

REGIO- AND STEREOSELECTIVE ADDITION OF N-p-TOSYL-TRICHLOROMETHYLMINE TO VINYL DIHYDRONAPHTHALENES¹

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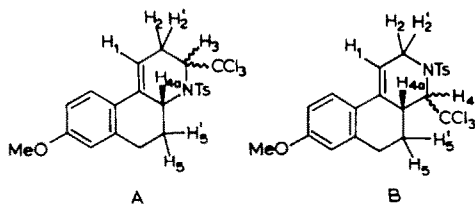
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Abstract—Imine 1 underwent regioselective addition to vinyl dihydronaphthalenes 2 and 3 to afford the cyclo-adducts 4, 5 and 6. The structures and stereochemistry of the latter adducts have been determined by PMR and X-ray analysis. Factors influencing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

In a preceding communication³ we described the cycloaddition of N-ethyloxycarbonylmethylene sulfonamide to vinyl dihydronaphthalene 2 and have shown the potential synthetic utility of such a heterocycloaddition.

In pursuing this investigation imine 1⁴ 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 inter alia the presence of olefinic (δ 5.96, H₁), CHCl₃ (δ 5.07, H₃) and CH-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 ($J_{4a,5} = 12.0$; $J_{4a,3} = 3.0$; $J_{2,4a} = 3.0$ Hz) which excludes the alternative structure B because the maximum possible number of couplings expected for the remaining CH-NTs proton is two ($J_{2,2'}$ and $J_{2,4a}$).

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 H₁ 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 H₃ 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 α -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 trichloromethyl substituent, (ii) an axial position for H_{4a}, (iii) a *cis*-relation for H₃ 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

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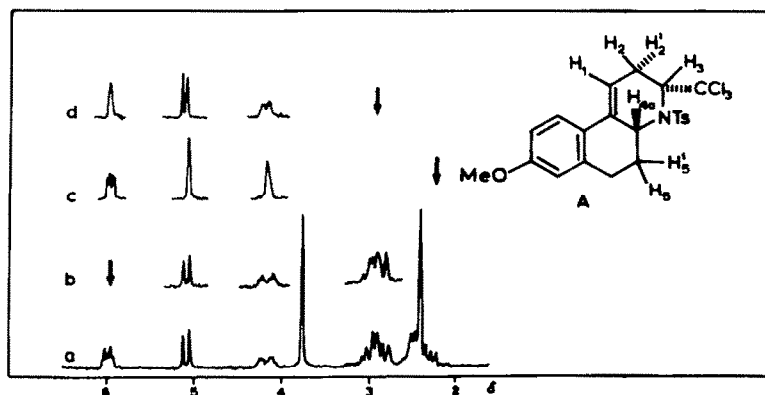


Fig. 1.

method of van der Meer⁶ 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.[‡]

The origin of the unique regioselectivity⁹ 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

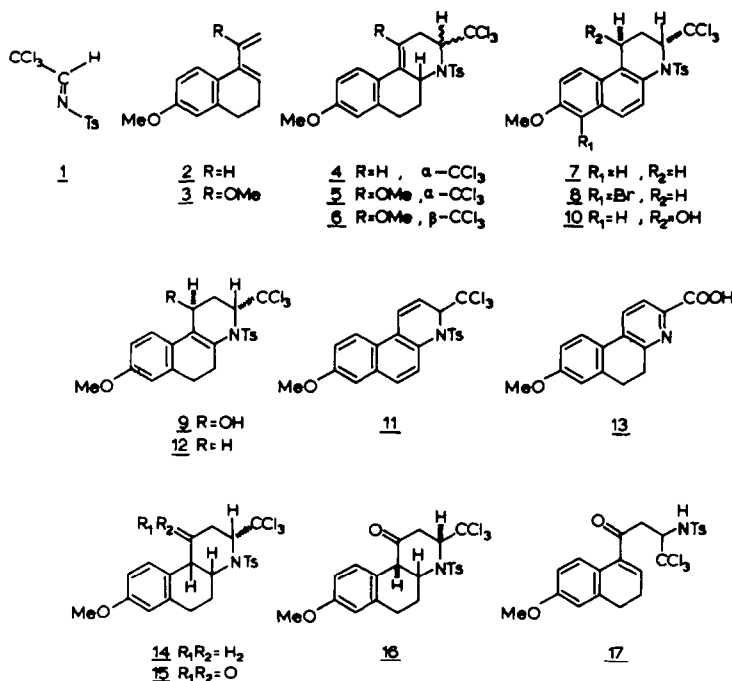
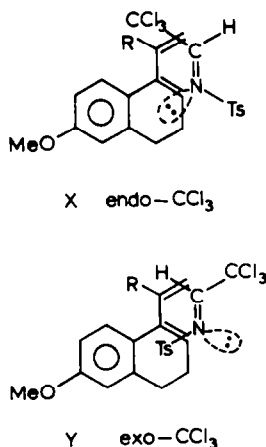


Table 1.^a

Compound	Fragment	$H^{\oplus}$	(M-Ts) [⊕]	(M- CCl_3) [⊕]	(M-Ts- CCl_3 -H) [⊕]
1		8	12	12	100
2		27	12	7	100
5		180	100	25	100

^a Relative intensities determined against (M-273)[⊕] = 100%.



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 $J_{2,3} + J_{7,8} = 16$ 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 heterocyclic 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_4 and C_1 atoms (Fig. 2). The drawing has been made according to the X-ray data.

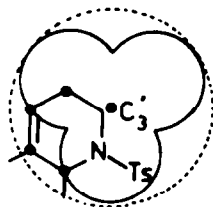


Fig. 2.

The formation of **10** can be explained in the following manner. While aromatization of ring B is known¹¹ 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 epoxide¹² 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 $\text{CH}_2\text{-CH}_2$ fragment also showed coupling constants $J_{1,2} + J_{1,2} = 9$ Hz and $J_{2,3} + J_{7,8} = 14.5$ Hz, thus exhibiting similar PMR characteristics as compared to **10** and also indicating a strong resemblance in conformation between **9** and **10**.

*In the model system i a value of 12.5 c/s was found for $J_{3,8}^{\text{trans}}$. $J_{3,8}^{\text{cis}}$ was estimated as 8.0 c/s according to the "Simeq" computer programme analysis developed by Dr. C. W. F. Kort of this laboratory.

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 $\text{C}_{4a}\text{-C}_{10b}$ 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 $\text{C}_1\text{-C}_{10b}$ double bond in **4** HBr-elimination occurs and under influence of the liberated acid partial isomerization of the $\text{C}_1\text{-C}_{10b}$ 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 $\text{C}_1\text{-X}$, $\text{C}_{10}\text{-H}$ 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 $\text{W}_{4a}^{1/2}$. From the spectrum of **15** the following parameters were obtained: $J_{4a,10b} = 8.5$ Hz, $\delta\text{H}_{10} = 6.74$ and $\text{W}_{4a}^{1/2} = 26$ Hz. The latter value is indicative for a *trans*-diaxial position for H_{4a} and one of the C_3 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 $\text{C}_{10b}\text{-C}_1\text{-C}_2$ 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

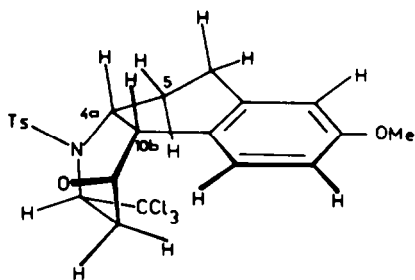


Fig. 3.

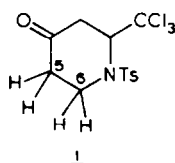


Fig. 4.

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 piperidone¹⁸ 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.p.s are uncorrected. Analyses were carried out by Messrs. H. Pieters of the Micro-analytical Department of this laboratory. IR-spectra were taken on a 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 Nazarov¹⁹ 2 was obtained in 78% yield; b.p.: 110–113°/0.1 mm $n_D^{20} = 1.591$.

N-Tosyl-3-trichloromethyl-8-methoxy-2,3,4,4a,5,6-hexahydrobenzo(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.: $C_{22}H_{20}O_4NSCl_3$ (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 Hajos¹⁹ 3 was obtained as an 80% pure oil.

N-Tosyl-1,8-dimethoxy-3-trichloromethyl-2,3,4,4a,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): 184–187.5°; 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.: $C_{22}H_{20}O_4NSCl_3$ (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_5 ; 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.: $C_{22}H_{20}O_4NSCl_3$ (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-tetrahydrobenzo(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-hexahydrobenzo(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 *p*-60–80/ $CHCl_3$ as an eluant. From the first fraction *N*-tosyl-3-trichloromethyl-8-methoxy-3,4-dihydrobenzo(f)quinoline 11 was isolated, yield: 20% m.p. ($CHCl_3/EtOH$): 188–190°; PMR δ (NC_3D_3): 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_5 ; 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.: $C_{22}H_{18}O_4NSCl_3$ (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-trichloromethyl-8-methoxy-1,2,3,4-tetrahydrobenzo(f)quinoline 7 was obtained in a nearly pure form; yield: 20%; m.p. 180–190°; PMR δ (NC_3D_3): 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_3D_3): 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.: $C_{22}H_{18}O_4NSCl_3Br$ (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 CCl₄ 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 $\lambda_{\text{max}}^{\text{EtOH}}$: 225 (27,000) and 293 (15,400) nm; PMR $\delta(\text{CDCl}_3)$: 240 (s) ArCH₃; 3.77 (s) OCH₃; 5.02 (t, J = 6.5 c/s) H₃; 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(CHCl₃): 1720 (C=O); 1350, 1160 (SO₂) cm⁻¹; PMR $\delta(\text{CDCl}_3)$: 2.44 (s) ArCH₃; 3.1 (m) H₂ and H_{10b}; 3.74 (s) OCH₃; 4.45 (m) H_{4a}; 5.76 (q, X part = ABX, J_{AX} = 8.5, J_{BX} = 1.5 c/s) H₃; 7.35 (d) and 7.84 (d) tosyl; UV $\lambda_{\text{max}}^{\text{EtOH}}$: 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.: C₂₂H₂₂O₄NSCl₃ (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 CHCl₃ was stirred for 20 hr and then repeatedly extracted with 2 N NaHCO₃, sat NaCl aq and dried. After evaporation of the solvent and trituration pure 16 was obtained, yield: 80%; m.p. (EtOH): 181–184°C; IR(CHCl₃): 1720 (C=O); 1320, 1150 (SO₂) cm⁻¹; PMR (CDCl₃): 2.43 (s) ArCH₃; 3.2 (AB part of AB 2H) H₂; 3.73 (s) OCH₃; 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) H₃; 7.31 (d, J = 8.5 c/s) H₁₀; 7.31 (d) and 7.88 (d) tosyl; UV $\lambda_{\text{max}}^{\text{EtOH}}$: 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.: C₂₂H₂₂O₄NSCl₃ (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 H₂O and extracted with CHCl₃. After work-up 17 was isolated, yield: 84%; m.p. (EtOH): 193–194°C; IR(CHCl₃): 3300 (NH); 1670 (C=C=O); 1340, 1160 (SO₂) cm⁻¹; PMR $\delta(\text{CDCl}_3)$: 2.32 (s) ArCH₃; 3.3 (AB-part of ABX-system, J_{AB} = 17, J_{AX} = J_{BX} = 5 c/s) CH₂; 3.79 (s) OCH₃; 4.95 (m) H₃; 5.71 (d, J = 10 c/s) NH; 7.22 (d) and 7.80 (d) tosyl; 7.44 (d) H₈, (J = 9.5 c/s); UV $\lambda_{\text{max}}^{\text{EtOH}}$: 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.: C₂₂H₂₂O₄NSCl₃ (502.85): C, 52.54; H, 4.41; N, 2.78; S, 6.37; Cl, 21.17%).

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