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REGIO- AND STEREOSELECTIVE ADDITION OF N-*p*-TOSYL-TRICHLOROMETHYLIMINE TO VINYL DIHYDRONAPHTHALENES[1]

R. P. LOVEN[2a], W. A. ZUNNEBELD[2b] and W. N. SPECKAMP*
Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

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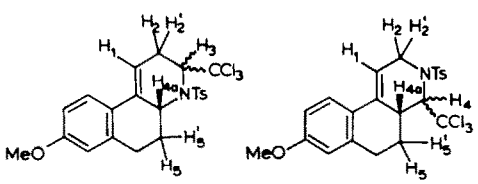
Abstract—Imine **1** underwent regioselective addition to vinyl dihydronaphthalenes **2** and **3** to afford the cyclo-adducts **4**, **5** and **6**. The structures and stereochemistry of the latter adducts have been determined by PMR and X-ray analysis. Factors influencing the mode of addition are discussed. Epoxidation and bromination of **4** led to the formation of aromatizated products. Hydrolysis of **5** and **6** gave the corresponding ketones which underwent facile ringopening via a retro-Michael type of reaction.

In a preceding communication[3] we described the cycloaddition of N-ethyloxycarbonylmethylene sulfonamide to vinyldihydronaphthalene **2** and have shown the potential synthetic utility of such a heterocycloaddition.

In pursuing this investigation imine **1**[4] was condensed with diene **2** to give a single crystalline 1:1 adduct in 72% yield.[5] Chromatographic examination of the mother liquor gave no indication for the presence of different types of adduct, the main side product being dimers of diene **2**. The structure of the adduct was deduced from its PMR-spectrum (Fig. 1a) which shows interalia the presence of olefinic (δ 5·96, H_1), C$\underline{H}$CCl$_3$ (δ 5·07, H_3) and C$\underline{H}$-NTs (δ 4·14, H_{4a}) protons.



Both possible types of adduct **A** and **B** however, would be expected to show similar splitting patterns and in order to establish its structure unequivocally decoupling experiments were carried out. After irradiation at δ 5·96 (Fig. 1b) the absorption at 4·14 (H_{4a}) can be recognized as a doublet of triplets ($J_{4a,5}$ = 12·0; $J_{4a,5'}$ = 3·0; $J_{2,4a}$ = 3·0 Hz) which excludes the alternative structure **B** because the maximum possible number of couplings expected for the remaining C$\underline{H}$-NTs proton is two ($^2J_{2,2'}$ and $^4J_{2,4a}$).

Further information on the stereochemistry of **4** can also be derived from the PMR data. Irradiation of the highfield allylproton (δ 2·17, Fig. 1c) gives a quartet for H_1 with respective J values of 7·0 and 2·5 Hz, of which the former vanishes upon irradiation at δ 2·70 (Fig. 1d). Furthermore the large coupling $J_{4a,5}$ = 12·0 Hz disappears upon irradiating at δ 2·17 while H_3 collapses to a singlet (Fig. 1c).

Combination of the PMR spectral data allow the following conclusions to be drawn for the magnitude of the different coupling constants: $J_{1,2}$ = 7·0 Hz; $J_{1,2'}$ = 2·5 Hz; $J_{1,4a}$ = 3·0 Hz; $J_{2',3}$ = 7·5 Hz; $J_{2,3}$ = 0·5 Hz; $J_{2,4a}$ = 3·0 Hz; $J_{2',4a}$ = 0·5 Hz and $J_{4a,5}$ = 12·0 Hz.

On the assumption of a—modified—Karplus equation to be valid model studies allowed a full configurational assignment of the molecule encompassing the following features: (i) a pseudo-axial position for the trichloro methyl substituent, (ii) an axial position for H_{4a}, (iii) a *cis*-relation for H_3 and H_{4a}, and (iv) a near-boat form for the heterocyclic ring. These conclusions were fully verified by an X-ray analysis according to the heavy-atom

*To whom all inquiries should be directed.

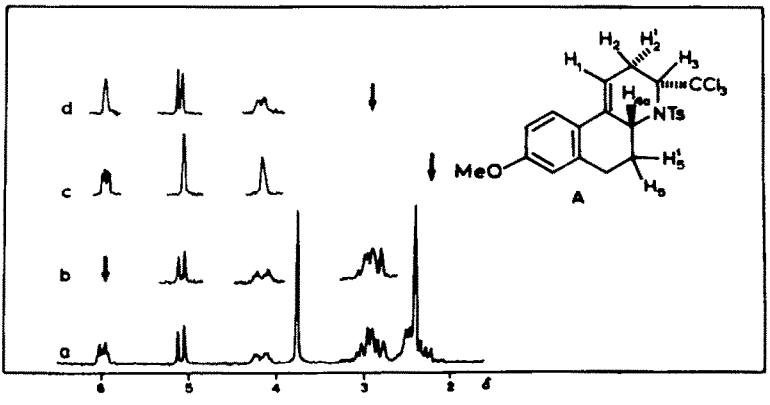


Fig. 1.

method of van der Meer[6] which in addition showed the sulfonyl group to be almost in the C-N-C plane thus favouring a trigonal nitrogen atom in the crystalline state.[7]

On the contrary, addition of **1** to diene **3** gave a mixture of two 1:1 adducts which on the basis of the following spectral evidence were assigned structures **5** and **6**. Both PMR and mass spectra of **4** and **5** are very similar and differ in considerable degree from the spectral data of **6**. In particular the coupling constants—$J_{2,3}$ and $J_{2',3}$—are of diagnostic value; the respective magnitudes being 1·5 and 7·5 Hz in adduct **5** and 5·0 and 8·0 Hz in adduct **6***.

Furthermore the aromatic C_{10}-H proton is located at 7·55 in **6** and 7·98 in **5**, indicating a considerable van der Waals interaction in the latter isomer. Combination of the aforementioned data and model studies led to the assignment of near-boat conformations of both **5** and **6** with the CCl_3-substituent pseudo-axial in **5** and pseudo-equatorial in **6**. Analysis of the data from Table 1 in which the important mass spectral fragments are summarized supports the structural assignments.

Mechanistically it is of interest to note the constancy of the ratio 5/6—being 1·5 as determined via PMR integration of the crude reaction mixture—upon carrying out the cycloadditions at different temperatures and in different solvents.†

In benzene at 20° a yield of 80% of crystalline (**5** + **6**) is obtained which drops to 35% in diethyl ether as the solvent, the ratio **5**/**6** however being constant. A change in temperature did also not affect the latter ratio. These observations tend to support the view of considering these reactions as genuine cycloadditions.[8]

The origin of the unique regioselectivity[9] of the addition of **1** to **2** is presumably caused by two factors: (i) a favoured E-conformation for the imine **1**, and (ii) the severe steric interaction between C_5-CH_2 and the substituent on imine carbon, favouring a transition state **X**. In case of increasing repulsion of the large trichlorogroup with the diene substituent R the addition may also take place via transition state **Y**—leading to the *exo*-adduct **6** together with the "normal" *endo*-adduct **5**. Similar observations have been made recently by Krow c.s.[10] in reactions of cyclic dienes with imine **1**.

In order to obtain chemical evidence on the interrelation between adducts **4**, **5** and **6** peracid oxidation of **4** was carried out. Depending on the reaction time and temperature oxidation with *m*-Cl-perbenzoic acid in 1,2 dichloroethane afforded the air-sensitive **9** in varying amounts. The main product, however, proved to be the

*Coupling constants were determined via appropriate decoupling experiments. The $H_2H_2H_3$ system in **5** was of AMX, in **6** of ABX type.

†Reactions were carried out in benzene at 20° and 80°, in diethyl ether at 10° and 35°.

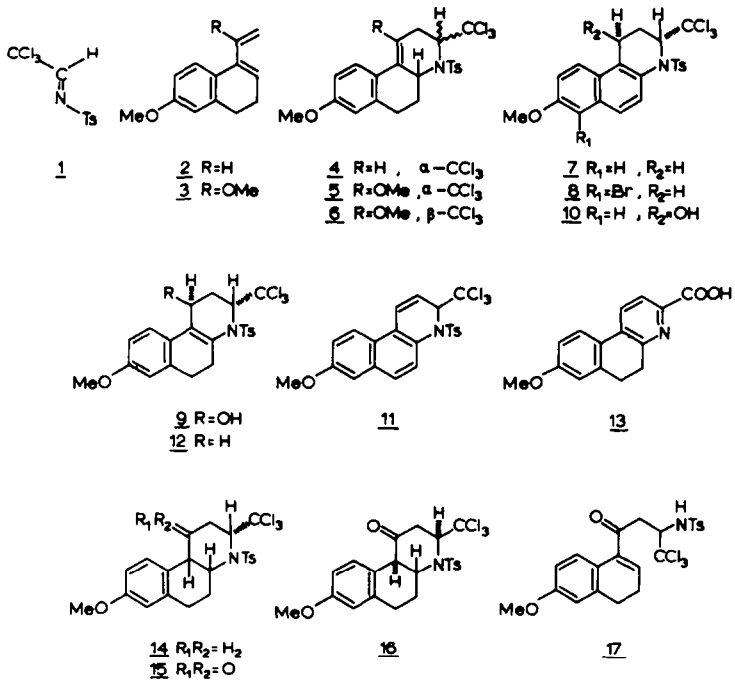
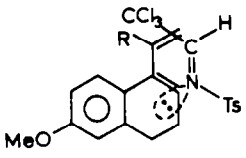


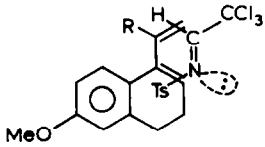
Table 1.[a]

Compound \ Fragment	$M^{\oplus\cdot}$	$(M-Ts)^{\oplus}$	$(M-CCl_3)^{\oplus}$	$(M-Ts-CCl_3-H)^{\oplus}$
4	8	12	12	100
5	27	12	7	100
6	180	100	25	100

[a] Relative intensities determined against $(M-273)^{\oplus}$ = 100%.



X endo–CCl_3



Y exo–CCl_3

aromatized hydroxy derivative **10** after stirring the crude oxidation mixture for 24 hr in acetone. Its structure could be established unequivocally via analysis of its UV, mass and PMR-spectral data. The J values found $J_{2,3}+J_{2',3}=16$ Hz, $J_{1,2}+J_{1,2'}=7$ Hz are indicative for an equatorial position of the trichloromethyl-substituent thus inferring a conformational change of the hererocyclic ring. From the latter J values a *β-axial*-position of the hydroxygroup is deduced which is conceivable in view of the steric effect of the trichloromethylgroup. α-Attack is almost excluded for steric reasons as shown from a projection of the CCl_3 group on the plane through the N, C_{4a} and C_1 atoms (Fig. 2). The drawing has been made according to the X-ray data.

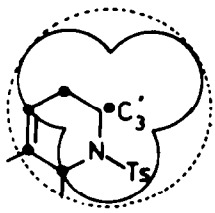


Fig. 2.

The formation of **10** can be explained in the following manner. While aromatization of ring B is known[11] to occur in some estrogens upon peroxidation of the 9,11-double bond the concurrent introduction of an 11-hydroxy function has not been reported earlier. A possible reaction pathway may be found in the acid catalyzed ring opening of the initially formed epoxide[12] followed by peroxidation of the resulting dihydronaphthalene and subsequent aromatization. TLC analysis of the epoxidation mixture allowed the isolation of **9**, although it was still contaminated with some **10**. **9** Was identified from its PMR spectral data which in addition to the presence of the CH_2-CH_2 fragment also showed coupling constants $J_{1,2}+J_{1,2'}=9$ Hz and $J_{2,3}+J_{2',3}=14{\cdot}5$ Hz, thus exhibiting similar PMR characteristics as compared to **10** and also indicating a strong resemblance in conformation between **9** and **10**.

Upon boiling the epoxidation product **10** with HCl/EtOH the unsaturated compound **11** was formed. The latter product was also the chief component of the mixture after treatment of **4** with 1 equiv of bromine in CCl_4. Its structure was indicated by the two independent modes of formation and confirmed via UV and PMR spectral data. A second product of the latter reaction was the dihydro-analogue **7**, characterized by its different UV,[13] the presence of four protons in the region δ 1·4–3·4 in the PMR spectrum and by mass spectral data. Upon use of two equivalents of bromine the reaction products were **11** and the 7-bromo-substituted benzo[f]quinoline **8**, strongly resembling **7** in its spectroscopic data.

Treatment of **7** with Br_2/CCl_4 gives exclusively **8**, no trace of **11** being formed. Thus in the formation of **7** and **11** from **4** different pathways have to be followed. This assumption can be verified further when the behaviour of the C_{4a}-C_{10b} unsaturated isomer **12**, obtained via acid catalyzed isomerization of **4**, is studied. Upon Br_2/CCl_4 treatment of **12**, **7** is found as the single product.

A rationale for this behaviour can be given in the following way: after bromine addition to the C_1-C_{10b} double bond in **4** HBr-elimination occurs and under influence of the liberated acid partial isomerization of the C_1-C_{10b} double bond takes place. The primary bromination adduct then gives rise to **11** while the isomerized product leads to **7**. The difficulty in brominating **7** at C-1 almost certainly finds its origin in steric factors, such as the proximity of the large CCl_3-group and the unfavourable peri-interactions of C_1-X, C_{10}-H in the product.

Finally it is of interest to note that upon carrying out the bromine addition to **4** in $CHCl_3$ the ratio **7**:**11** changes in favour of **7** presumably because of the enhanced solubility of HBr in $CHCl_3$ thus promoting the isomerization of **4**.

Hydrolysis of **4** gave in strongly alkaline medium a small quantity of the pyridine-carboxylic acid **13** in addition to large amounts of unidentified material. On the contrary treatment of **11** under similar circumstances led to simultaneous rearrangement and aromatization.[14]

Acid hydrolysis of adducts **5** and **6**, however, under mild conditions (HBr/HOAc/$CHCl_3$ r.t.) gave two ketones **15** and **16** which were formed at different rates and for which structural assignments were based upon the respective PMR spectra featuring characteristic values for $J_{4a,10b}$, δH_{10} and $W_{4a}^{1/2}$. From the spectrum of **15** the following parameters were obtained: $J_{4a,10b}=8{\cdot}5$ Hz, $\delta H_{10}=6{\cdot}74$ and $W_{4a}^{1/2}=26$ Hz. The latter value is indicative for a *trans*-diaxal position for H_{4a} and one of the C_5 protons. The value of $J_{4a,10b}$ is more difficult to interpret. *cis*-Geometry in the corresponding carbocyclic series usually leads to J values of 5·0 Hz.[15] In the spectrum of **14** a value of 3·0 Hz for $J_{4a,10b}$ is found. However, PMR-analysis of an analogous ketone* reveals coupling constants of 8·0 Hz for a *cis* relationship of the corresponding protons. Therefore the aforementioned data are in good agreement for a model which is given in Fig. 3 in which H_{10} is situated at a distance of 2·8 Å above the C_{10b}-C_1-C_2 plane in the C=O shielding zone.[16] In the second isomer **16** the value of $J_{4a,10b}=12$ c/s proves a *trans* fusion of the heterocyclic ring.[17]

Finally when **5** or **6** were heated in EtOH/HCl ring cleavage occurred and **17** was obtained in 80%. Under similar conditions the latter product was also formed starting from ketone **16**. Its structure was inferred from PMR data, showing the presence of a doublet at 5·71 (N-H) and a multiplet at 4·95 (CH-CCl_3) the former signal

*In the model system i a value of 12·5 c/s was found for $J_{5,6}^{trans}$. $J_{5,6}^{cis}$ was estimated as 8·0 c/s according to the "Simeq" computer programme analysis developed by Dr. C. W. F. Kort of this laboratory.

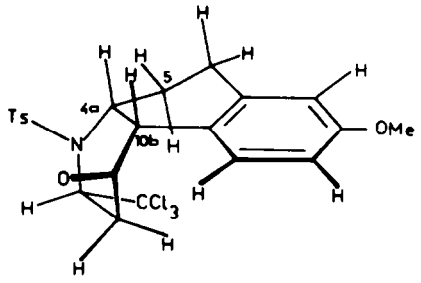


Fig. 3.

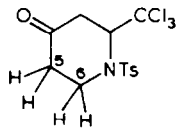


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Fig. 4.

disappearing upon addition of D_2O and the latter simplifying to a triplet. Mass and UV data supported structure **17** the formation of which can be depicted as an acid catalyzed fragmentation. Under similar conditions, however, the monocyclic N-tosyl piperidone[18] is not affected indicating that the steric compression in the tricyclic adducts **5**, **6** and **16** promotes the ringopening.

In summary the addition of imines **1** to polycyclic dienes is to be viewed upon as an expedient method for the synthesis of polyfunctional heterocyclics provided means can be found for a selective degradation of the trichlorogroup. In a further communication a rational method for the achievement of this goal will be presented.

EXPERIMENTAL

All m.ps are uncorrected. Analyses were carried out by Messr. H. Pieters of the Micro-analytical Department of this laboratory. IR-spectra were taken on an Unicam SP-200 as KBr-tablets. The NMR-spectra were determined on a Varian HA-100 in $CDCl_3$, unless otherwise stated, with TMS as internal standard, δ values are given in ppm. Mass spectra were obtained on an AEI spectrometer type MS 9-H. The UV spectra were measured on a Cary-14 in ethanol.

N-*Trichloroethylidene* - p - *toluenesulfonamid* **1**. By the procedure of Albrecht,[4] **1** was obtained in 83% yield, m.p. (C_6H_6): 119–122°; IR(CCl_4): 1645 (C=N); 1360, 1170 (SO_2); PMR ($CDCl_3$): 2·45 (s) $ArCH_3$; 7·40 (d) and 7·85 (d) tosyl; 8·45 (s) CH=N.

1 - *Vinyl* - 6 - *methoxy* - 3,4 - *dihydronaphthalene* **2**. By the procedure of Nazarov[19] **2** was obtained in 78% yield; b.p.: 110–113°/0,1 mm $n_D^{20} = 1{\cdot}591$.

N - *Tosyl* - 3 - *trichloromethyl* - 8 - *methoxy* - 2,3,4,4a,5,6 - *hexahydro* - *benzo(f)quinoline* **4**. Compound **2** (50 mmol) was added to a soln of **1** (50 mmol) in 60 ml benzene. After 16 hr the solvent was evaporated and the residue was triturated with EtOH, yield: 72%; m.p. (EtOH): 188–189°; UV: λ_{max}^{EtOH}: 263(19,600), 294(3,350) nm. Found: C, 54·3; H, 4·6; O, 9·9; N, 2·9; S, 6·8; Cl, 22·0. Calc.: $C_{22}H_{22}O_3NSCl_3$ (486·8); C, 54·28; H, 4·56; O, 9·86; N, 2·88; S, 6·59; Cl, 21·85%).

1 - (1' - *Methoxyvinyl*) - 3,4 - *dihydro* - 6 - *methoxy* - *naphthalene* **3**, By the procedure of Hajos[19] **3** was obtained as an 80% pure oil.

N - *Tosyl* - 1,8 - *dimethoxy* - 3 - *trichloromethyl* - 2,3,4,4*a*,5,6 - *hexahydrobenzo(f)quinolines* **5** *and* **6**. To **1** (4·7 mmol) a soln of **3** (4·7 mmol) in 12 ml benzene was added. After 23 hr the solvent was evaporated and the residue was triturated with EtOH. First **6** crystallized, yield: 27%; m.p. (EtOH): 184·5–187·5°; IR($CHCl_3$): 1640 (C=C–OCH_3) 1320, 1150 (SO_2) cm^{-1}; PMR δ ($CDCl_3$): 2·34(s) $ArCH_3$; 3·57(s) C=C–OCH_3; 3·64(s) arom. OCH_3; 4·48 (diff. d, J = 12·0 c/s) H_{4a}; 5·46 (d.d. J = 5 and 8 c/s) H_5; 7·12(d) and 7·77(d) tosyl; 7·76 (d, J = 8·5 c/s) H_{10}; UV: λ_{max}^{EtOH}: 228 (15,500 sh); 270 (16,400) nm. (Found: C, 53·6; H, 4·7; N, 2·7; S, 6·3; Cl, 20·5. Calc.: $C_{23}H_{24}O_4NSCl_3$ (516·87); C, 53·44; H, 4·68; N, 2·71; S, 6·20%).

5 was obtained as second crop. Yield: 14%; m.p. (EtOH): 202–205°; IR($CHCl_3$): (C=C–OCH_3); 1350, 1340, 1320, 1150 (SO_2) cm^{-1}; PMR δ($CDCl_3$): 2·39(s) Ar-CH_3; 3·75(s) arom. OCH_3; 4·25 (diff. t) H_{4a}; 5·21 (d. d. J = 7·5 and 1·5 c/s) H_3; 7·26(d) and 7·67(d) tosyl; 7·98 (d, J = 8 c/s) H_{10}; UV λ_{max}^{EtOH}: 235 (15,400 sh); 264 (20,800) (Found: C, 53·6; H, 4·7; N, 2·7; S, 6·3; Cl, 20·5. Calc: $C_{23}H_{24}O_4NSCl_3$ (516·87); C, 53·44; H, 4·68; N, 2·71; S, 6·20; Cl, 20·58%).

Epoxidation of **4**. To **4** (0·41 mmol) dissolved in 2 ml 1,2-dichloro-ethane *m*-chloroperbenzoic acid (1·2 mmol) was added. After 1 hr the soln was extracted with 2 N KOH aq (5 times). The PMR spectrum of the crude product indicated a complicated mixture. When this mixture—in which **9** and **10** were absent—was stirred in acetone in an open vessel for 65 hr N - *tosyl* - 1 - *hydroxy* - 3 - *trichloromethyl* - 8 - *methoxy* - 1,2,3,4 - *tetrahydro* - *benzo(f)quinoline* **10** was formed in 60% yield; m.p. (MeOH): 168–173°; IR($CHCl_3$): 3480(OH); 1330, 1150(SO_2) cm^{-1}; PMR δ($CDCl_3$): 2·38(s) $ArCH_3$; 2·5(m) OH (this signal vanishes by shaking $CDCl_3$-solution with D_2O); 3·90(s) OCH_3; 5·50(m) H_1; 5·65 (d·d. J = 7·5 and 9 c/s) H_3; 7·64(d), 7·98(d) tosyl; UV λ_{max}^{EtOH}: 233(44,000); 240(45,000); 271(10,000); 281(8,000); 294(5,500); 320(2,500) nm.

Mass: 499 (M) 10%; 382 (M-CCl_3) 19%; 364 (M-CCl_3-H_2O) 73%; 344 (M-tosyl) 31%; 227 (M-CCl_3-Ts) 94%; 209 (M-CCl_3-tosyl-H_2O) 100%. (Found: C, 52·8; H, 4·0; N, 2·8; S, 6·4; Cl, 21·2. Calc.: $C_{22}H_{20}O_4NSCl_3$ (500·83); C, 52·65; H, 3·90; M, 2·89; S, 6·43; Cl, 21·12%.)

In a second experiment the crude reactionproduct contained 25% N - *tosyl* - 3 - *trichloromethyl* - 8 - *methoxy* - 1,2,3,4,5,6 - *hexahydro* - *benzo(f)quinoline* **9**. It appeared impossible to isolate pure **9**. **9** Was obtained as a crystalline product (m.p. 153–155°) contaminated with 25% **10** after repeated thick-layer chromatography (silicagel F 254, Merck, eluant: $CHCl_3$/EtOAc = 97/3).

Bromination of **4**. A soln of Br_2 (10 mmol) in 50 ml CCl_4 was added to a soln of **4** (10 mmol) in 100 ml CCl_4 at 0°. Instantaneous formation of HBr occurred. After 2 hr at 0° and 20 hr at r.t. the soln was evaporated to dryness and triturated with EtOH. The crude product—containing major products **7** and **11** and minor products **8** and **12**—was passed through a column of Al_2O_3 with pa 60–80/$CHCl_3$ as an eluant. From the first fraction N - *tosyl* - 3 - *trichloromethyl* - 8 - *methoxy* - 3,4 - *dihydro* - *benzo(f)quinoline* **11** was isolated, yield: 20% m.p. ($CHCl_3$/EtOH): 188–190°; PMR δ(NC_5D_5): 1·98(s) $ArCH_3$; 3·74(s) OCH_3; 6·18 (d, J = 6 c/s) H_3; 6·43 (d·d. J = 6 and 9 c/s) H_2; 6·93 (d) and 7·58 (d) tosyl; 7·48 (d, J = 9 c/s) 7·91 (d, J = 9 c/s)H_5 and H_6; 8·35 (d) H_{10}; UV λ_{max}^{EtOH}: 228 (34,000), 249 (39,000); 255 (43,500); 309 (5,500); 321 (5,800); 345 (3,200); 356 (3,100) nm. (Found: C, 54·7; H, 3·9; O, 10·1; N, 2·9; S, 6·5; Cl, 22·3. Calc.: $C_{22}H_{18}O_3NSCl_3$ (482·8): C, 54·73; H, 3·76; O, 9·94; N, 2·90; S, 6·64; Cl, 22·03%). **11** Was also formed when **4** (1 mmol) was epoxidized and subsequently boiled with a mixture of 30 ml EtOH and 5 ml conc HCl for 0·5 hr. The PMR spectrum indicated 65% formation of **11**. From the second fraction N - *tosyl* - 3 - *trichloro* - *methyl* - 8 - *methoxy* - 1,2,3,4 - *tetrahydro* - *benzo(f)quinoline* **7** was obtained in a nearly pure form; yield: 20%; m.p. 180–190°; PMR δ(NC_5D_5): 2·07(s) $ArCH_3$; 1·4–3·4 (m) CH_2-CH_2; 3·79 (s) OCH_3; 5·75 (t, J = 7·5 c/s) H_3; 6·98 (d) and 7·5 (d) tosyl; 7·78 (d) H_{10}; 7·90 (AB, J = 9 c/s) H_5 and H_6.

Bromination under the same conditions in $CHCl_3$ as solvent instead of CCl_4 gave mainly **7**.

Bromination under the same conditions with two equivs Br_2 instead of one yielded a mixture of **11** and **8**. **8** could be purified by crystallization from $CHCl_3$/EtOH, yield: 33%; m.p. 251–253°; PMR δ(NC_5D_5): 2·08 (s) $ArCH_3$; 1·5–3·5 (m) CH_2-CH_2; 3·82 (s) OCH_3; 5·77 (t, J = 7·5 c/s) H_3; 7·01 (d) and 7·60 (d) tosyl; 7·90 (d) H_{10}; 8·24 (AB, J = 9 c/s) H_5 and H_6; UV λ_{max}^{EtOH}: 232·5 (42,000); 247 (53,500); 278 (7,500; 293 (7,000); 305 (5,700); 332,5 (2,400); 346 (2,600) nm. (Found: C, 47·0; H, 3·6; O, 8·6; N, 2·5; S, 5·6; Cl, 18·9; Br, 14·2%. Calc.: $C_{22}H_{19}O_3NSCl_3Br$ (563·7): C, 46·87; H, 3·40; O, 8·51; N, 2·49; S, 5·69; Cl, 18·87; Br, 14·18%).

Bromination of **7** instead of **4** under the same conditions gave **8** in 90% yield.

Bromination of **12** instead of **4** under the same conditions gave a mixture of **7** and **8**.

N - *Tosyl* - 3 - *trichloromethyl* - 8 - *methoxy* - 1,2,3,4,5,6 - *hexahydro* - *benzo(f)quinoline* **12**. After stirring **4** in a 0·1 M soln of CCl_4 for 20 hr at r.t, in presence of two drops of HBr-HOAc soln, the solvent was evaporated and the residue triturated with EtOH, yield of **12** (PMR): quantitative; m.p. 145 (dec); UV λ_{max}^{EtOH}: 225 (27,000) and 293 (15,400) nm; PMR $\delta(CDCl_3)$: 240 (s) $ArCH_3$; 3·77 (s) OCH_3; 5·02 (t, J = 6·5 c/s) H_3; 7·22 (d) and 7·58 (d) tosyl.

N - *Tosyl* - 1 - *oxo* - 3*α* - *trichloromethyl* - 8 - *methoxy* - 1,2,3,4,4a,5,6,10b - *octahydro* - *benzo(f)quinoline* **15**. Procedure as for **16**, reaction time 70 hr, yield: 75%; m.p. (EtOH): 189–192°C; IR($CHCl_3$): 1720 (C=O); 1350, 1160 (SO_2) cm^{-1}; PMR $\delta(CDCl_3)$: 2·44 (s) $ArCH_3$; 3·1 (m) H_2 and H_{10b}; 3·74 (s) OCH_3; 4·45 (m) H_{4a}; 5·76 (q, X part = ABX, J_{AX} = 8·5, J_{BX} = 1·5 c/s) H_3; 7·35 (d) and 7·84 (d) tosyl; UV λ_{max}^{EtOH}: 229 (22,300); 263 (3,200 sh); 275 (3,000); 283 (2,400) nm. (Found: C, 52·4; H, 4·4; N, 2·9; S, 6·2; Cl, 21·2. Calc.: $C_{22}H_{22}O_4NSCl_3$ (502·85): C, 52·54; H, 4·41; N, 2·78; S, 6·37; Cl, 21·17%).

N - *Tosyl* - 1 - *oxo* - 3*β* - *trichloromethyl* - 8 - *methoxy* - 1,2,3,4,4a,5,6,10b - *octahydro* - *benzo(f)quinoline* **16**. A soln of **6** (0·12 mmol) and a few drops of 40% HBr/HOAc in 4 ml $CHCl_3$ was stirred for 20 hr and then repeatedly extracted with 2 N $NaHCO_3$, sat NaCl aq and dried. After evaporation of the solvent and trituration pure **16** was obtained, yield: 80%; m.p. (EtOH): 181–184°; IR ($CHCl_3$): 1720 (C=O); 1320, 1150 (SO_2) cm^{-1}; PMR ($CDCl_3$): 2·43 (s) $ArCH_3$; 3·2 (AB part of AB 2H) H_2; 3·73 (s) OCH_3; 3·98 (d, J = 12 c/s) H_{10b}; 4·3 (double triplet J = 12 and 3 c/s) H_{4a}; 5·60 (q, X part ABX, J_{AX} = 8·0, J_{BX} = 4·0 c/s) H_3; 7·31 (d, J = 8·5 c/s) H_{10}; 7·31 (d) and 7·88 (d) tosyl; UV λ_{max}^{EtOH}: 235 (15,400 sh); 264 (20,800) nm. (Found: C, 52·4; H, 4·3; N, 2·8; S, 6·3; Cl, 21·1. Calc.: $C_{22}H_{22}O_4NSCl_3$ (502·85): C, 52·54; H, 4·41; N, 2·78; S, 6·37; Cl, 21·17%).

N - *Tosyl* - 1 - (1' - *oxo* - 3' - *amino* - 4',4',4', - *trichloro)butyl* - 3,4 - *dihydroxy* - 6 - *methoxy* - *naphthalene* **17**. Compound **6** (0·17 mmol) was dissolved in a boiling mixture of 1·7 ml conc HCl and 17 ml EtOH in about 0·5 hr. The soln was refluxed for another 2·5 hr, poured in H_2O and extracted with $CHCl_3$. After work-up **17** was isolated, yield: 84%; m.p. (EtOH): 193–194°; IR($CHCl_3$): 3300 (NH); 1670 (C=C–C=O); 1340, 1160 (SO_2) cm^{-1}; PMR $\delta(CDCl_3)$: 2·32 (s) $ArCH_3$; 3·3 (AB-part of ABX-system, J_{AB} = 17, J_{AX} = J_{BX} = 5 c/s) CH_2; 3·79 (s) OCH_3; 4·95 (m) H_3; 5·71 (d, J = 10 c/s) NH; 7·22 (d) and 7·80 (d) tosyl; 7·44 (d) H_8, (J = 9·5 c/s); UV λ_{max}^{EtOH}: 220 (22,400), 279 (4,300), 302 (3,050 sh) nm. (Found: C, 52·6; H, 4·3; N, 2·19; S, 6·5; Cl, 21·4. Calc.: $C_{22}H_{22}O_4NSCl_3$ (502·85): C, 52·54; H, 4·41; N, 2·78; S, 6·37; Cl, 21·17%).

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