1.5 mmol) was nitrosated with $Na^{15}NO_2$ (300 mg, 4.3 mmol) in formic acid (10 mL) at 0 °C. After the usual workup, the nitrosourea (200 mg, 60%) was obtained: mp 86–87 °C; ^1H NMR ($CDCl_3$) 1.20–2.20 (m, 10 H, CH_2), 3.55 (td, CH_2Cl, $^2J_{^{15}N-H}$ = 1.6 Hz, NH exchangeable); mass spectrum, *m/e* (relative intensity; calcd value) 237.0845 (0.59; $C_9H_{16}{}^{37}Cl^{14}N^{15}N_2O_2$, 237.0842), 235.0870, (1.83; $C_9H_{16}{}^{35}Cl^{14}N^{15}N_2O_2$, 235.0870), 111.0034 (1.24; $C_2H_5{}^{37}Cl^{14}N^{15}NO$, 111.031), 109.0062 (3.82; $C_2H_5{}^{35}Cl^{14}N^{15}NO$, 109.0062), 83.0853 (100.00; C_6H_{11}, 83.0845).

1-(Fluoroethyl)-3-cyclohexyl-1-nitrosourea-*1*,*N*$_1$-$^{15}N_2$ (8a). Potassium cyanate (1.32 g, 15 mmol) was added to a solution of 2-fluoroethylamine-^{15}N hydrochloride [1.35 g, 15 mmol; which in turn was prepared by the procedure of Montgomery et al.[14] for the unlabeled compound from (2-fluoroethyl)phthalimide] in water (10 mL), and the solution was stirred for 6 h. The solid which precipitated (1.2 g, 67%) was collected after the reaction mixture was cooled.

To the above fluoroethylurea-*1*-^{15}N (1.20 g, 10 mmol) in formic acid (10 mL) was added solid sodium nitrite-^{15}N (1.5 g, 21 mmol) in portions at 0 °C, and the mixture was stirred for 1 h. The reaction mixture was stirred for an additional 30 min after slow addition of water (15 mL). The solid which precipitated was collected and crystallized (350 mg, 26%) from ether and petroleum ether, giving purified **8a**: mp 80 °C (for unlabeled, 81–83 °C); NMR ($CDCl_3$) 4.20 (dt, 2 H, CH_2CH_2F, $^2J_{H-F}$ = 24.0 Hz), 4.38 (dt, 2 H, CH_2CH_2F, $^1J_{H-F}$ = 48.8 Hz), 5.70 (br m, 1 H, NH, exchangeable), 5.90 (br m, 1 H, NH exchangeable); mass spectrum, *m/e* (relative intensity; calcd value) 137.0384 (3.61, M^+, $C_3H_6NO_2{}^{15}N_2F$), 137.0385), 94.0327 (100.00; $C_2H_5FO^{15}N_2$, 94.0327).

1,3-Bis(2-chloroethyl)-1-nitrosourea-2-^{13}C=*O*,^{15}N=*O* (1b). This compound was prepared by starting from $^{13}COCl_2$ and employing the procedures described for **13** or **1a** to afford 36% of 1,3-bis(2-chloroethyl)urea (**17**) which was subsequently nitrosated with $NaNO_2$ in HCOOH acid to give **1b** in 50% yield: mp 30 °C; mass spectrum, *m/e* (relative intensity; calcd value) 217.0004 (3.24 M^+; $C_4{}^{13}C_1H_9{}^{35}Cl^{37}ClN_2{}^{15}N_1O_2$, 217.0046), 215.0073 (3.79, M^+; $C_4{}^{13}C_1H_9{}^{35}Cl^{35}ClN_2{}^{15}N_1O_2$, 215.0075).

3-Cyclohexyl-1-(2-chloroethyl)-1-nitrosourea-2-^{13}C=*O*,^{15}N=*O* (2c). To a solution of cyclohexylamine (100 mg, 1 mmol) and triethylamine (1 mL excess) in water (20 mL) was added 1,3-bis(2-chloroethyl)-1-nitrosourea (**1b**; 100 mg, 0.46 mmol), and the reaction mixture was stirred for 4 h at ambient temperature. The solid which separated was collected to afford the urea **18**, 80 mg (86%). The above urea (80 mg) was nitrosated with $Na^{15}NO_2$ (150 mg, 2.17 mg) and after the usual workup afforded the nitrosourea **2c**: 50 mg (62%); pale yellow solid; mp 86 °C; mass spectrum, *m/e* (relative intensity; calcd value 237.0910 (1.87; $C_8{}^{13}C_1H_{16}{}^{37}Cl^{35}ClN_2{}^{15}N_1O_2$, 237.0905), 235.0935 (5.52, M^+; $C_8{}^{13}C_1H_{16}{}^{35}Cl_2N_2{}^{15}N_1O_2$, 235.0935).

^{18}O Exchange of the Carbonyl Oxygen of BCNU (1). A solution of 0.05 mmol of **1** in a mixture of 0.1 mL of acetonitrile and 0.9 mL of $H_2{}^{18}O$ (22% enrichment) with potassium phosphate buffer (pH 7.2) was sealed in a Reacti-vial for 12 h at 25 °C. The reaction mixture was extracted with ether (3 × 10 mL), the extract dried (Na_2SO_4), and the solvent removed. The residue was analyzed by mass spectrometry. The carbonyl oxygen containing fragment (*m/e* 56.0154, relative intensity 8.8, calcd for $C_2H_2NO^+$ *m/e* 56.0138) was compared with $C_2H_2N^{18}O$ (*m/e* 58.0) and found to be ca. 1% enriched in ^{18}O.

Note. All nitrosoureas should be handled with extreme care owing to their potential mutagenicity.

Acknowledgment. This investigation was supported by Grant 1-R01-CA21488-01 awarded by the National Cancer Institute, DHEW, and by a grant from the Provincial Cancer Hospitals Board. S.M.S.C. acknowledges the award of an Alberta Heritage Foundation for Medical Research Post-Doctoral Fellowship. We thank Dr. Tom Nakashima and Mr. Glen Bigam and their associates for extensive NMR measurements.

Registry No. **1**, 154-93-8; **1** (C=^{18}O), 79664-68-9; **1a**, 79664-69-0; **1b**, 79664-70-3; **2**, 13010-47-4; **2a**, 79664-71-4; **2b**, 79664-72-5; **2c**, 79664-73-6; **2d**, 79664-74-7; **3**, 33073-59-5; **4**, 54749-90-5; **5**, 60784-46-5; **6**, 2365-30-2; **7**, 13908-93-5; **7a**, 79664-75-8; **8**, 69112-98-7; **9**, 13908-91-3; **10**, 59960-30-4; **11**, 6296-45-3; **12**·HCl (X = Cl), 79664-76-9; **12**·HCl (X = F), 79664-77-0; **13**, 79664-78-1; **14**, 79664-79-2; **15**, 79664-80-5; **16** (R = H), 79664-81-6; **16** (R = C_6H_{11}), 79664-82-7; **17**, 79664-83-8; **18**, 79664-84-9; 2-chloroethylamine, 689-98-5; 2-fluoroethylamine, 406-34-8; (2-chloroethyl) isocyanate, 1943-83-5; cyclohexyl isocyanate, 3173-53-3; *trans*-4-methylcyclohexyl isocyanate, 32175-00-1; 2-deoxy-D-glucos-2-yl isocyanate, 79664-85-0; isocyanic acid, 75-13-8; (2-hydroxyethyl) isocyanate, 4747-84-6; (2-fluoroethyl) isocyanate, 505-12-4; ethyl (2-chloroethyl)carbamate, 6329-26-6; (2-bromoethyl)phthalimide-^{15}N, 58551-02-3; (2-fluoroethyl)phthalimide-^{15}N, 79680-95-8; aminoethanol-^{15}N·HCl, 58265-67-1; cyclohexylamine-^{15}N, 78441-12-0; aniline-^{15}N, 7022-92-6.

Supplementary Material Available: Figures 2–5 containing NMR spectra data for **1a**, **1b**, **2a**, and **6** (six pages). Ordering information is given on any current masthead page.

Benzo- and Indoloquinolizines. 21.[1] Allylic Strain Competition in 4b,5,6,7,8,8a,10,11,16,16b-Decahydrodibenz[*f*,*h*]indolo[2,3-*a*]quinolizine Isomers. Detection of Boat Conformers by Carbon-13 Nuclear Magnetic Resonance

D. Tourwé,* E. De Cock, and G. Van Binst

Vrije Universiteit Brussel, Laboratorium voor Organische Chemie, Pleinlaan 2, B-1050 Brussel, Belgium

Received August 1, 1980

The concept of allylic strain between the benzene or the indole ring and the benzylic carbon–carbon bond is used to explain the conformational equilibria in the 4b,5,6,7,8,8a,10,11,16,16b-decahydrodibenz[*f*,*h*]indolo[2,3-*a*]quinolizine isomers, in 5,6,8,9-tetrahydro-14b*H*-benz[*h*]indolo[2,3-*a*]quinolizine, and in their indole *N*-methyl analogues. The conformational changes were monitored by ^{13}C chemical shifts. Boat conformers with bowsprit–flagpole interactions between γ-positions show upfield shifts, whereas these are not observed for δ-interacting groups.

Comparison of the ^{13}C NMR spectra of the *rel*-(4bβ,8aα,16bβ)-**1a** and the *rel*-(4bα,8aβ,16bβ)-**2a** isomers has indicated the cis-cisoid-trans conformation[2] **4a** for the latter (Chart I).[4] The *trans*-quinolizidine conformation **5a** was excluded because of the very similar chemical shifts

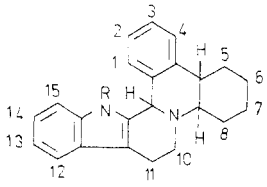
(1) Part 20: F. Vlaeminck, E. De Cock, D. Tourwé, and G. Van Binst, *Heterocycles*, **15**, 1213 (1981).

(2) For a discussion of the conformational equilibria in these compounds, see ref 3.

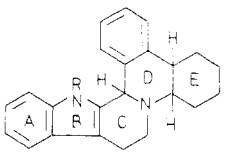
(3) G. Van Binst and D. Tourwé, *Org. Magn. Reson.*, 6, 590 (1974).

0022-3263/81/1946-5321$01.25/0

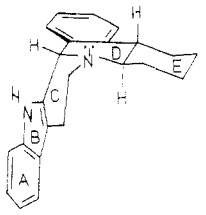
Chart I[a]



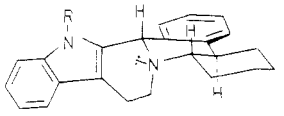
1 rel-(4bS,8aα,16bβ)
1a R=H
1b R=CH_3



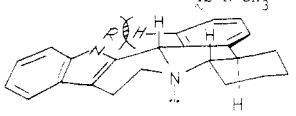
2 rel-(4bα,8aS,16bβ)
2a R=H
2b R=CH_3



3 rel-(4bβ,8aα,16bS)
cis-transoid-trans conformation
3a R=H
3b R=CH_3



4 rel-(4bα,8aβ,16bS)
cis-cisoid-trans conformation
4a R=H
4b R=CH_3

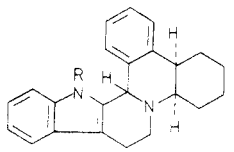


5 rel-(4bα,8aβ,16bβ)
trans-transoid-trans conformation 5a R=H
5b R=CH_3

[a] Cis relates to the C/D ringfusion, transoid relates to the lone pair-H8a orientation, and trans to the D/E ringfusion.

of the N_{16}–H (**2a**) and the N_{16}–CH_3 (**2b**) compounds. In the latter, the strong steric interaction between the C_1 H and the N_{16} CH_3 precludes a trans C/D ring junction, **5b**. It was anticipated that N_{16}-methylation of **1a** and **2a** would not influence the *cis*-quinolizidine conformations **3** and **4**.

We now report the results of a ^{13}C study of the N_{16}-methyl-*rel*-(4bβ,8aα,16bβ)-**1b** and the *rel*-(4bα,8aα,16bβ)-**6b** isomers, as well as of **8a** and its *N*-methyl derivative **8b** (Chart II).



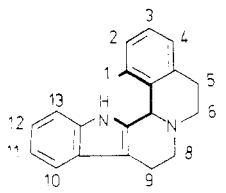
rel-(4bS,8aα,16bS) 6a R=H
6b R=CH_3

Results and Discussion

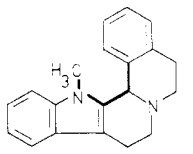
The ^{13}C spectrum of the N_{16}-methyl-*rel*-(4bα,8aβ,16bβ) isomer **2b** is identical within 0.8 ppm (except for C16b which experiences a γ shift)[4] with that of its unmethylated analogue **2a**, proving that both compounds have the same *cis*-quinolizidine conformation (**4a** and **4b**, Chart I).

Unexpectedly, N-methylation of **1a**, which also has a cis C/D ring junction (see **3a**),[3,4] completely changes the chemical shifts. The shift of 22.8 ppm for C_{11} is characteristic of an unhindered position, thus excluding conformation **3b**. The upfield shifts of C_{4b} (2.9 ppm) and C_{16b} (5.0 ppm) can be interpreted as due to the bowsprit–

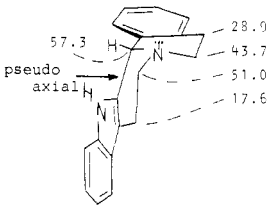
Chart II



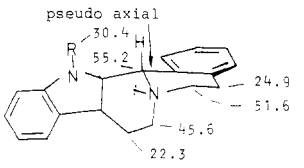
8a



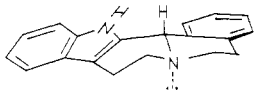
8b



cis_1 conformation 9a
(δ for R=H)

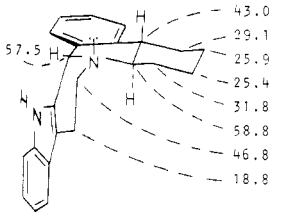


cis_2 conformation 9b
(δfor R= CH_3)

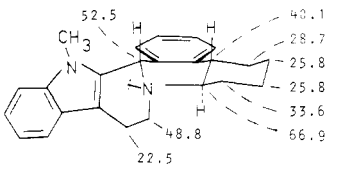


trans conformation 9c

flagpole interaction in a boat conformation[7] of the D-ring compound **7**. This conformation also explains the



1a rel-(4bS,8aα,16bS)
cis-transoid-trans conformation 3a
($N-CH_3$: conformation 3b)



1b rel-(4bS,8aα,16bβ)
cis-transoid-trans (ring D-boat) conformation 7

downfield shifts of C_8 (2.6 ppm) and C_{8a} (8.1 ppm), which no longer have γ interactions with C_{10} and C_{11}, respectively.

Thus, methylation of the N_{16} indole nitrogen has different conformational consequences for **3a** and **4a**. The reason for this difference is that although both **3a** and **4a** have cis C/D ring junctions, they are of different types. This distinction is shown in 5,6,8,8a-tetrahydro-14b*H*-benz[*h*]indolo[2,3-*a*]quinolizine **8** (Chart II), for which the three conformations **9a–c** are possible. The chemical shifts of C_5 and C_9 exclude the trans conformation **9c**[5,6,9,10] but indicate the cis_1 conformation **9a** for the unmethylated compound **8a** and the cis_2 conformation **9b** for its methylated derivative **8b**. Dreiding models do not indicate any difference in steric interaction between the group at N_{16} and the hydrogen at C_1 for both cis conformers. The different conformations must therefore be explained by the allylic strain[11] between the aromatic rings and the benzylic carbon–carbon bond, which forces the group attached to it into a pseudoaxial position.

(4) G. Van Binst, D. Tourwé, and E. De Cock, *Org. Magn. Reson.*, 8, 618 (1976).

(5) E. Wenkert, H. P. S. Chawla, C.-J. Chang, D. W. Cochran, E. W. Hagaman, J. C. King, and K. Orito, *J. Am. Chem. Soc.*, **98**, 3645 (1976).
(6) M. Lounasmaa and M. Hämeilä, *Tetrahedron*, **34**, 437 (1978).
(7) As for cyclohexene, the name boat is used instead of half-boat.[8]
(8) R. Bucourt, *Top. Stereochem.*, 8 (1974).
(9) D. Tourwé and G. Van Binst, *Heterocycles*, **9**, 507 (1978).
(10) M. Sugiura, N. Takao, K. Iwasa, and Y. Sasaki, *Chem. Pharm. Bull.*, **26**, 1168, 1901 (1978).
(11) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5492, 5493 (1965); F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

Table I. 270-MHz ^{1}H NMR Parameters of the C_{10}-C_{11} Fragment

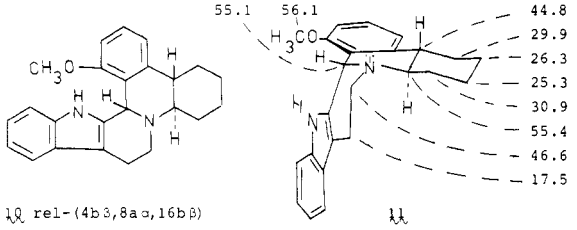
parameter[b]	compd 11	1a[a]	6a[a]
$\delta(H_{10}$-eq)	3.80	3.48	3.67
$\delta(H_{10}$-ax)	3.30	3.15	3.33
$\delta(H_{11}$-ax)	2.97	2.88	2.96
$\delta(H_{11}$-eq)	2.59	2.70	2.64
$\delta(H_{16b})$	5.65	5.30	5.25
$^2J(10)$	−14.1	−13.5	−14.3
^3J(10-eq,11-ax)	5.3	5.3	4.9
^3J(10-eq,11-eq)	0	3.5	~1
^3J(10-ax,11-ax)	12.2	9.5	11.9
^3J(10-ax,11-eq)	4.9	5.2	5.1
$^2J(11)$	−16.0	−15.7	−16.6
^5J(11-ax,16b)	2.5	~2.4	2.4
^5J(11-eq,16b)	2.2	~2.0	2.0

[a] Values from ref 3. [b] Chemical shifts are given in δ units and J values in hertz.

In compounds **8** there is competition between the allylic strains imposed by the benzene and the indole rings. In **8a** the benzene ring induces the strongest interaction (heavy lines in **8a**) and forces the C_{14b} indole bond into the pseudoaxial position. The introduction of the more bulky methyl group on methylation of the N_{16} indole nitrogen reverses the situation (heavy lines in **8b**), leading to the cis_2 conformation **9b**.

Analogously, the cis_1 conformation of **3a** changes to cis_2 conformation **7** on N-methylation, while the cis_2 conformation of **4a** is not affected. The trans-fused E ring in **1b** does not allow a further ring inversion of the D ring during this process but keeps ring D in a boat conformation.

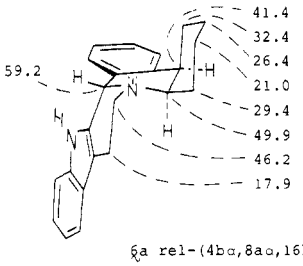
Additional evidence for the allylic strain competition between the indole and benzene rings is provided by the 1-methoxy derivative **10**. The ^{13}C chemical shifts of C_{8a}



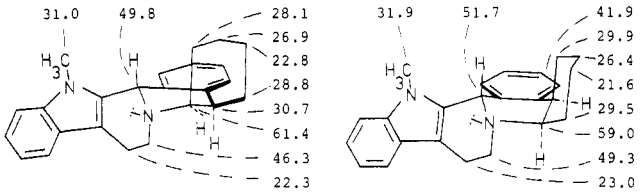
10 rel-(4bβ,8aα,16bβ) 11 cis-transoid-trans conformation

and C_{16b} confirm a cis_1 conformation, **11**, indicating that the type of cis conformation is not controlled by steric interaction between the substituents at C_1 and N_{16}.

Comparison of the ^{13}C chemical shifts of **3a** and **11** indicates that the former is not conformationally homogeneous and apparently contains some isomer with D-ring boat conformation **7**. Taking the chemical shifts of C_{4b} and C_{8a} in **7** (N_{16}–CH_3) and in **11** as representative for those in conformations **7** (N_{16}–H) and **3a**, respectively, the conformational equilibrium in **1a** can be calculated. This indicates the presence of about 30% of the D–boat form. This value for the equilibrium could not be confirmed by a low-temperature spectrum because of the limited solubility of **1a**. However, the vicinal coupling constants of the C_{10} and C_{11} methylene hydrogens, which were obtained from the 270-MHz proton spectra, also show averaged values for **1a**, whereas those obtained for **11** correspond closely to those of the *rel*-(4bα,8aα,16bβ) isomer **6a** (Table I). The latter compound also has a cis_1-type conformation, **12**,[3,4] and a conformational change can therefore be expected on N-methylation. The ^{13}C spectrum of the methyl derivative **6b** at −100 °C shows two sets of signals as shown in **13** and **14** that correlate with each other to give the observed averaged room-temperature spectrum. Both **13**



6a rel-(4bα,8aα,16bβ)
cis-transoid-cis conformation 12



cis-transoid-cis conformation 13 70 % — 100°C — cis-transoid-cis (ring-D boat) conformation 14 30 %

6b rel-(4bα,8aα,16bβ)

and **14** have a cis_2 conformation. A double ring inversion of the D and E rings and an inversion at nitrogen converts **13** into **14**, which also has a boat-form D ring. The driving force for the inversions is relief of the allylic interaction between bonds indicated in heavy lines in **13**.

Conclusion

The concept of allylic interaction with aromatic rings can explain the preferred conformations in these compounds. The stronger interaction of a benzene ring compared with that of an indole ring can have conformational consequences in alkaloids that contain a benzo- or an indoloquinolizidine segment. Allylic strain can be relieved by formation of boat conformers. An example of such strain relief is found in the 8-azaestrone isomers studied by Brown.[12]

^{13}C NMR is a useful method for detecting conformational changes in multiring compounds; the ^{1}H NMR spectra of the *N*-methyl derivatives reported in this paper could not be analyzed, even at 270 MHz.

Experimental Section

The natural-abundance ^{13}C NMR spectra were obtained by using Bruker HX-270 (67.9 MHz) and WH-90 (22.6 MHz) spectrometers, equipped with a Nicolet 1080 and a BNC 12 computer, respectively. The sample concentration was 100–200 mg in 1.3 mL of $CDCl_3$. The low-temperature spectra of **6b** were run in CS_2 with 10% internal acetone-d_6. Chemical shift differences between both solvents did not exceed 0.5 ppm. The temperature was controlled with a Bruker B-ST100/700 temperature-control unit. Signal multiplicity was determined on gated decoupled spectra. The C-16b signal was assigned by selective ^{1}H decoupling. The assignment of the remaining signals was done by comparison with spectra of 1,2,3,4,4a,5,6,10b-octahydro-6-phenylphenanthridines as described in previous papers.[4,13]

***trans*-2-(3-Methoxyphenyl)cyclohexylamine (15)** was obtained by reduction of *trans*-1-(3-methoxyphenyl)-2-nitrocyclohexane[14] with Fe/CH_3COOH according to the procedure of Cochran.[15] After distillation at 96 °C (0.05 torr) a yield of 64% was obtained. The oil can be crystallized from *n*-hexane; mp 41.5–42 °C. The hydrochloride was recrystallized from 2-propanol; mp 203–203.5 °C (lit.[14] mp 202–203 °C).

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***trans*-1-(Formylamino)-2-(3-methoxyphenyl)cyclohexane (16)** was obtained by refluxing **15** in ethylformate during 18 h.[16] After distillation at 164–166 °C (0.04 torr), a light yellow oil is obtained in 95% yield: IR (NaCl, film) 3270 (NH), 1660 (CO); NMR ($CDCl_3$) shows *Z* (77%) and *E* (23%) rotamers about the amide bond, δ 7.85 (CHO (*Z*), d, J_{NH-CHO} = 0.9 Hz), 7.59 (CHO (*E*), d, J_{NH-CHO} = 11.7 Hz); mass spectrum *m/z* (relative intensity) 233 (2, $M^{+\cdot}$), 188 (100).

7-Methoxy-*trans*-1,2,3,4,4a,10b-hexahydrophenanthridine (17) was obtained as byproduct in the synthesis of the 9-methoxy isomer **18**. A 10.5-g sample of **16** was heated with 105 g of polyphosphoric acid at 115 °C for 5 h. After cooling, the reaction mixture was poured into 400 mL of ice–water and carefully made basic with NaOH. After extraction with ether, drying over $MgSO_4$ and evaporation of the solvent, the residue was distilled at 117.5 °C (0.04 torr). The ^1H NMR spectrum of the colorless oil indicates a mixture of 7-methoxy (15%) and 9-methoxy (85%) derivatives (H_6 integration). By column chromatography on alumina (Merck Co., activity II–III) with petroleum ether–ether (90/10) elution, both compounds can be separated. One obtains 0.75 g of **17** and 6.18 g of **18**.

17: mp 100–101 °C; IR (KBr) 1615 (C=N); mass spectrum, *m/z* (relative intensity) 215 (91, $M^{+\cdot}$, $C_{14}H_{17}NO$), 186 (100, $C_{12}H_{12}NO$); NMR δ 8.70 (H_6, d, *J* = 3.1 Hz), 7.32–6.79 (3 H_{arom}), 3.86 (OCH_3), 2.84 (H_{4a}), 2.43–1.28 (H_{alif}).

18: mp ($HClO_4$) 184–185 °C; IR (KBr) 1625 (C=N); mass spectrum, *m/z* (relative intensity) 215 (100, $C_{14}H_{17}NO$), 186 (99, $C_{12}H_{12}NO$); NMR δ 8.22 (H_6, d, *J* = 3.1 Hz), 7.22–6.77 (3 H_{arom}), 3,84 (OCH_3), 2.88 (H_{4a}), 2.41–1.25 (H_{alif}).

Indole N-Methylation. The procedure of Morrison[17] was followed on 100-mg samples of the parent compounds.[3,16,18,19] The compounds were purified by column chromatography on alumina with ether elution; yield 80–85%. After crystallization from ethanol the following compounds were obtained: **1b**, mp 186–187 °C. Anal. Calcd for $C_{24}H_{26}N_2$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.10; H, 7.53; N, 8.26. **6b**, mp 158–158.9 °C. Found: C, 84.30; H, 7.55; N, 8.29. **8b**, mp 182–184 °C. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72. Found: C, 83.12; H, 7.05; N, 9.90.

4b,5,6,7,8,8a,10,11,16,16b-Decahydro-1-methoxydibenz[*f*,*h*]indolo[2,3-*a*]quinolizine (10). Tryptophyl bromide (210 mg) and **17** (215 mg) were heated for 4 h at 100–120 °C. Glacial acetic acid (10 mL) was added, and the solution was refluxed overnight. The precipitated hydrobromide salt was filtered, and the free base was liberated with dilute NaOH. Crystallization from ethanol gave 57% of **10**: mp 175–175.5 °C; mass spectrum, *m/z* (relative intensity) 358 (100, $C_{24}H_{26}N_2O$). Anal. Calcd for $C_{24}H_{26}NO$: C, 80.45; H, 7.26; N, 7.82. Found: C, 80.32; H, 7.15; N, 8.01.

Registry No. 1b, 79549-36-3; **6b**, 79549-37-4; **8b**, 79517-39-8; **10**, 79517-40-1; **15**, 32948-96-2; **15**·HCl, 32928-84-0; **16**, 79517-41-2; **17**, 79517-42-3; **18**, 79517-43-4; *trans*-1-(3-methoxyphenyl)-2-nitrocyclohexane, 32928-86-2; tryptophyl bromide, 3389-21-7.

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Photochemistry of Vinyl Halides. Formation of Benzofurans by Photolysis of β-(*o*-Methoxyphenyl)vinyl Bromides

Tatsuo Suzuki, Tsugio Kitamura, Taka-aki Sonoda, Shinjiro Kobayashi, and Hiroshi Taniguchi*

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

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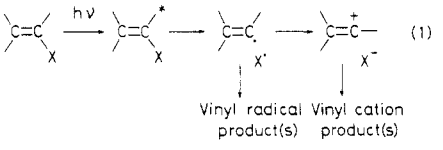
Photolysis of β,β-bis(*o*-methoxyphenyl)-substituted vinyl bromides gave benzofuran derivatives which are derived from an intramolecular nucleophilic attack of the methoxyl group on an intermediate vinyl cation. With α-aryl-substituted vinyl bromides, only one type of benzofuran derivative was detected. However, when the α substituent was a hydrogen or a methyl group, two isomeric benzofurans were formed, one via the unrearranged vinyl cation and the other via an (*o*-methoxyphenyl)-rearranged vinyl cation. Irradiation of α-methyl-β,β-bis(*o*-methoxyphenyl)vinyl bromide in nucleophilic solvent, i.e., methanol, did not result in solvent-incorporated products. In the photolysis of β-(*o*-methoxyphenyl)-substituted vinyl bromides a selectivity–reactivity relationship between the cyclization and the rearrangement of the intially formed vinyl cation was observed.

It is well-known that irradiation of vinyl halides gives products derived from vinyl radicals as the reactive intermediates.[1] However, it was recently found that an ionic itermediate, i.e., a vinyl cation, was also generated in the course of the photolysis of vinyl halides.

We reported that in the photolysis of 1,1-diaryl-2-haloethylenes[2] and 1,1-diaryl-2-halopropenes[3] the corresponding vinyl cations were generated by an internal electron transfer in the vinyl radical pairs which were initially formed by homolytic fission of the carbon–halogen bond (eq 1). McNeely and Kropp reported that solvent-incorporated products were obtained in the photolysis of alicyclic vinyl halides and suggested that vinyl cations



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which were formed by an electron transfer were the product-forming intermediates.[4] Likewise, Sket and Zupan also suggested that the photolysis of 1,1-diphenyl-2-haloethylenes gave diphenylacetylene via a vinyl cation.[5]

Solvolytically generated vinyl cations have been extensively studied since 1964.[6] In this field, we reported that the solvolysis of α-aryl-β,β-bis(*o*-methoxyphenyl)vinyl halides gave two isomeric benzofuran derivatives (eq 2).[7]

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