6$).[9]—Tris-(*p*-bromophenyl)amine was oxidised with antimony pentachloride as described by Ledwith.[9]

Tris-(p-bromophenyl)ammonium Tetrafluoroborate (6: X = BF_4).—Silver tetrafluoroborate (0.435 g) in ether (42 ml) was treated with tris-(*p*-bromophenyl)amine (0.8 g). The solution was flushed with N_2 for 10 min and cooled to −30 °C. A solution of iodine (0.33 g) in ether (5 ml) was added. After the mixture had warmed to room temperature it was filtered and the solid extracted with dichloromethane (5 × 2 ml). The extract was poured into dry ether (40 ml) at −20° and the blue crystals of the *tetrafluoroborate* (6; X = BF_4) were collected (0.69 g, 73.5%); $\nu_{max.}$ 1 600, 1 490, 1 390, 1 355, 1 155, 1 120, 1 080, 1 050, 940, and 855 cm^{-1}, $\lambda_{max.}$ 723 nm (ε 22 800) (Found: C, 37.9; H, 2.4; Br, 42.7; N, 2.4. $C_{18}H_{12}BrN_3,BF_4$ requires C, 38.0; H, 2.1; Br, 42.4; N, 2.5%).

Oxygenation of Ergosteryl Acetate (1; R = Ac) *with the Radical Cation* (6; X = $SbCl_6$).—The acetate (1; R = Ac) (100 mg) in dichloromethane (14 ml) at −78 °C in the *dark*, was treated with the ammoniumyl salt (6; X = $SbCl_6$) (10 mg) in dichloromethane (1 ml) with dry oxygen bubbling

[36] P. Bladon, *J. Chem. Soc.*, 1955, 2176.
[37] H. Wieland, *Ber.*, 1909, **42**, 3020.

through the solution. After 5 min saturated aqueous sodium hydrogen carbonate (1 ml) was added, and the mixture warmed to 0 °C. P.l.c. of the dichloromethane layer gave the peroxide (2; R = Ac) (96 mg, 95%). Similarly the radical cation (6; X = BF_4) gave the peroxide (2; R = Ac) (96%).

Reaction of Lumisteryl Acetate (3; R = Ac) *with the Ammoniumyl Salts* (6; X = $SbCl_6$ *or* BF_4).—The acetate (3; R = Ac) (100 mg) in dichloromethane (10 ml) in the dark at −78 °C with oxygen bubbling through the solution was treated with the radical cation (6; X = $SbCl_6$ or BF_4) (10 mg) in dichloromethane (1 ml). *No* peroxide (4; R = Ac) was detected after 2 h. Similarly, no reaction was observed at room temperature.

Oxygenation of Tetraphenylfuran (7) *with Trityl Tetrafluoroborate.*—The furan (7) (150 mg) in dichloromethane (15 ml) at −78 °C, with oxygen bubbling through the mixture, was treated with trityl tetrafluoroborate (30 mg) in dichloromethane (1 ml). After 2 h (irradiation: laboratory lighting) the usual work-up gave *cis*-dibenzoylstilbene (8) (103 mg, 67%), m.p. 214—216° (from light petroleum) (lit.,[10] 212°).

Oxygenation of Tetraphenylfuran (7) *with the Radical Cation* (6; X = BF_4).—The furan (7) (100 mg) in dichloromethane (10 ml) in the dark at room temperature with oxygen bubbling through the solution was treated with the salt (6; X = BF_4) (20 mg) in dichloromethane (1 ml). After 2 h work-up in the usual way gave the stilbene (8) (31 mg, 30%). No reaction was observed at −78 °C. The salt (6; X = $SbCl_6$) gave the stilbene (8) (10%).

Reaction of p-*Mentha*-1,3-*diene* (9) *with Trityl Tetrafluoroborate and Oxygen.*—A mixture of *p*-menthadienes (100 mg; 51% 1,3-diene (9)] in dichloromethane (10 ml) at −78 °C with oxygen bubbling through the solution was treated with trityl tetrafluoroborate (20 mg) in dichloromethane (1 ml). After 1.5 h (exposure to laboratory lighting), work-up in the usual way gave 1,4-epidioxy-*p*-menth-2-ene (10) (57 mg, 90%), identical with an authentic sample.[38]

Reaction of p-*Mentha*-1,3-*diene* (9) *with the Radical Cations* (6; X = $SbCl_6$ *or* BF_4^-).—The menthadiene mixture (150 mg) in dichloromethane (10 ml) at −78 °C with oxygen bubbling through in the dark was treated with the salt (6; X = BF_4) (25 mg). After 2 h, work-up in the usual way gave the peroxide (10) (52 mg, 55%). The salt (6, X = $SbCl_6$) gave (10) (16%).

Reaction of 1,1′-*Bicyclohexenyl* (11) *with Trityl Tetrafluoroborate.*— 1,1′-Bicyclohexenyl [12] (11) (287 mg) in dichloromethane (10 ml) at −78 °C with oxygen bubbling through (exposure to laboratory lighting) was treated with trityl tetrafluoroborate (30 mg) in dichloromethane (1.5 ml). After 1.5 h work-up in the usual way gave the *cis*-peroxide (12) (217 mg, 64%), m.p. 51—53° (lit.,[13] 54°).

Reaction of 1,1′-*Bicyclohexenyl* (11) *with the Radical Cation* (6, X = BF_4).—The diene (11) (234 mg) in dichloromethane (10 ml) at −78°, with oxygen bubbling through in the dark, was treated with the cation radical (6; X = BF_4) (100 mg) in dichloromethane (2 ml). After 3 h work-up in the usual way gave the *cis*-peroxide (12) (206 mg, 74%).

Bicyclohexylidene-2,2′-*diol* (13).—The peroxide (12) (25 mg) in ethanol (10 ml) was hydrogenated (1 atm) over Raney nickel (10 mg). Work-up gave the diol (13) (19 mg, 76%), m.p. 148—149°(from methanol–light petroleum)(lit.,[13] 147—149°).

Oxygenation of 1,3-*Diphenylisobenzofuran* (14).[14]—The furan (14) (135 mg) in dichloromethane (20 ml) at −78 °C, with oxygen bubbling through the illuminated (laboratory lighting) solution, was treated with trityl hexachloroantimonate (172 mg). After 1 h the solution was warmed to 0 °C and aqueous 0.1N sodium hydroxide (5 ml) added. The dichloromethane layer was separated, dried (Na_2SO_4), and evaporated to give, after p.l.c., *o*-dibenzoylbenzene (15) (123 mg, 86%), m.p. 147—148° (lit.,[15] 146—147°).

Similar use of the cation (6; X = $SbCl_6$) in the dark gave *o*-dibenzoylbenzene (15) (90%).

Tris-(p-*tolyl*)*ammoniumyl Hexachloroantimonate* (21; X = $SbCl_6$, R = Me).—Tritolylamine[39] (290 mg) in dichloromethane (5 ml) was treated with antimony pentachloride (600 mg) in dichloromethane (5 ml). The mixture was poured into light petroleum (50 ml) and the blue crystalline *hexachloroantimonate* (21; X = $SbCl_6$, R = Me) (500 mg) filtered off; $\nu_{max.}$ 1 580, 1 510, 1 330, 1 175, 1 020, 930, and 840 cm^{-1}, $\lambda_{max.}$ 673 nm (ε 25 400) (Found: C, 40.4; H, 3.6; N, 2.3. $C_{21}H_{21}Cl_6NSb$ requires C, 40.6; H, 3.4; N, 2.3%).

Tris-(p-*tolyl*)*ammoniumyl Tetrafluoroborate* (21, R = Me, X = BF_4).—Tritolylamine (800 mg) and silver tetrafluoroborate (400 mg) in ether under N_2 at −30 °C were treated with iodine (250 mg) in ether (50 ml). The solution was warmed to room temperature and filtered, and the solid was extracted with dichloromethane (5 × 2 ml). The extract was poured into ether (40 ml) at −20°. Light petroleum (40 ml) was added to precipitate the salt (21; R = Me) (520 mg, 49%), $\lambda_{max.}$ 674 nm (ε 23 900). No further data were obtained because of its instability.

Tris-(p-*methoxyphenyl*)*ammoniumylaminium Hexachloroantimonate* (21; X = $SbCl_6$, R = OMe).—The salt (21; R = OMe, X = $SbCl_6$) was made as for (21; X = $SbCl_6$, R = Me) but from tris-(*p*-methoxyphenyl)amine; [39] $\nu_{max.}$ 1 580, 1 510, 1 480, 1 390, 1 330, 1 280, 1 160, 1 140, 1 020, 930, 920, 870, 860, 800, and 740 cm^{-1}, $\lambda_{max.}$ 723 nm (ε 24 400). Similarly prepared, the *tetrafluoroborate* (21; R = OMe, X = BF_4) had $\nu_{max.}$ 1 580, 1 500, 1 470, 1 390, 1 355, 1 340, 1 315, 1 160, 1 120, 1 080, 1 035, 940, 925, and 850 cm^{-1}, $\lambda_{max.}$ 723 nm (ε 25 550) (Found: C, 59.8; H, 5.0; N, 3.1. $C_{21}BF_4N_3$ requires C, 59.7; H, 5.0; N, 3.3%).

Tris-(p-*chlorophenyl*)*ammoniumyl Hexachloroantimonate* (21; R = Cl, X = $SbCl_6$).—Tris-(*p*-chlorophenyl)amine [39] (25 mg) in dichloromethane (4 ml) was treated with antimony pentachloride (50 mg) in dichloromethane (1 ml). The mixture was poured into ether to give the salt (21; R = Cl, X = $SbCl_6$) (38 mg, 64%), $\nu_{max.}$ 1 580, 1 560, 1 500, 1 320, 1 180, 1 100, 1 020, and 850 cm^{-1}, $\lambda_{max.}$ 702 nm (ε 24 100).

Tris-(p-*chlorophenyl*)*ammoniumyl Tetrafluoroborate* (21; R = Cl, X = BF_4).—The preparation was carried out as for the *p*-tolyl case (21; R = Me, X = BF_4). The salt (21; R = Cl, X = BF_4) had $\lambda_{max.}$ 701 nm (ε 19 200) $\nu_{max.}$ 1 580, 1 560, 1 500, 1 390, 1 355, 1 320, 1 160, 1 080, 1 050, 1 020, 940, 855, and 845 cm^{-1}. Its instability prevented characterisation.

Tris-(p-*iodophenyl*)*ammoniumyl Hexachloroantimonate* (21; R = I, X = $SbCl_6$).—Tris-(*p*-iodophenyl)amine [40] (400 mg) in dichloromethane (10 ml) was treated with antimony pentachloride (400 mg) in dichloromethane (1 ml). The mixture was poured into ether–light petroleum (1 : 1) (50 ml) at −30 °C to give the salt (21; R = I, X = $SbCl_6$) (450 mg), $\lambda_{max.}$ 794 nm (ε 25 050), $\nu_{max.}$ 1 550, 1 180, 1 060, 1 010, and 840 cm^{-1}.

N-(p-*Chlorophenyl*)*di*-p-*tolylamine.*—*p*-Chloroaniline (25 mg), *p*-iodotoluene (100 g), potassium carbonate (20 g), and copper bronze (1 g) were refluxed in nitrobenzene (50 ml) for 5 days. The mixture was steam distilled and the residue

extracted with dichloromethane (200 ml). The dried (Na_2SO_4) extract was evaporated and the residue chromatographed on alumina (550 g) (elution with light petroleum). *N*-(p-*Chlorophenyl*)-*di*-p-*tolylamine* (9.5 g, 16%), m.p. 106—107° (from light petroleum) was isolated; $\nu_{max.}$ 1 600, 1 590, 1 510, 1 490, 1 330, 1 180, 1 110, 1 015, and 840 cm^{-1} (Found: C, 78.3; H, 5.9; N, 4.4. $C_{20}H_{18}ClN$ requires C, 78.0; H, 5.9; N, 4.8%).

N-(p-*Chlorophenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (22; R = Cl).—*N*-(*p*-Chlorophenyl)di-*p*-tolylamine (250 mg) in dichloromethane (3 ml) was treated with antimony pentachloride (500 mg) in dichloromethane (1 ml). The mixture was poured into dry ether (20 ml) and light petroleum (10 ml) to give the *salt* (22; R = Cl) (380 mg, 73%), $\nu_{max.}$ 1 575, 1 515, 1 490, 1 320, 1 170, 1 100, 1 015, 925, 840, and 830 cm^{-1}, $\lambda_{max.}$ 685 nm (ε 24 900) (Found: C, 36.9; H, 2.8; N, 1.8. $C_{20}H_{18}Cl_7NSb$ requires C, 37.4; H, 2.7; N, 2.2%).

N-(p-*Bromophenyl*)*di*-p-*tolylamine*.— *N*-Phenyldi-*p*-tolylamine [41] (2 g) in dichloromethane (10 ml) was treated dropwise with bromine (1.2 g) in dichloromethane (5 ml). The mixture was evaporated to give N-(p-*bromophenyl*)*di*-p-*tolylamine* (2.1 g, 82%), m.p. 103.5—104.5° (from ethanol), $\nu_{max.}$ 1 610, 1 580, 1 510, 1 490, 1 470, 1 320, 1 280, 1 080, 1 010, 830, 730, 715, and 700 cm^{-1} (Found: C, 68.2; H, 5.2; N, 4.1. $C_{20}H_{18}BrN$ requires C, 68.2; H, 5.2; N, 4.0%).

N-(p-*Bromophenyl*)*di*-p-*tolylammonium Hexachloroantimonate* (22; R = Br).—Prepared as for (22; R = Cl) this had $\lambda_{max.}$ 689 nm (ε 25 600), $\nu_{max.}$ 1 580, 1 565, 1 175, 1 080, 1 015, 930, 840, and 835 cm^{-1}. Its instability prevented further characterisation.

N-(p-*Iodophenyl*)*di*-p-*tolylamine*.— *N*-Phenyldi-*p*-tolylamine [41] (2 g) in ethanol (50 ml) containing red mercury(II) oxide (3 g) was heated at reflux, and iodine (2.5 g) was added over 30 min. The solution was cooled and filtered and the mercury(II) salts were washed with dichloromethane (5 × 5 ml). The filtrate was evaporated and the residue chromatographed over alumina to give N-(p-*iodophenyl*)*di*-p-*tolylamine* (1.9 g, 65%), m.p. 88—89° (from light petroleum), $\nu_{max.}$ 1 605, 1 575, 1 510, 1 490, 1 470, 1 320, 1 280, 1 180, 1 005, 840, 825, 750, and 715 cm^{-1} (Found: C, 60.2; H, 4.5; N, 3.6. $C_{20}H_{18}IN$ requires C, 60.2; H, 4.5; N, 3.5%).

N-(p-*Iodophenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (22; R = I).—Prepared as for (22; R = Cl) this had $\lambda_{max.}$ 697 nm (ε 24 750), $\nu_{max.}$ 1 580, 1 560, 1 180, 1 070, 1 015, 930, and 840 cm^{-1} Its instability prevented further characterisation.

N-(p-*Cyanophenyl*)*di*-p-*tolylamine*.— *N*-(*p*-Bromophenyl)-di-*p*-tolylamine (4.5 g) and anhydrous copper(II) cyanide (2.5 g) in pyridine (6 ml) were heated under reflux. After 1 day more cyanide (1.5 g) was added, followed by further portions (1 g and 0.5 g) after 2 and 3 days, respectively. After 4 days, the mixture was poured into ammonia solution (*d* 0.88; 10 ml). Benzene (10 ml) was added and the mixture filtered. The solids were washed with ether (50 ml). The organic layer was separated, washed with aqueous 2N-ammonia (2 × 20 ml), 2N-hydrochloric acid (2 × 20 ml), saturated aqueous sodium chloride (2 × 20 ml), and water (2 × 20 ml). Drying (Na_2SO_4), evaporation, and chromatography (alumina) of the residue gave N-(p-*cyanophenyl*)*di*-p-*tolylamine* (3.5 g, 90%), m.p. 127.5—128.5° (from light petroleum), $\nu_{max.}$ 2 250, 1 610, 1 600, 1 530, 1 510, 1 340, 1 305, 1 275, 1 180, and 830 cm^{-1} (Nujol) (Found: C, 84.5; H, 6.0; N, 9.5. $C_{21}H_{18}N_2$ requires C, 84.5; H, 6.1; N, 9.4%).

N-(p-*Cyanophenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (22; R = CN).—*N*-(*p*-Cyanophenyl)di-*p*-tolylamine (50 mg) in dichloromethane (1 ml) was treated with antimony pentachloride (100 mg) in dichloromethane (1 ml). The mixture was poured into ether (10 ml) and light petroleum (5 ml) to give the *salt* (22; R = CN) (66 mg, 61%), $\lambda_{max.}$ 712 nm (ε 23 600), $\nu_{max.}$ 1 595, 1 580, 1 510, 1 340, 1 180, 1 175, 930, 850, and 840 cm^{-1} (Found: C, 39.8; H, 2.9; N, 4.4. $C_{21}H_{18}Cl_6N_2Sb$ requires C, 39.9; H, 3.0; N, 4.3%).

N-(p-*Nitrophenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (22; R = NO_2).—*N*-(*p*-Nitrophenyl)di-*p*-tolylamine [42] (200 mg) in dichloromethane (1 ml) was treated with antimony pentachloride (400 mg) in dichloromethane (0.5 ml) under argon. The green solution was poured into light petroleum (25 ml) to give the salt (22; R = NO_2) (260 mg, 63%), $\lambda_{max.}$ 680 (ε 13 200), $\nu_{max.}$ 1 575, 1 540, 1 350, 1 170, 865, and 840 cm^{-1}. Its instability prevented further characterisation.

N-(p-*Methoxycarbonylphenyl*)*di*-p-*tolylamine*.— *N*-(*p*-Cyanophenyl)di-*p*-tolylamine (250 mg) in methanol (5 ml) saturated with hydrogen chloride, was heated at reflux overnight. The solution was evaporated and the residue chromatographed (alumina) to give N-(p-*methoxycarbonylphenyl*)*di*-p-*tolylamine* (250 mg), m.p. 85—86° (from light petroleum): $\nu_{max.}$ (Nujol) 1 720, 1 610, 1 530, 1 300, 1 200, 1 140, 855, and 800 cm^{-1} (Found: C, 79.9; H, 6.4; N, 4.4. $C_{22}H_{21}NO_2$ requires C, 79.7; H, 6.4; N, 4.2%).

N-(p-*methoxycarbonylphenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (22; R = CO_2Me).—The above amine (50 mg) in dichloromethane (2 ml) was treated with antimony pentachloride (90 mg) in dichloromethane (1 ml). The mixture was poured into ether (25 ml) and light petroleum (15 ml) to give the salt (22; R = CO_2Me) (78 mg, 78%), $\lambda_{max.}$ 701 nm (ε 24 100), $\nu_{max.}$ 1 720, 1 580, 1 320, 1 170, 1 120, 1 020, 970, 930, 870, and 835 cm^{-1}. Its instability prevented further characterisation.

Tris-(2,4-*dichlorophenyl*)*amine*.—Triphenylamine was treated with sulphuryl chloride,[43] to give tris-(2,4-dichlorophenyl)amine, m.p. 77—79° (lit.,[43] 78—79°).

Tris-(2,4-*dichlorophenyl*)*ammoniumyl Hexachloroantimonate* (23; R = Cl, X = $SbCl_6$) *and Tetrafluoroborate* (23; R = Cl, X = BF_4).—These salts proved too unstable to be isolated. Spectra were recorded by forming the salts with 2 equiv. of antimony pentachloride and 1 equiv. of silver tetrafluoroborate and iodine, respectively.

Tris-(2,4-*dibromophenyl*)*amine*.— Tris-(*p*-bromophenyl)-amine was treated with bromine in the presence of a steel catalyst to give tris-(2,4-dibromophenyl)amine, m.p. 214—216° (lit.,[44] 218—220).

Tris-(2,4-*dibromophenyl*)*ammoniumyl Hexachloroantimonate* (23; R = Br, X = $SbCl_6$) *and Tetrafluoroborate* (23; R = Br, X = BF_4).—These salts proved too unstable to be isolated and spectra were recorded as described for the analogous chloride compounds.

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N-(3,5-*Bismethoxycarbonylphenyl*)*di*-p-*tolylamine*.— Dimethyl 5-iodoisophthalate [45] (10.66 g), ditolylamine (6.4 g), potassium carbonate (4 g), copper bronze (0.5 g), and crystal of iodine were heated together at 180 °C for 3 days. The mixture was cooled and extracted with boiling chloroform (5 × 100 ml). The extract was evaporated and the residue chromatographed (alumina) [elution with benzene–light petroleum (3 : 17)] to give the *amino-diester* (5.2 g, 41%), m.p. 157.5—158.5° (from light petroleum), $\nu_{max.}$ (Nujol) 1 740, 1 600, 1 510, 1 345, 1 250, 825, 760, and 740 cm^{-1} (Found: C, 74.3; H, 6.1; N, 3.5. $C_{24}H_{23}NO_4$ requires C, 74.0; H, 6.0; N, 3.5%).

N-(3,5-*Bismethoxycarbonylphenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (24; R = CO_2Me).—This radical cation was too unstable to be isolated as a crystalline compound, but spectra were recorded on solutions of the salt obtained by treatment of the tertiary amine with 2 equiv. of antimony pentachloride in dichloromethane; $\lambda_{max.}$ 705 nm (ε 23 350), $\nu_{max.}$ (CH_2Cl_2) 1 720, 1 575, 1 515, 1 470, 1 350, 1 330, 1 205, 1 170, 1 030, 1 010, 940, and 835 cm^{-1}.

N-(3,5-*Dimethoxyphenyl*)*di*-p-*tolylamine*.— 1-Iodo-3,5-dimethoxybenzene [46] (2.64 g), ditolylamine (1.93 g), potassium carbonate (1.2 g), copper bronze (0.2 g), and a crystal of iodine were heated, neat, at 200 °C for 3 days. The mixture was cooled and extracted with boiling chloroform (5 × 50 ml). The extract was evaporated, the residue dissolved in benzene (75 ml), and light petroleum (75 ml) added to precipitate tars. The mother liquor was decanted and evaporated. The residue was chromatographed (alumina) (elution with 10% benzene–light petroleum) to give N-(3,5-*dimethoxyphenyl*)*di*-p-*tolylamine* (600 mg, 18%), m.p. 121—122.5° (from light petroleum), $\nu_{max.}$ 1 600, 1 510, 1 300, 1 245, 1 200, 1 155, 1 065, 835, 760, and 700 cm^{-1} (Found: C, 79.0; H, 6.9; N, 4.2. $C_{22}H_{23}NO_2$ requires C, 79.3; H, 7.0; N, 4.2%).

N-(3,5-*Dimethoxyphenyl*)*di*-p-*tolylammoniumyl Hexachloroantimonate* (24; R = OMe).—This salt was too unstable to be isolated. Spectra were recorded on a solution prepared in the usual way; $\nu_{max.}$ (CH_2Cl_2) 1 640, 1 555, 1 520, 1 470, 1 370, 1 290, 1 220, 1 180, 1020, and 840 cm^{-1}.

Oxygenation of Ergosteryl Acetate (1; R = Ac) *with Amine Radical Cations*.—The oxygenation reactions with the amine radical cations described above are summarised in Table 9. The reactions were conducted with exclusion of light unless otherwise stated. Oxygen was bubbled through the solutions. Reactions were followed by t.l.c. and the yields of the peroxide (2; R = Ac) are as obtained by p.l.c. after the usual work-up.

Oxygenation of Ergosteryl Acetate (1; R = Ac) *with Lewis Acids. General Procedure*.—Lewis acid solutions were prepared by addition of the Lewis acid (0.1—1.0 mmol) to a flask containing freshly distilled dichloromethane (10 ml). Dichloromethane (25 ml) was distilled into a flame-dried flask containing ergosteryl acetate (1; R = Ac) (50 mg). Oxygen was passed through the solution as it was cooled to −78°. The Lewis acid solution was added to the stirred mixture, and the reaction was monitored by t.l.c. and/or u.v. The results are listed in Tables 2—7. In Table 3 some catalysts caused ergosteryl acetate (1; R = Ac) to isomerise to the 6,8(14),22-triene (25). Isolated by p.l.c. it had m.p. 120—121° (from light petroleum) (lit.,[47] 119—120.6°), $\lambda_{max.}$ 255 nm (ε 22 500), $[\alpha]_D^{21}$ −97.8°.

Reaction of Ergosteryl Acetate (1; R = Ac) *with the Radical Cation* (6; X = $SbCl_6$) *under Nitrogen at Room Temperature*.—The acetate (1; R = Ac) (220 mg) in dichloromethane (100 ml) at 20 °C was treated with the radical cation (6; X = $SbCl_6$) (900 mg) in acetonitrile (100 ml), added dropwise over 1.5 h under N_2. Methanol (100 ml) was added to the mixture and the solution evaporated at 20 °C. The residue was chromatographed (silica) (elution with light petro-

TABLE 9

Ergosteryl acetate (1; R = Ac) (mg)	CH_2Cl_2 (ml)	Temp. (°C)	Radical cation (mg)	Reaction time (h)	Peroxide (2; R = Ac) (%)
100	10	−78	(21; R = Me) [a] (15)	3	0
100	10	−78	(21; R = OMe) [a] (15)	3	0
100	10	−78	(21; R = Cl) [b] (20)	0.1	51
100	10	20	(21; R = Cl) [b] (20)	1	<5
100	10	−78	(21; R = Cl, X = BF_4) (20)	0.15	>95
100	10	−78	(21; R = I) [a] (15)	0.5	>95
100	10	20	(21; R = I) [a] (15)	0.5	55
100	10	−78	(22; R = Cl) [a] (20)	2	0
100	10	−78	(22; R = H) [a] (25)	2	0
100	10	−78	(22; R = Br) (20)	2	0
100	10	−78	(22; R = I) (20)	2	0
50	10	−78	(22; R = CN) (10)	0.1	>95
50	10	20	(22; R = CN) (10)	1	42
50	10	−78	(22; R = NO_2) (25)	0.1	>95
50	10	20	(22; R = NO_2) (25)	0.5	60
50	10	−78	(22; R = CO_2Me) (25)	1	>95
50	10	20	(22; R = CO_2Me) (25)	1	55
44	20	−78	(23; R = Cl, X = $SbCl_6$) [c] (15)	0.25 [d]	>95
44	30	−78	(23; R = Cl, X = BF_4) [c] (27.5)	0.15 [d]	>95
44	20	−78	(23; R = Br, X = $SbCl_6$) [c] (20)	0.25 [d]	>95
44	30	−78	(23; R = Br, X = BF_4) [c] (40)	0.25 [d]	>95
100	10	−78	(24; R = CO_2Me) [c] (20)	1.25 [d]	85
100	10	−78	(24; R = OMe) [c] (22.5)	2 [d]	0

[a] Both X = $SbCl_6$ and X = BF_4 were used. [b] X = $SbCl_6$. [c] Prepared *in situ*. [d] Conducted in room lighting.

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leum). P.l.c. gave the anthrasteroid acetate (27; R = Ac) (170 mg, 77%), $\nu_{max.}$ 1 745, 1 250, and 1 040 cm^{-1}, $\lambda_{max.}$ 270 and 280 nm (ε 23 620 and 3 880). The acetate (27; R = Ac) was converted into the alcohol (27; R = H) and benzoylated (benzoyl chloride–pyridine) to give the benzoate (27; R = Bz), m.p. 128.5—129.5° (lit.,[35] 128.5—129.5°), identical (i.r., u.v., and n.m.r. spectra, and m.p. and mixed m.p.) with an authentic sample.

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