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Tetramethyldiamidophosphoric acid chloride mediated epoxide–diene conversion and steroidal aromatization

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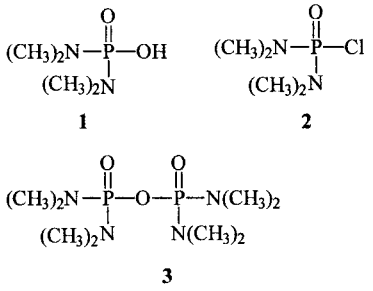
Abstract—The reaction of tetramethyldiamidophosphoric acid chloride with epoxides in the presence of a trace amount of water furnished 1,3-dienes in good yield. The conversion works with open chain and cyclic epoxides. A C–C bond cleavage reaction occurs if the epoxide contains a quaternary carbon. Application of this method to epoxy sterols afforded ring A aromatic steroids in good yield. The aromatization works via dienol-benzene rearrangements and is independent of the C-3 stereochemistry. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

While the deoxygenation of an epoxide to an olefin is a well known reaction,[1] there is little by way of precedent[2] for the direct conversion of epoxides to dienes other than reactions of selected epoxides with phosphates,[3] phosphoranes,[4] and ethyl metaphosphates.[5a] Recently Hendrickson et al. described the direct elimination of epoxides to dienes in 50–85% yields using phosphonium anhydrides.[5b] Preliminary investigations of the scope and mechanism of this epoxide–diene interconversion revealed that the generality of the published methods is limited.[6]

Although the HMPA-mediated dehydration of alcohols to olefins is well known, the conversion of an epoxide to a diene under similar conditions represented an interesting extension of this reaction. But studies of this epoxide to diene interconversion show that the generality was also limited. The suggested mechanism ascribes that tetramethyldiamidophosphoric acid (**1**), formed by hydrolysis of HMPA, could have an important role.[7a–f]

The aim of this work was to generate tetramethyldiamidophosphoric acid (**1**) and react it with epoxides. For this purpose tetramethyldiamidophosphoric acid chloride (**2**) was chosen as a starting material according to the procedure of Heath et al.[8] Le Roux et al.[9] showed that this compound is stable in acidic medium (J_{P-Me}=9 Hz) but gives octamethyldiamidopyrophosphate (**3**) (J_{P-Me}=10.3 Hz) in alkali medium. The free acid **1** should be produced from its chloride **2** under Heath's conditions.[8]

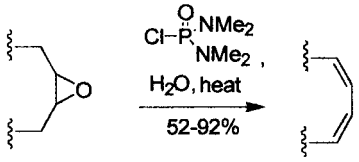


1 **2**

3

2. Results and discussion

According to Scheme 1, epoxycyclooctane (**4a**) was heated at 140–150°C with **2** (5 ml per mmol of epoxide) in the presence of a trace amount of water, and the reaction was conveniently monitored by GLC using internal standards. After 30 min no more starting material was present. The crude reaction mixture was worked up by dilution with water and was extracted with ether or hexane. The analysis of the product by NMR, IR and GLC indicated that the epoxide was effectively dehydrated to give 1,3-cyclooctadiene (**5a**) in 92% yield. Repeating this reaction under anhydrous conditions with distilled **2** under argon gave only a trace amount of diene **5a**. This result indicated that water was necessary for this conversion.



4a-h **5a-h**

Scheme 1.

Keywords: epoxides; dienes; steroid and sterols; aromatization.

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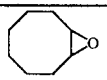
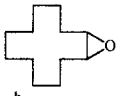
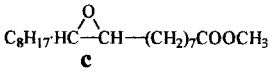
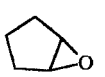
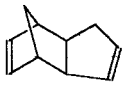
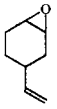
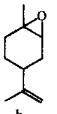
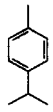
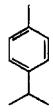
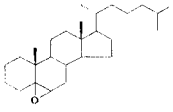
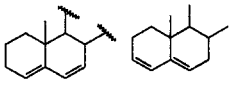
Table 1. Tetramethyldiamidophosphoric acid chloride mediated epoxide–diene conversion

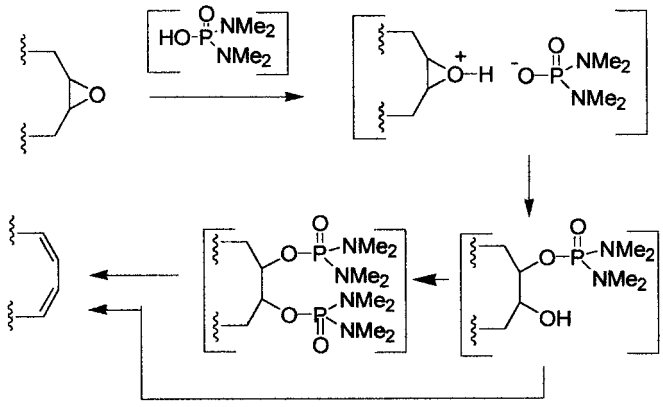
Starting Material[a] 4	Reaction Time	Product 5	Yield (%)
 **a**	30 min.	 **a**[e]	92[c]
 **b**[b]	40 min	 **b**[f]	74[c]
 **c**	1 h	C_7H_{15}-CH=CH-CH=CH-$(CH_2)_5COOCH_3$ **c**	76[c,d]
 **d**	1 h	 **d**	52[c]
 **e**[b]	1h	 **e**	78[c]
 **f**[b]	1h	 **f**	76[c], 73[g]
 **g**	2 h	 **f**	71[c], 70[g]
 **h**[13]	2 h	 **g** **h**	73[g]

[a]Commercially available epoxides are used.
[b]*cis-trans* Mixture.
[c]The yields are determined by GLC (column: HP-1, detector: FID, initial: 120°C, oven: 150°C, final: 200°C) using internal standards.
[d]Part of the ester is hydrolyzed during the conversion.
[e]*cis–cis* Isomer.
[f]Mixture of isomers (92:8).
[g]Isolated yield of the isomeric mixture.

The commercial cyclododecane epoxide, a mixture of *cis* and *trans* isomers (2:1) (**4b**), is also dehydrated using the same procedure as for **4a**.[10] The cyclododecadiene (**5b**) was isolated in 74% yield as a mixture of isomers (GLC: 92:8, 1*E*, 3*Z* is the major isomer).

The deoxygenation of the open chain epoxide methyl oleate epoxide[6] (**4c**) affords an isomeric mixture of 1,3-diene **5c** in 76% yield. Under similar conditions cyclopentene oxide (**4d**) furnished dimeric cyclopentadiene (**5d**) in 52% yield and the crude product contains undefined polymeric material. Heating of 4-vinyl-1-cyclohexene-1,2-epoxide (**4e**) with **2** furnished ethylbenzene (**5e**) in 78% yield and limonene oxide (**4f**) afforded 1-isopropyl-4-methyl benzene (**5f**) in 76% yield after epoxide–diene conversion and isomerization of the triene to the aromatic ring. Triene 5-isopropenyl-2-methyl-1,3-cyclohexadiene (**6**) before isomerization was detected when the reaction was stopped after 10 min and the crude product was analysed by ^{1}H NMR spectrum (δ 4.76 CH_2 protons) and GC–MS.[11a,12] From the same crude mixture the compounds **7** was also detected using GC–MS (4–5%, M^+ 132) and characterised as 2,4-DNP derivative.[11b]

Interestingly, 1-isopropyl-4-methylbenzene (**5f**) was also obtained from deoxygenation of α-pinene oxide (**4g**) in 71% yield. During this conversion, C–C bond cleavage and elimination, followed by isomerization, occurs to give benzene derivative **5f** via formation of stable carbonium ions. Treatment of (20*R*)-5α,6α-epoxycholestane (**4h**) with **2** as described above afforded a mixture of products. The products are identified as cholesta-4,6-diene (**5g**) (major product) and cholesta-3,5-diene (**5h**) (minor product)(GLC 5:1 mixture, mp 78–79°C, total yield 73%).



Scheme 2.

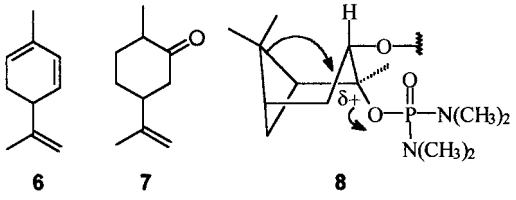
The chromatographic separation of the isomers was unsuccessful. The product mixture was characterised using NMR spectroscopy (δ 5.38–5.98 olefinic protons) and GLC (comparing of the mixture with authentic samples[12]). Only one reaction is described in the literature for the formation of 3,5- and 4,6-cholestadiene in 1:1 ratio starting from isomeric 5,6-epoxycholestanes by using aluminum alkoxides.[13,14] The deoxygenation reactions of epoxides with **2** in the presence of a trace amount of water are summarised in Table 1.

As shown in the following illustrative examples the simple elimination process with secondary alcohols with tetramethyldiamidophosphoric acid chloride (**2**) for 1–4 h in the presence of trace amount of water afforded olefins in good yields (yields by distillation or chromatography):

1. cyclohexanol→cyclohexene (55%)
2. menthol→3-menthene and 2-menthene (61 and 23%)
3. cholesterol→cholesta-3,5-diene (85%)
4. borneol→camphene (77%)
5. *cis*-1,5-cycloocatanediol→*cis*, *cis*-1.5-cyclooctadiene (82%)

With this additional information we considered that in the dehydration reaction with tetramethyldiamidophosphoric acid chloride (**2**) in the presence of trace amount of water the formation of tetramethyldiamidophosphoric acid (**1**) and HCl is the key step. As suggested in Scheme 2 the conversion may work via monophosphonate, and or bis-phosphonate intermediates. No cyclic 1,3,2-dioxaphospholan is detected during the reactions.

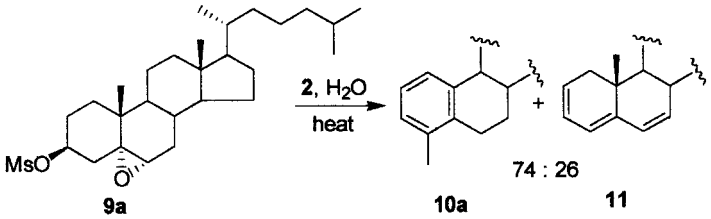
In the reaction of α-pinene oxide (**4g**) with **2**, epoxide ring opening, followed by polarisation of a C-2α–O bond (**8**) and axial cleavage mode of reaction via formation of carbocation by the phosphonate departing would be followed by a series of elimination to give the double bonds.



6 **7** **8**

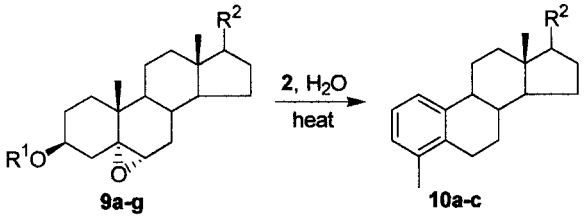
This simple conversion of alkenes through their epoxides to the dienes has been applied to epoxy sterols in order to prepare ring A aromatized steroids. Monoaromatic steroids are of considerable interest both from a biological and chemical viewpoint. They represent one of the important classes of naturally occurring, biologically active compounds, namely the estrogens that comprise the female sex hormones. The estrogens enjoy an extensive range of use in therapy. Considerable effort has been directed towards the synthesis of estrogens and other analogues of ring A aromatic steroids.[15] Investigation of possible routes to the synthesis of estrogenic hormones has led to numerous approaches to access the A ring aromatic skeleton.[16–23]

The dienol–benzene aromatization reaction of ring A of the steroids is one example of a more general class of steroid aromatization reactions which requires two double bond equivalents and a carbonium ion source in order to proceed.[24,25] The cationic spiro intermediate, which is characteristic of the dienol–benzene rearrangement, may be derived from a range of compounds including the 3β-mesyloxy-5α-6α-epoxides. Our initial attention was focused on the reaction of tetramethyldiamidophosphoric acid chloride with epoxy sterols for obtaining ring A aromatization via dienol-benzene rearrangement. The methanesulfonate of



9a **10a** **11**

Scheme 3.



Scheme 4.

3β-hydroxyl-5α,6α-epoxy cholestane (**9a**) and tetramethyldiamidophosphoric acid chloride (**2**) was heated with a trace amount of water and the reaction was monitored by TLC. After 2 h almost all of the starting material was consumed and two UV active spots were observed with R_f values of 0.64 and 0.60. The fractions were separated by column chromatography and identified as 4-methyl-19-norcholesta-1,3,5(10)-triene (**10a**, 45%)[26] and cholesta-2,4,6-triene (**11**, 16%).[27] The ^{1}H NMR spectrum of **10a** showed the migration of C-19 (methyl group) from C-10 to C-4 giving a singlet at 2.18 ppm (3 protons) and three aromatic protons between 7.01–7.19 as multiplet (Scheme 3).

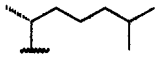
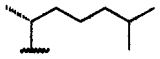
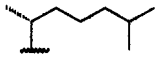
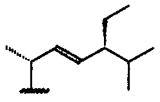
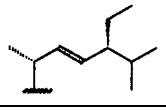
Assignment of the 2,4,6-triene **11** structure rather than the isomeric 1,3,5-triene rested on the analysis of the NMR spectrum (^{1}H, ^{13}C, DEPT, COSY). The ^{1}H NMR spectrum shows two spin system for H-6 and H-7, three spin system for H-2, H-3 and H-4 consistent only with 2,4,6-triene. In addition, the allylic H-1 ethylene signals in COSY NMR of 2,4,6-triene **11** showed only geminal and allylic coupling to H-2. The chemical shift of δ 0.95 for the C-19 angular methyl group in **11** was consistent with the values reported in the literature for related systems.[28,29] Monitoring of the reaction by GLC showed that the triene formed first then aromatization occurred (during the first 5–10 min the triene is the major product). This showed that the aromatization and migration of the methyl group may proceed via formation of the 2,4,6-triene.

Heating of the methanosulfonate of 3β-hydroxyl-5,6-epoxy cholestane (**9a**) with tetramethyldiamidophosphoric acid chloride (**2**) for 3 h (the reaction was monitored by TLC using reference compounds) furnished aromatized compound **10a** as a major product in 66% yield after purification. Under similar conditions 3β-methanosulfonate of 5α,6α-androstan-17-one (**9d**) and stigmasterol (**9f**) gave A ring aromatization products 4-methylestra-1,3,5(10)-triene-17-one (**10b**) and 4-methylstigmast-1,3,5(10),22-tetraene (**10c**) in 71% and 73% respectively (Scheme 4).

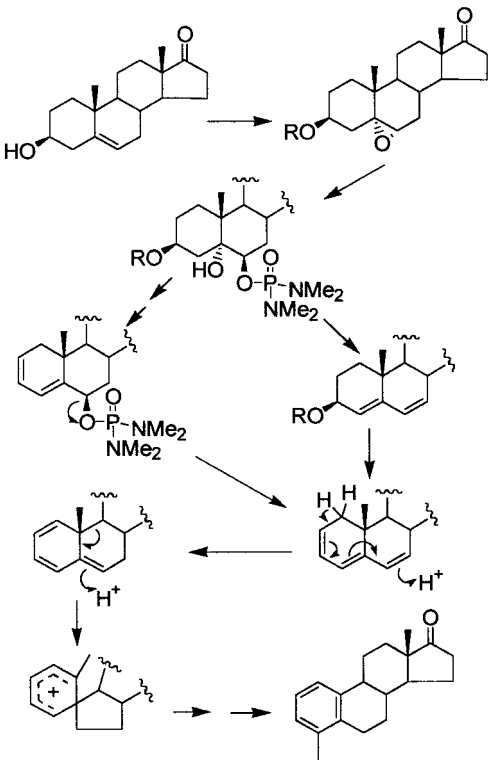
The sterols are converted to the 5α,6α-epoxide derivatives with *m*-chloroperbenzoic acid.[27,30] The methanesulfonate of 5α,6α-epoxy sterols are prepared using methane sulfonyl chloride and triethylamine according to the literature procedure.[31,32]

The conversion of methanosulfonates **9a**, **9d** and **9f** to the aromatized derivatives involved the thermal elimination of methanesulfonic acid, epoxide–diene conversion and prototropic rearrangements. That the methanesulfonic acid was not essential for the conversion of the epoxide to the diene and subsequent aromatization was demonstrated by the reaction of **9b**, **9c**, **9e**, and **9g** in tetramethyldiamidophosphoric acid chloride, which also afforded the expected ring A aromatization products **10a**, **10b** and **10c** in one step and good yields as shown in Scheme 4. Treatment of 3α-hydroxy-5α,6α-epoxycholestane **9c** with tetramethyldiamidophosphoric acid chloride gave 4-methylestra-

Table 2. Ring A aromatization of 5α,6α-epoxy-sterols

Starting material[a] **9**	C-3 Stereochem.	R^1	R^2	Reaction time (h)	Product **10**	Yield (%)
a[b]	β	CH_3SO2^-		3	**a**[i]	66
b[c]	β	H		4	**a**	63
c[d]	α	H		4	**a**	64
d[e]	β	CH_3SO2^-	O	3	**b**[j]	71
e[f]	β	H	O	4	**b**	70
f[g]	β	CH_3SO2^-		3	**c**[k]	73
g2[h]	β	H		3	**c**	69

[a] The starting materials are synthesized according to the literature procedure and the spectroscopic data are in agreement with the published values.
[b] Mp 148–150°C (Lit.[32] 146–150°C.
[c] Mp 143–145°C (Lit.[30] 144–145°C).
[d] Mp 124–125°C (Lit.[33] 124–125°C).
[e] Mp 168–170°C (Lit.[34] 168–172°C).
[f] Mp 228–229°C (Lit.[35] 229–230°C).
[g] Mp 157–160°C (Lit.[21] 162–164°C).
[h] Mp 147–150°C (Lit.[21] 149–151°C).
[i] Mp 48–49°C (Lit.[26a] 49°C).
[j] Mp 190–192°C (Lit.[36a] 191–192°C).
[k] Mp 115–116°C (Lit.[21] 116–118°C).



Scheme 5.

1,3,5(10)-triene-17-one (**10a)** in 64% yield. This experiment showed that the aromatization reaction is independent of the C-3 stereochemistry. The results of the ring A aromatization are summarized in Table 2.

A proposed mechanism for this tetramethyldiamidophosphoric acid chloride mediated reaction of epoxy sterols is shown in Scheme 5. The initial reaction of epoxide with tetramethyldiamidophosphoric acid involves proton transfer and ring opening. A series of elimination reactions (elimination of methanesulfonate, water and tetramethyldiamidophosphate) and prototropic rearangements furnishes the 2,4,6-triene. The 2,4,6-triene would then isomerize to the 1,3,5-triene and could then be protonated at C-6 to generate the spiro intermediate characteristic of the dienol-benzene rearrangements.[18–20]

3. Conclusions

In conclusion, we have developed an efficient and convenient route for epoxide–diene conversion. These results show that epoxide–diene conversion occurs when epoxides are treated with tetramethyldiamidophosphoric acid chloride (**2**). The conversion works with open chain and cyclic epoxides. A C–C bond cleavage reaction occurs if the epoxide contains a quaternary carbon. The formed polyenes are isomerizing to the most stable structures. The reaction is simple, tetramethyldiamidophosphoric acid chloride (**2**) is commercially available and the yields are good Application of this method to the epoxy sterols furnished A ring aromatized steroids in good yields. The aromatization works via formation of a 2,4,6-triene. Aromatization of 3-substituted 5α,6α-epoxides proceeds with hydroxy and methanosulfonate and is independent of the C-3 stereochemistry. This process offers an attractive alternative to other multistep procedures.

4. Experimental

All reagents were of commercial quality and reagent quality solvents were used without further purification. IR spectra were determined on a Philips model PU9700 spectrometer. ^{1}H NMR spectra were determined on a Bruker 400 MHz FT spectrometer. GLC analyses were determined on a HP 5890 gas chromatograph. Mass spectra were obtained on VGTrio2 spectrometer at ionisation energy of 70 eV.

4.1. Reactions with tetramethyldiamidophosphoric acid chloride. General procedure

1 mmol of epoxide was dissolved in 5 ml tetramethyldiamidophosphoric acid chloride and to this solution was added 1–2 drops of water. The mixture was heated at 140–150°C and then diluted with 5 ml of water while still warm and extracted with 30 ml of ether or hexane. Organic layer was washed with 5 ml of 1N HCl solution and brine, dried over $MgSO_4$. Evaporation of solvent gave the 1.3-diene. GLC conditions (Inlet temp. 150°C, oven 90°C, detec. temp. 200°C).

4.2. Representative examples

4.2.1. 1,3-Cyclooctadiene (5a). According to the general procedure, the reaction of cyclooctene oxide (126 mg, 1 mmol) afforded cyclooctane-1.3-diene in 92.5% yield (GLC; column: HP-1, detector: FID, initial: 120°C, oven: 150°C, final: 200°C).

4.2.2. 1,3-Cyclododecadiene (5b). According to the general procedure, cyclododecane epoxide (**4b**) (182 mg, 1 mmol) gave cyclododecadiene (**5b**) (122 mg, 74%) as a colourless liquid after purification of the crude product (PTLC, silica gel 60, EtOAc/ hexane 1:20). IR(TF): 2950–2850, 1455, 1366 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.11–1.73 (m,12, 6 CH_2), 2.01–2.48 (m, 4, 2 allyl. CH_2), 5.31–5.78 (m, 2, *CH*–CH_2–), 6.12– 6.47 (m, 2, CH–*CH*–*CH*–CH). ^{13}C NMR ($CDCl_3$): δ 21.92, 22.18, 22.52, 22.62, 22.72, 23.07, 23.46, 23.60, 23.76, 23.81, 24.16, 24.47, 24.98, 25.28, 25.90, 26.97, 27.21, 27.97, 28.97, 29.7, 127.10, 128.26, 129.50, 129.60, 130.27, 131.56, 134.2. GC–MS (isomeric mixtures, 92:8): (*m*/*z*) (%bp) 164 (M^+), 149, 135, 121, 107, 91, 79(bp), 67, 55. The structural data agree with those of lit.[5b,10]

4.2.3. Reaction of 5α,6α-epoxycholestane with 2: the synthesis of cholesta-4,6-diene (5g) and cholesta-3,5-diene (5h). In accordance with the general procedure the mixture of 5α,6α-epoxycholestane **4h** (3.3 g, 8 mmol) and **2** was refluxed for 4 h (checked by TLC. Petroleum ether: ether 10:1). The mixture was cooled and extracted with ether three times and was washed with water and $NaHCO_3$ solution three times and dried over anhydrous $MgSO_4$. The solution was filtered, concentrated and chromatographed on silica gel (Petroleum ether–ether 10:1) to

give a mixture of **5g** and **5h** (2.54 g, 73%) (5:1; GLC, OV 101 capillary column, 90°C) as a colourless solid, mp 77–79°C. ^{1}H NMR ($CDCl_3$): δ 0.66, 0.71, 0.82, 0.89 (methyl protons), 5.38–5.98 (vinylic protons). The structural data agree with those of literature.[12]

4.3. General procedure for epoxidation of sterols:[30–35]

To 25 mmol of sterol in 300 ml of $CHCl_3$ at 0°C was added 40 mmol of *m*-chloroperbenzoic acid portionwise. The mixture was stirred at °0C for 1 h and filtered. The filtrate was washed successively with saturated $NaHCO_3$, H_2O, and brine. The solution was dried over anhydrous $MgSO_4$ and the crude product was purified by column chromatography or crystallization.

4.4. General procedure for methanesulfonate of epoxysterols:[21,32,34]

To a 20 mmol solution of epoxysterol in 60 ml of CH_2Cl_2 at 0°C under argon atmosphere was added 60 mmol of Et_3N followed by slow addition of 25 mmol of methanesulfonyl chloride. The mixture was stirred for 1 h at 0°C and diluted with cold water. The solution was extracted twice with 100 ml of CH_2Cl_2. The organic layer was washed successively with H_2O to neutral pH and with brine. The solution was dried over $MgSO_4$, filtered, and concentrated to afford crude product which was chromatographed on silica gel using 3:1 hexane–EtOAc.

4.5. Reactions with tetramethyldiamidophosphoric acid chloride. General procedure

1 mmol of epoxy sterol was dissolved in 10 mmol (10 equiv.) tetramethyldiamidophosphoric acid chloride and to this solution was given 1 drop of water. The mixture was heated at 140–150°C for 1–4 h and then diluted with 5 ml of water while still warm and extracted with 25 ml of ether. The ether layer was washed with 10 ml of 1N HCl solution and brine, dried over $MgSO_4$. Evaporation of solvent gave the product. GLC conditions (Inlet temp. 150°C, oven 90°C, detec. temp. 200°C, column, SE-30 fused silica gel capillary column (15 M).

4.5.1. Synthesis of 4-methyl-19-norcholesta-1,3,5(10)-triene (10a) and cholesta-2,4,6-triene (11). According to the general procedure **9a** (480 mg,1 mmol) afforded after 2 h reflux and chromatographic separation (EtOAc: hexane 1:5) of **10a** (164 mg, 45%) as a colourless solid (mp 48–49°C, Lit.[26] 49°C): ^{1}H NMR ($CDCl_3$): δ 0.76 (s, 3H, C-18 CH_3), 0.82 (d, J=7.4 Hz, 3H,C-21 CH_3), 0.92,(d, 6H, C-26, 27 CH_3), 2.18 (s, 3H, C-4 CH_3), 7.01, 7.13, and 7.19 (3m, 3H, Ar-H), and **11** (59 mg, 16%) as a colourless solid (mp 70–72°C, Lit.[27] 70–71°C):^{1}H NMR ($CDCl_3$): δ 0.74 (s, 3H, C-18 CH_3), 0.81 (d, J=6.4 Hz, 3H, CH_3), 0.87 (d, J=6.4 Hz, 3H, CH_3), 0.95 (s, 3H, C-19 CH_3), 1.07 (d, J=6.5 Hz, 3H, C-21 CH_3), 5.54 (dd, J=1.1 and 5.5 Hz, 1H, C-4 H), 5.62 (dd, J=9.5 Hz, 1H, C-6 H), 5.66 (dddd, J=2.6, 6.4, 9.1, and 1.1 Hz, 1H, C-2 H), 5.72 (ddd, J=3.2, 9.1 and 5.5 Hz, 1H, C-3 H), 5.93 (dd, J=1.9 Hz, 1H, C-7 H). ^{13}C NMR ($CDCl_3$): δ ppm 12.1 15.2 18.9, 21.2, 23.1, 23.3, 24.4, 24.5, 28.4, 28.6, 35.9, 36.2, 36.6, 36.8, 37.3, 39.9, 40.3, 43.5, 51.9, 54.9, 56.8 (21 saturated carbons),119.1 123.9, 125.2, 128.3, 131.2 (5 olefinic C–H),143.2(one olefinic quatenary carbon). The structural data agree with those of literature.[26]

4.5.2. 4-Methylestra-1,3,5(10)-triene-17-one (9b).[36] ^{1}H NMR ($CDCl_3$): δ 0.93 (s, 3H, C-18 CH_3), 2.24 (s, 3H, C-19 CH_3), 7.03, 7.16, and 7.23 (3 m, 3H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 13.6, 20.2, 21.5, 25.7, 26.3, 26.8, 32.1, 35.8, 37.3, 45.1, 47.6, 51.2, 123.4, 125.7, 128.1, 134.8, 136.6, 139.9, 220.1. The structural data agree with those of literature.[36]

4.5.3. (20*R*, 22*E*,24*S*)-4-Methylstigmast-1,3,5(10),22-tetraene (10c).[21] ^{1}H NMR ($CDCl_3$): 0.74 (s, 3H, C-18 CH_3), 0.81 (t, J=7.2 Hz, 3H, C-29 CH_3), 0.83 (d, J=6.5 Hz, 3H, CH_3), 0.89 (d, J=6.5 Hz, 3H, CH_3), 1.03 (d, J=6.5 Hz, 3H, C-21 CH_3), 2.22 (s, 3H, C-4 CH_3), 4.92-5.23 (m, 2H, vinylic H), 6.98–7.25 (m, 3H, Ar-H). The structural data agree with those of literature.[21]

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CH_3), 1.27–1.42 (m, 1H, CH), 1.51–1.62 (m, 1H, CH), 1.78 (broad s, 3H, CH3), 1.88–2.01 (m, 2H, CH_2), 2.02–2.20 (m, 2H, CH_2), 2.35–2.45 (m, 1H, CH), 2.87 (m,1H, CH), 4.80 (m, 2H, CH_2), 7.98, 8.26, 9.18 (3H, Ar-H), 11.25 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 16.7, 20.8, 31.14, 32.50, 35.93, 39.98, 45.89, 96.30, 110.63, 116.32, 123.56, 130.0, 145.66, 147.33, 162.21. MS (70 eV, *m/z*): 332 (M^+), 317, 297, 271, 255, 135, 122, 107, 93, 79, 67, 55.

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