100. The Double *Bamford-Stevens* Reaction with Tricyclo [5.1.0.0^{3,5}] octane-2,6-dione (Bis-homo-*p*-quinone[1]). Synthesis and Reactions of 4,5-Dihydro-4,5-methano-1,7-diaza-7a*H*-indene (4,5-Homo-1,7a-diaza-indene)[2]

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Zusammenfassung. Alkalische Zersetzung der bis-*p*-Toluol-sulfonylhydrazone **3** und **4** von sowohl *anti*- (**1**) wie auch *syn*-Bis-homo-*p*-chinon (**2**) ergab 4,5-Homo-1,7-diaza-inden (**5**). Das Produkt hat Eigenschaften eines Pyrazols und eines Olefins. Durch katalytische Reduktion entstand 6,7-Dihydro-4,5-homo-1,7-diaza-inden (**12**) und bei der Bromierung in Äthanol 3,6α-Dibrom-7β-äthoxy-4,5-homo-1,7a-diaza-inden (**11**). Spektroskopische Daten gaben Aufschluss über die Konstitutionen von **5**, **11** und **12**, über die bevorzugte Konformation von **11** und **12**, und über die Konfiguration von **11**.

Die Umwandlung von **3** oder **4** zu **5** beinhaltet eine weitgehende Umlagerung des Ringskeletts, welche möglicherweise über das Diazo-carben **15** mit nachfolgender Fragmentierung des Cyclopropanringes zu einem Acetylen-olefin, anschliessender Cyclisierung zu einem Pyrazolring und schliesslich intramolekularer Anlagerung eines Pyrazolstickstoffatoms an die Dreifachbindung verläuft.

1. Introduction and Reaction. – Alkaline thermal decomposition of *p*-toluenesulfonyl-hydrazones (*Bamford-Stevens* reaction [1]) in aprotic solvents usually first produce diazo-compounds [2], which are converted either to nitrogen-containing heterocycles [3] or *via* carbenes to rearranged [4] or fragmented [5] products. In the present paper we describe the *Bamford-Stevens* reaction with the bis-*p*-toluenesulfonyl-hydrazones (**3** and **4**) of the recently synthesised [6] bis-homo-*p*-quinones (**1** and **2**)[4]), in which both types of behaviour are observed in the same reaction.

The bis-*p*-toluenesulfonyl-hydrazone of *anti*-bis-homo-*p*-quinone (**3**) was subjected to thermolytic decomposition with sodium hydride or methoxide in diglyme at about 190°, to yield 60% of only one product as a colourless oil which solidified at –20°. The corresponding reaction with the *syn*-bis-homo-*p*-quinone-bis-*p*-toluenesulfonyl-

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[1]) The prefix «homo-» before a trivial name signifies in general that the system (chain or ring) has been enlarged by one carbon member. The special case of double bond to cyclopropane modification has received individual attention in connection with *Winstein*'s homoconjugation concept. For brevity's sake we call in the following text compounds (**1**) and (**2**) *anti*- and *syn*-bis-homo-*p*-quinone.

[2]) For brevity's sake we call compounds in this series homo-diaza-indenes. Other names of **5**, in accord with the IUPAC-rules of nomenclature would be 7,8-dihydro-7,8-methano-pyrazolo [2,3a] pyridine or 1,10-diaza-tricyclo[5.3.0.0^{4,6}]deca-2,7,9-triene.

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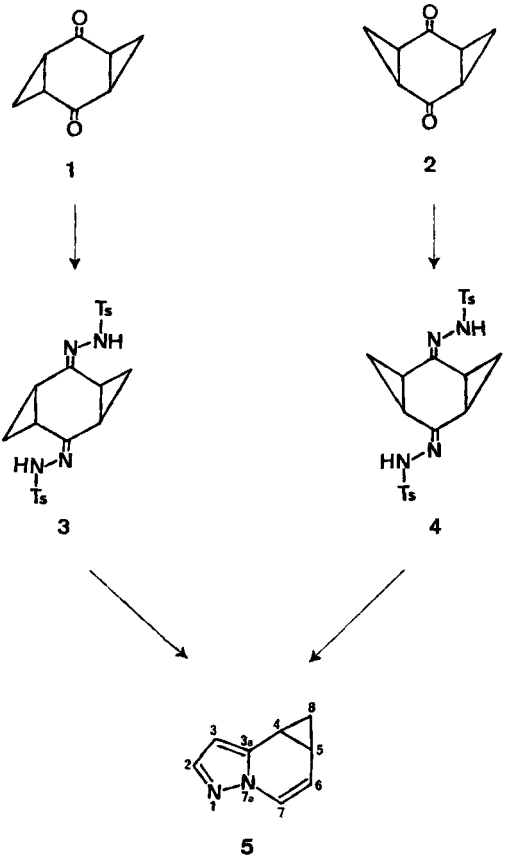
[4]) In the course of this work it was found that the cyclisation of *cis,trans,cis*-2,4,6,8-tetrabromocyclooctane-1,5-dione to *anti*-1,3-dibromo-bis-homo-*p*-quinone could also be performed by dehydrobromination with 1,4-diaza-bicyclo[2.2.2]octane (92% yield) and with 1,5-diaza-bicyclo[4.3.0]nona-5-ene (60% yield). These reactions are described in the Expt. Part.

hydrazone (**4**) gave the same product in 40% yield. Its structure was deduced as 4,5-homo-1,7a-diaza-indene (**5**) by spectral analysis and confirmed by bromination and hydrogenation. Since the formation of **5** from **3** and **4** involves skeletal rearrangements, which are not immediately transparent, we present the derivation of the structure and the reaction products of **5** in some detail.

2. Structure of 4,5-homo-1,7a-diaza-indene (5). – Elemental analysis and the mass spectrum (M^+ = base peak = 132 *m/e*) indicate a molecular formula of $C_8H_8N_2$. The IR. spectrum suggests the presence of cyclopropane-C–H (3010 cm^{-1}), C=C (1655 cm^{-1}, see also later) and C=N (1560 cm^{-1}) groupings.



The high field signal group (above 3 ppm) of the ^{1}H-NMR. spectrum can be interpreted as belonging to a four proton coupling system, with three of these protons (δ = 2.46, 1.49 and 0.06 ppm) possessing just the expected three couplings and one of them (δ = 1.88 ppm) being involved, in addition, in one extra-system coupling (see below). The coupling constants show that this four-proton signal group is typical for a 1,2-*cis*-disubstituted cyclopropane [7], namely one *geminal* coupling of 4 Hz, two *trans* couplings of 5 Hz and three *cis* couplings of 8–9 Hz.

The chemical shifts, assigned on the basis of these coupling constants are in agreement with the magnetic shielding effects expected for the indicated partial structure (compare Fig. 1) as follows: The signal with the unusually high δ-value (0.06 ppm) is the one which shows a *geminal* and two *trans* couplings. It is, therefore, assigned to the single hydrogen on the 'inside' of the cyclopropane ring (*endo*-H–C(8)),

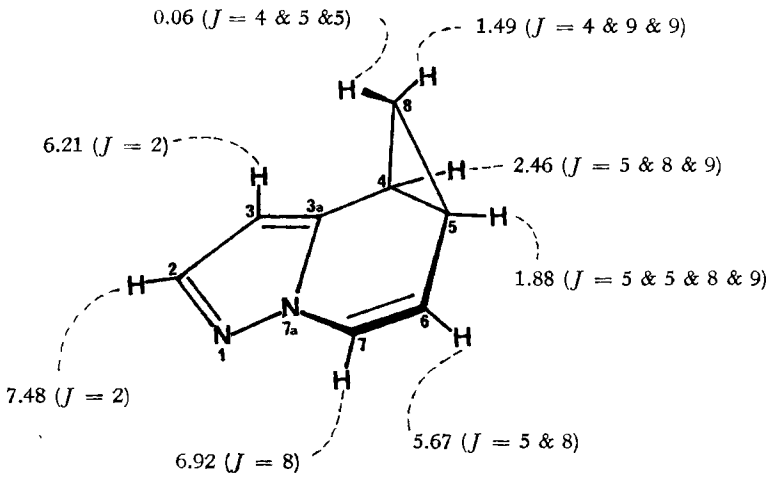


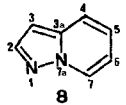
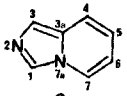
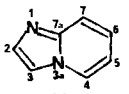
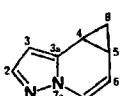
Fig. 1. *Chemical shifts* (in ppm, TMS = 0) *and coupling constants* (in Hz) *of the* ^{1}*H-NMR.-spectrum of 4,5-homo-1,7a-diaza-indene* (**5**)

which sits directly above the rest of the molecule. The other signal with the *geminal* coupling (δ = 1.49 ppm) clearly belongs to *exo*-H–C(8). The remaining two signals of the four proton coupling system must be assigned to two hydrogens on the 'outside' of the cyclopropane ring, since each of them takes part in one *trans* and two *cis* couplings; the one at lower field (δ = 2.46 ppm) is considered to be due to H–C(4), which sits in a benzyl-type position (α- to pyrazole, see below) and the one at higher field (δ = 1.88 ppm, with the extra-system coupling mentioned above) is attributed to H–C(5).

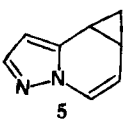
This extra-system coupling of 5 Hz shows that H–C(5) has a *vicinal* neighbour, H–C(6), to which the signal with J = 5 Hz (δ = 5.67 ppm) must be assigned. The second coupling (J = 8 Hz) in this latter signal reveals that H–C(6) has another *vicinal* neighbour, namely H–C(7) with δ = 6.92 ppm (J = 8 Hz). The chemical shifts (δ = 5.67 and 6.92 ppm) and the coupling (J = 8 Hz) of H–C(6) and H–C(7) identify them as *cis* disposed vinyl hydrogens; the very low value of H–C(7) (δ = 6.92 ppm) shows that it can hardly be *geminal* to carbon (the lowest value calculated according to [8] would be *geminal* to phenyl: δ = 6.33 ppm) so that C(7) must be bound to a nitrogen atom (N(7a)).

The above arguments establish a partial structure which include positions 4,5, 6,7,7a and 8 of formula **5**. There remain 3 carbon, 1 nitrogen and 2 hydrogen atoms to be placed, which can be reconciled with further spectral properties only by including these atoms along with C(3a) and N(7a) in a pyrazole nucleus. The UV. maximum at 255 nm (ε = 8740) agrees with a pyrazole structure involved in further

Table 1. *Comparable ^{1}H-NMR. signals due to the pyrazole hydrogens and ^{13}C-NMR. signals due to the five- and six-membered ring carbons of 1,7a-(**8**), 2,7a-(**9**) diaza-7aH-indene and 1,3a-diaza-3aH-indene (**10**) and 4,5-homo-1,7a-diaza-indene (**5**)*

	^{1}H-NMR.		**^{13}C-NMR.** (ppm)							
			Ring-position							
	Assignment and chemical shift (ppm)	J value (Hz)	1	2	3	3a	6	7	7a	Lit.
 **8**	H–C(2) $\delta = 7.80$ H–C(3) $\delta = 6.38$	$J_{2,3} = 2.18$	N	141.29	96.25	139.5	110.83	128.08	N	[10–12]
 **9**	H–C(1) $\delta = 7.93$ H–C(3) $\delta = 7.27$	$J_{1,3} = 0$	128.36	N	119.94	130.64	112.65	122.81	N	[10] [11]
 **10**	H–C(2) $\delta = 7.48$ H–C(3) $\delta = 7.48$	–	N	134.05	113.41	N	112.19	126.96	145.60	[10] [11]
 **5**	H–C(2) $\delta = 7.48$ H–C(3) $\delta = 6.21$	$J_{2,3} = 2$	N	140.0	103.4	136.8	111.2	123.5	N	

conjugation [9] (compare with the hydrogenation product below) and the IR. band at 1560 cm^{-1} is also characteristically found [9] in pyrazoles.



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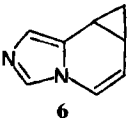

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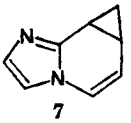

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The three possible ways to construct a pyrazole nucleus lead to structures **5**, **6** and **7**. In Table 1, our product is compared with the three corresponding diaza-indenes **8**, **9** and **10**. The large difference in chemical shifts ($\Delta\delta$ = 1.27 ppm) of the two pyrazole hydrogens (δ = 6.21 and 7.48 ppm) shows that only one of them is *geminal* to nitrogen. This excludes structures **6** and **7**, as can be verified by comparisons of the corresponding signals in **8**, **9** and **10**, shown on the left part of Table 1. Only 1,7a-diaza-7a*H*-indene (**8**) has a similar $\Delta\delta$-value (1.42 ppm) and a similar coupling constant (J = ~2 Hz) between the two pyrazole hydrogens as our product, to which, therefore, structure **5** must be assigned.

This structure (**5**) receives strong confirmation from the ^{13}C-NMR. spectra: The chemical shifts (in ppm) and the multiplicities permit the following assignments (compare Fig. 2). The 3 signals in the low field group (δ = 140.0/*d*, 136.8/*s* and 123.5/*d*) correspond to the three triligant carbons attached to one nitrogen [13] (C(2), C(3a) and C(7)), the first and the third with one hydrogen and the second with none. The weak intensity of the 136.8 ppm signal is due to the long relaxation time of C(3a) which carries no hydrogen. The two signals in the middle field group (δ = 111.2/*d* and 103.4/*d*) correspond to the two triligant carbons (C(6) and C(3)), both carrying one hydrogen, and the three signals in the high field group (δ = 13.85/*d*, 13.05/*d* and 9.76/*q*) correspond to the three quadriligant carbons (C(4), C(5) and C(8)) in the cyclopropane ring [13], the first two being associated with one hydrogen and the third with two strongly non-equivalent ($\Delta\delta$ = 1.43 ppm) hydrogens.

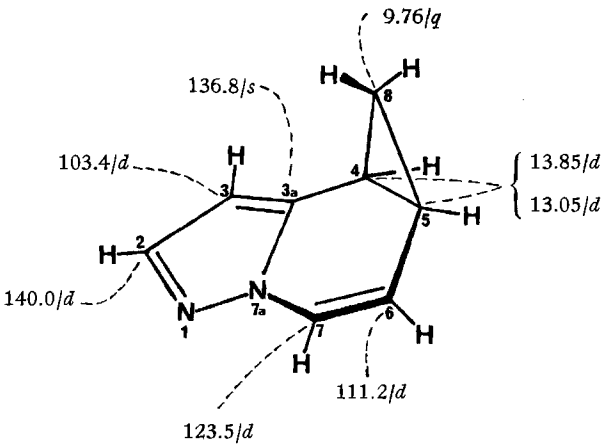


Fig. 2. *Chemical shifts* (in ppm, TMS = 0) *and multiplicities due to proton coupling of the* ^{13}*C-NMR. spectrum of 4,5-homo-1,7a-diaza-indene* (**5**)

On the right part of Table 1 the chemical shifts of the ^{13}C-NMR. signals due to the different carbons according to our assignment in structure **5** are compared with known [11] signals of 1,7a- (**8**), 2,7a-(**9**) diaza-7a*H*-indene and 1,3a-diaza-3a*H*-indene (**10**). Here, again, the best agreement is with the 1,7a-diaza-structure **8**.

3. Reaction products. – With $HClO_4$, 4,5-homo-1,7a-diaza-indene (**5**) formed a perchlorate which, although not purified, manifested itself through its chromatography- and solubility-behaviour, an IR. band (film) at 3150 cm^{-1} (N^+–H) and its NMR.-spectrum in deuterioacetone with the same signal and coupling pattern as the free base but with all the signals shifted downfield by 0.3 to 0.9 ppm.

With bromine in ethanol, 4,5-homo-1,7a-diaza-indene (**5**) yielded 45% of a viscous product (**11**), b.p. 82–85°/0.02 Torr, which was shown to be $C_{10}H_{12}Br_2N_2O$ by elemental analysis and mass spectrum (M^+ 338/336/334 *m/e*). This implied that an addition reaction with solvent participation (bromoethoxylation) as well as a substitution reaction (bromination) had taken place. The presence of an ethoxyl group in the bromination product (**11**) was substantiated by the first fragment peak (293/291/289 *m/e*) in the mass spectrum and by the NMR. signals at $\delta = 3.68/q$ and $1.00/t$, both with $J = 8$ Hz.

An evident candidate for the electrophilic substitution reaction is the pyrazole nucleus and, indeed, the NMR. spectrum of the bromination product (**11**) shows that only one of the pyrazole hydrogens, namely H–C(2), which gives a signal at 7.46 ppm (in **5** it was at 7.48 ppm), is left. The other one (H–C(3), which in **5** had produced a signal at 6.21 ppm) has been replaced by a bromine atom. The substitution at C(3) agrees with the regiospecificity of the corresponding bromination of 1,7a-diaza-7a*H*-indene (**8**) [12]. The continued presence of the 1570 cm^{-1} IR. band in **11** shows that the pyrazole ring is still intact. This is supported by the UV.-maximum at 233 nm ($\varepsilon = 5400$), which is about 23 nm higher than that of pyrazole itself, in agreement with the expected [9] [14] effect of two alkyl groups and one bromine as pyrazole substituents.

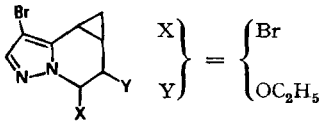
The C(6)–C(7) double bond in **5** is the evident candidate for the addition reaction. Indeed, the bromination product (**11**) no longer exhibits the IR. band 1655 cm^{-1} which had been attributed to the C(6)–C(7) double bond in **5**. Moreover, the ^{1}H-NMR. signals assigned to H–C(6) and H–C(7) are moved upfield by the bromoethoxylation (**5** → **11**) from 5.67 to 4.82 ppm and from 6.92 to 5.62, both keeping their multiplicities but with reduced coupling constants ($J_{H-C(6)/H-C(7)}$ 8 → 2 Hz and $J_{H-C(5)/H-C(6)}$ 5 → 2 Hz). The signal due to H–C(7) ($\delta = 5.62$ ppm) shows an additional small splitting (1 Hz) with H–C(5) ($\delta = 2.12$ ppm) established by decoupling, which is considered to be due to a W-geometry (see below).

The cyclopropane ring evidently remained intact during the bromination-bromoethoxylation; for the ^{1}H-NMR. spectrum of product **11** shows the same four-proton coupling system due to H–C(5), H–C(4), *exo*-H–C(8) and *endo*-H–C(8) as the educt **5**. Only H–C(5) possesses extra-system coupling, in this case two: the *vicinal* coupling with H–C(6) ($J = 2$ Hz) and the W-coupling ($J = 1$ Hz) mentioned above. Of interest is the reversal of the order of the chemical shifts due to the *exo*- and *endo*-H–C(8) as a result of the bromoethoxylation. In **5** the δ-values are 1.49 and 0.06 ppm, in **11** they are 1.34 and 1.54 ppm (see below).

The evidence just presented shows that only the C(6)–C(7) double bond is involved in the bromoethoxylation. The eight isomers which can be thought of as a result of this reaction are assembled in Table 2.

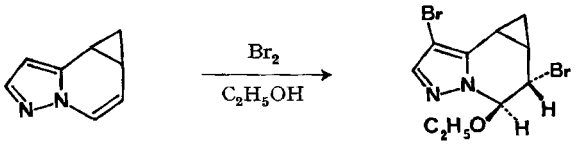
The following observations and considerations offer several independant arguments for a decision as to which isomer[5]) is formed in the above reaction: 1) Models

Table 2. *Isomers of 3,6-dibromo-7-ethoxy- resp. 3,7-dibromo-6-ethoxy-1,7a-diaza-indene*[5])

	6α, 7α	6β, 7α	6β, 7β	6α, 7β
6-bromo-7-ethoxy-isomers	**A**	**B**	**C**	**D**
7-bromo-6-ethoxy-isomers	**E**	**F**	**G**	**H**

show that a conformation with W-geometry between H–C(5) and H–C(7) can be reached only by the 7β-isomers (compare Fig. 4). The observed coupling of 1 Hz between these protons thus eliminates the 7α-isomers, namely **A**, **B**, **E** and **F**. 2) The chemical shift of the H–C(6) signal (δ = 4.82 ppm, which is the one of the H–C(6)/H–C(7) pair with the lower δ-value and without the W-coupling) corresponds better to the estimated value [15] for a methine hydrogen in approximately this environment *geminal* with bromine (δ = ~4.6 ppm) than for a similar methine hydrogen *geminal* to an ether oxygen (δ = ~4.2 ppm). This eliminates the 6-ethoxy-isomers, namely **E**, **F**, **G** and **H**. 3) Preliminary bromonium ion formation might be expected to occur preferentially from the α-side[5]) of **5**, because of some hindrance on the β-side due to the cyclopropane ring. This would exclude the β-bromo-isomers, namely **B**, **C**, **G** and **H**. 4) Attack of ethanol should take place *anti-periplanar* to bromine. This eliminates the *cis* isomers, namely **A**, **C**, **E** and **G**. 5) This attack of the ethanol oxygen should occur at the more electrophilic carbon (C(7)) of the intermediate bromonium ion. This supports the above elimination of the 6-ethoxy-isomers **E**, **F**, **G** and **H**.

D is the only isomer which is not eliminated by any argument. It is the 6α-bromo-7β-ethoxy-isomer, which is shown in formula **11**.



5 **11**

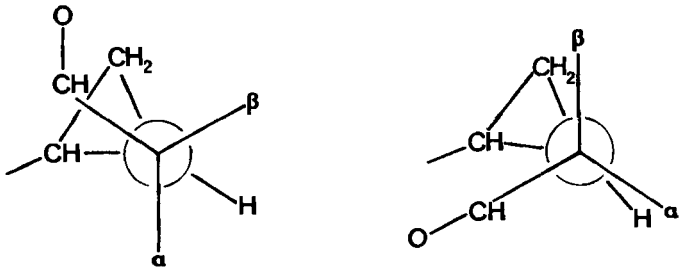
Compound **11** can exist as two conformers[6]), one with Br–C(6) and C_2H_5O–C(7) both axial (**a**) and the other with these substituents both equatorial (**b**). We conclude

[5]) We will call that side of the 4,5-homo-1,7a-diaza-indene (**5**) molecule and of its derivatives (**11** and **12**) which carries the cyclopropane ring the β-side, and the other the α-side.

[6]) Conformer **a** is the one with the 6α- and 7β-bonds directed axially; conformer **b** has these bonds located equatorially.

that conformer **a** is preferred for the following reasons: 1) In conformer **b**, the coupling between the *anti-periplanar* H–C(6) and H–C(7) should be much larger than the observed value of 2 Hz. 2) A W-geometry between H–C(5) and H–C(7) is only possible in conformer **a**. 3) The large downfield shift of *endo*-H–C(8) in the bromination product **11** ($\delta = 1.54$ ppm) as compared to the educt **5** ($\delta = 0.06$ ppm) indicates a through space proximity of a negative atom (the 7β-ethoxyl-oxygen) to *endo*-H–C(8), which is possible only in conformer **a**.

The factor which stabilises conformer **a**, despite the axial position of both ethoxyl and bromine, over conformer **b** may be that the C(5)–C(6) bond in the latter (**b**) must



conformer **a** conformer **b**

Fig. 3. *Projection view along the C(5)–C(6) bond of the two conformers of the 6,7-dihydro-4,5-homo-1,7a-diaza-indenes* **11** *and* **12**

be nearly eclipsed, whereas it can be comfortably staggered in the former (**a**) (compare Fig. 3). The assignments of the ^{1}H-NMR. signals to structure **11** are summarised in Fig. 4.

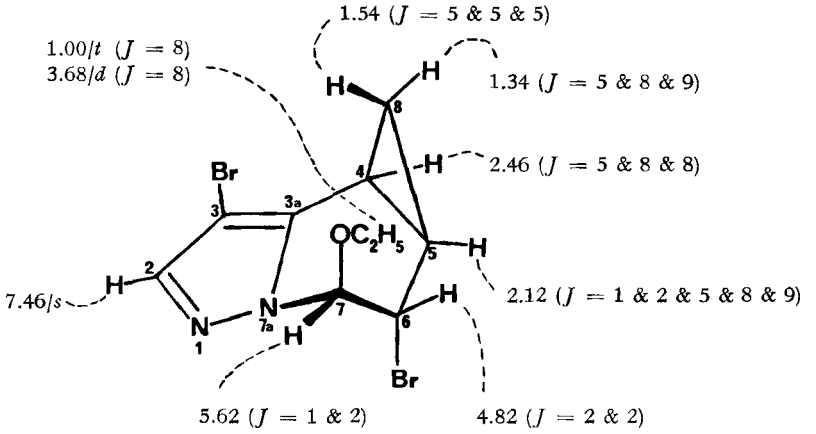
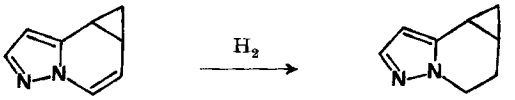


Fig. 4. *Chemical shifts* (in ppm, TMS = 0) *and coupling constants* (in Hz) *in the* ^{1}*H-NMR. spectrum of 3,6α-dibromo-7β-ethoxy-4,5-homo-1,7a-diaza-indene* (**11**)

Catalytic hydrogenation of 4,5-homo-1,7a-diaza-indene (**5**) with 5% palladium on carbon yielded a single product, $C_8H_{10}N_2$, which shows a mass spectrum with the

base peak being the molecular ion = 134 *m/e*. The 6,7-dihydro-4,5-homo-1,7a-diaza-indene structure **12** is assigned to it on the following basis:



5 **12**

The pyrazole ring was unaffected by the hydrogenation as evidenced by the UV. maximum at 222 nm ($\varepsilon = 7350$) characteristic [14] for a dialkyl-pyrazole, by the continued (see above) presence of the IR. band at 1560 cm^{-1} and by the typical [10] [12] ^{1}H-NMR. signals of H–C(2) at 7.33 and of H–C(3) at 6.10 ppm, both doublets with $J = 2$. These data, in fact, demonstrate the presence of a pyrazole nucleus more clearly than those of **5**.

The hydrogenation of **5** also left the cyclopropane ring intact: The ^{1}H-NMR. spectrum of **12** still has the four-proton coupling system, mentioned above with compounds **5** and **11**. While the signal of H–C(4) is not analysable (covered by the signals of Hα- and Hβ-C(6)), the typical *geminal*, *cis* and *trans* coupling pattern can be recognized in the *exo*- and *endo*-H–C(8) signals ($\delta = 1.02$ and 0.87 ppm). In addition to two *cis* and one *trans* coupling, the H–C(5) signal ($\delta = 1.63$ ppm) shows three more splittings with $J = 3$, 3 and 0.5 Hz. The two couplings of 3 Hz must be with the two *vicinal* hydrogens at C(6) and that of 0.5 Hz with one of the two hydrogens at C(7) (see below).

Only the double bond at C(6)–C(7) of **5** was affected by the hydrogenation: The product (**12**) no longer has the IR. band at 1655 cm^{-1} and the UV. maximum has shifted to 222 nm (in **5** it was 255 nm). The ^{1}H-NMR. spectrum shows the absence of non-aromatic vinyl hydrogens, but a new four-proton signal group has appeared in the $\delta = 4.5$ to 2.0 ppm range. Two of these signals overlap with the H–C(4) signal to a multiplet at $\delta = 2.3$–2.0 ppm; since they occur at higher field, they are assigned to the hydrogens at C(6). The other two signals ($\delta = 4.27$ and 3.65 ppm), which are clearly and separately visible at lower field, are assigned to the two hydrogens *geminal* with nitrogen (H_2–C(7)).

Further analysis of these signals leads to the conclusion that 6,7-dihydro-4,5-homo-1,7a-diaza-indene **12** (just as its 6α-bromo-7β-ethoxy-derivative **11**) exists preferentially as conformer **a**[6]) (see Fig. 3). The multiplicities of the two signals assigned to H_2–C(7) are: $\delta = 4.27$ ppm ($J = 0.5$, 4, 5 and 13 Hz); $\delta = 3.65$ ppm ($J = 7$, 10 and 13 Hz). Aside from the *geminal* ($J = 13$ Hz, with each other) and the two *vicinal* couplings ($J = 4$ to 10 Hz, with H_2–C(6)) experienced by each of the two protons in H_2–C(7), only the signal at $\delta = 4.27$ ppm shows an additional splitting of 0.5 Hz, which has been shown by irradiation to be a long range coupling with H–C(5). The required equatorial position for a W-arrangement with H–C(5) can be reached only by H_α–C(7), to which, therefore, the 4.27 ppm signal must be attributed. The fact that this long range coupling can be seen, means that conformer **a** (see Fig. 5) is highly populated in **12**. This is confirmed by the following two NMR.-observations: 1) Only the 3.65 ppm signal, which must belong to H_β–C(7), has a large *vicinal* coupling ($J = 10$ Hz). This means that H_β–C(7) prefers the axial position (as in conformer **a**)

where it has an axial *vicinal* neighbour, namely H_α–C(6). 2) The fact that the two *vicinal* couplings of H–C(5), not due to the cyclopropane hydrogens, are equal ($J = 3$ and 3 Hz) means that H–C(5) is located *syn-clinal* to *both* hydrogens at C(6), an arrangement characteristic for conformer **a** (compare Fig. 3). The presumed reason why 6,7-dihydro-4,5-homo-1,7a-diaza-indene (**12**) prefers conformer **a** is (as in **11**) the better staggering of the substituents at C(5) and C(6). Fig. 5 summarises our interpretation of the spectral data of the hydrogenation product on structure **12**.

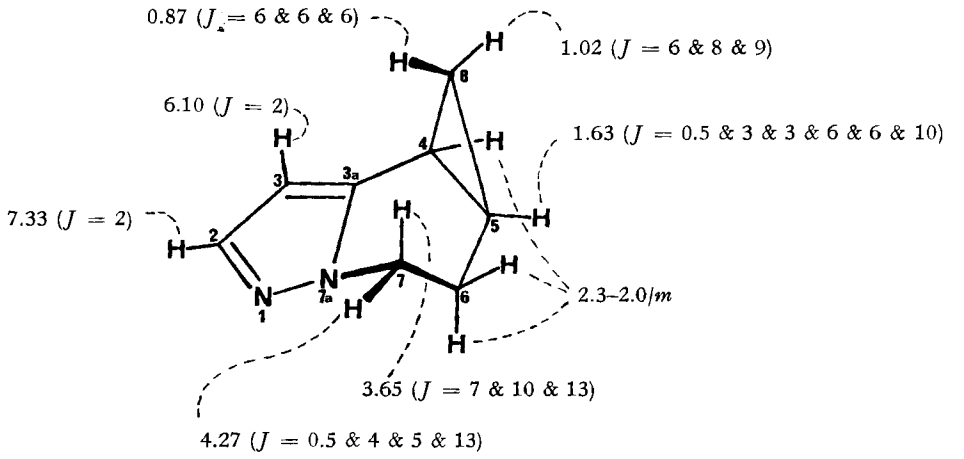


Fig. 5. *Chemical shifts* (in ppm, TMS = 0) *and coupling constants* (in Hz) *in the* ^1H*-NMR. spectrum of 6,7-dihydro-4,5-homo-1,7a-diaza-indene* (**12**)

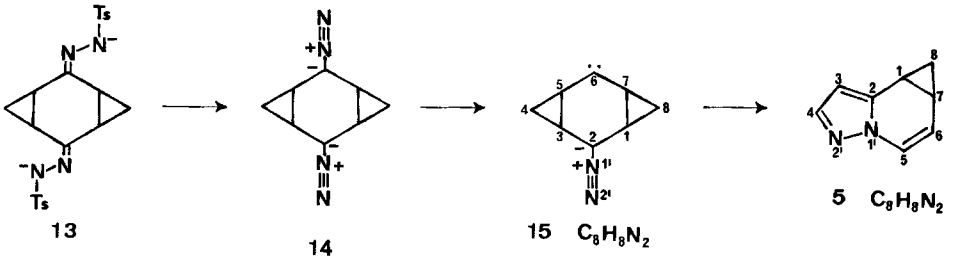
4,5-Homo-1,7a-diaza-indene (**5**) was unaffected by sodium ethoxide in hot ethanol, by thermolysis at 350° for 2 hours and by irradiation with a high pressure mercury lamp in ether alone or in the presence of benzophenone.

4. Mechanistic considerations. – In this section the *anti-* (**1**) and *syn-*(**2**)-bis-homo-*p*-quinones will be treated together simply as bis-homo-*p*-quinone since the alkaline decomposition of both bis-*p*-toluenesulfonyl-hydrazones (**3** and **4**) leads to the same product, 4,5-homo-1,7a-diaza-indene (**5**).

It is likely that the bis-anion of the bis-*p*-toluenesulfonyl-hydrazone (**13**) first decomposes to the bis-diazo-compound **14** ($C_8H_8N_4$). The composition of the final product **5** ($C_8H_8N_2$) requires the loss of two atoms of nitrogen somewhere along the process. It is reasonable to assume that N_2 is evolved from **14** in the first step, so that the diazo-carbene **15** is the high-energy intermediate from which the subsequent rearrangements proceed. The simplest rebonding we could think of is illustrated in reaction scheme 1, where the numbering of the major (= non-hydrogen) atoms of the intermediate **15** is transferred accordingly to the product **5**. Only four of these ten atoms of the system retain the same nearest neighbours in the process.

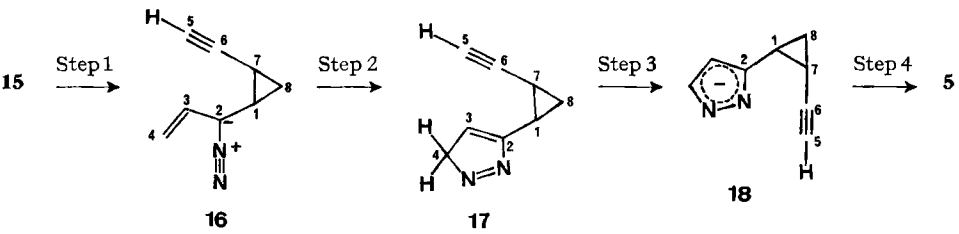
The detailed steps involved in this structural change are not yet known. In scheme 2 we present one possible formulation, in which the individual steps are numbered 1 to 4. In step 1 the carbenoid carbon induces a fragmentation of the cyclopropane ring to a double- and a triple-bond, a reaction type which has been

Scheme 1



observed previously [5]. Step 2 represents the well known [3b] [16] [17] cyclisation of a 3-diazo-propene derivative **16** to a substituted pyrazole **17**. In step 3 excess base abstracts a proton from the pyrazole [16] [18] to form the ethynyl-cyclopropyl-pyrazolyl anion **18**. The intramolecular addition of the pyrazole nitrogen to the triple bond in step 4, which finds an intermolecular analogy in the literature [16] [19], might take place during the working-up of the basic reaction medium.

Scheme 2



This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Sandoz AG* Basel. We thank the members of our research team for interesting discussions on this problem.

Experimental Part

General. — Melting points were taken in a sealed capillary tube with a heated oil bath apparatus; the temperatures are not corrected. The unqualified term 'dried' refers to the use of anhydrous magnesium sulfate, and 'petrol' refers to the fraction b.p. 40–60°. All compounds were analysed on thin layer chromatography (TLC.) plates prepared from *Macherey-Nagel* silica gel N—HR/UV_{254} or *Macherey-Nagel* aluminium oxide N/UV_{254}. Analytical gas-liquid chromatography was carried out on a *Varian* Aerograph model 1200; the results are reported as *GC.*: column material, column temperature, detector temperature, injector temperature, retention times of peaks (peak areas in % of total).

The *IR. spectra* were measured on a *Perkin-Elmer* 21 or 421 spectrometer. They are recorded as follows: (solvent or support): frequency in cm^{-1}, intensity as w = weak, m = medium and s = strong. *The mass spectra* were measured on a *CEC* 21–110 B or an *Atlas* CH-5 instrument. They are recorded as follows: (energy in eV): molecular ions and/or fragment ions in *m/e* (intensities relative to base peak in %, interpretation when evident). With the exception of the ions containing bromine (including all isotope peaks) only the peaks above *m/e* = 90 with intensities higher than 5% are recorded; for compounds of small molecular weight, peaks of lower *m/e* values are also given. *The electronic spectra* were measured on a *Beckman*-spectrophotometer ACTA-111. They are recorded as follows: (solvent): maximum in nm (extinction ε). *The* ^{1}*H-NMR. spectra*

were measured with an HA-100 instrument. They are recorded as follows: (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0)/multiplicity with *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet and *m* = multiplet (splitting *J* = Hz), relative integration in pr units (interpretation). The protons are identified by the number of the carbon atoms to which they are attached; the numbering corresponds to that given on the formulae in the text. *The* ^{13}*C-NMR. spectra* were measured on a *Varian* XL 100 instrument with *Fourier* transform. They are recorded as follows: (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0)/multiplicity with *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, (interpretation). The chemical shifts are obtained from proton-noise decoupled and the multiplicities from off-centre double resonance spectra; the carbon numbering corresponds to the formulae in the text.

We thank the MS.-laboratory (direction Prof. *M. Hesse*) for the mass spectra, the micro-laboratory (direction *H. Frohofer*) for the elemental analyses and the IR. spectra, and the NMR. laboratory (direction Prof. *W. v. Philipsborn*) as well as Mr. *M. Karpf* for the NMR. spectra.

Dehydrobromination of *cis, trans, cis*-2,4,6,8-tetrabromo-cyclooctane-1,5-dione. – a) *With 1,5-diaza-bicyclo[3.4.0]non-5-ene.* To a solution of 0.300 g (0.64 mmol) *cis,trans,cis*-2,4,6,8-tetrabromo-cyclooctane-1,5-dione, m.p. 220–222°, in 10 ml benzene, was added at room temperature 0.16 g (1.29 mmol) 1,5-diaza-bicyclo[3.4.0]non-5-ene with stirring. After 4$^1/_2$ h 2N sulfuric acid was added to the black oil and the product was extracted with chloroform. The extracts were washed with water, dried and evaporated to give a partially crystalline solid. Crystallisation from carbon tetrachloride gave 0.116 g (60%) *anti*-1,3-dibromo-bis-homo-*p*-quinone, m.p. 133–143°.

b) *With 1,4-diaza-bicyclo[2.2.2]octane.* A solution of 0.80 g (1.75 mmol) *cis,trans,cis*-2,4,6,8-tetrabromo-cyclooctane-1,5-dione, m.p. 220–222°, in 10 ml dry acetone, was treated with 0.6 g (5.4 mmol) 1,4-diaza-bicyclo[2.2.2]octane at room temperature. On completion of the addition a solid had precipitated out and TLC. indicated that the reaction was complete. The filtered solution was evaporated to dryness and the residue, dissolved in chloroform, was washed well with water, dried and evaporated to yield a crystalline product. Recrystallisation from chloroform gave 0.48 g (92%) *anti*-1,3-dibromo-bis-homo-*p*-quinone as white plates, m.p. 146.5–147.5° (Lit. [6], m.p. 146–147°, yield 80%). This sample was shown by mixed m.p. and its NMR. spectrum to be identical with an authentic sample [6].

Bis-p-*toluenesulfonyl-hydrazone of* anti-*bis-homo*-p-*quinone* (**1**). A solution of 0.50 g (3.68 mmol) *anti*-bis-homo-*p*-quinone (**1**), m.p. 186–187° [6] and 1.40 g (7.5 mmol) *p*-toluenesulfonyl-hydrazide in 15 ml ethanol was heated under reflux. After 15 min the product started to fall out of solution and after 60 min the precipitate was collected and washed well with ethanol. Due to its insolubility the anti-*bis-homo*-p-*quinone-bis*-p-*toluenesulfonyl-hydrazone* (**3**) (1.65 g) could not be recrystallised; it was dried under vacuum at ~100°. During the m.p. determination, decomposition was observed to start at ~200° and to continue until blackening occurred; at 252° the sample suddenly effervesced; yield 94%. – IR. (Nujol): 3235 m; 1600 w; 1380 s; 1335 s; 1165 s. – ^{1}H-NMR. (100 MHz, CF_3COOH): δ = 7.80/*d* (*J* = 8), 4 pr (aromatic H's); 7.36/*d* (*J* = 8), 4 pr (aromatic H's); 3.1–3.4/*m*, 2 pr; 2.8–3.1/*m*, 2 pr; 2.44/*s*, 6 pr (2 × CH_3); 2.3–2.8/*m*, 2 pr; 1.3–2.2/*m*, 4 pr; the non-interpreted signals could not be assigned reliably.

$C_{22}H_{24}N_4O_4S_2$	Calc.	C 55.9	H 5.12	N 11.9	S 13.6 %
(472.568)	Found	,, 56.07	,, 5.19	,, 12.14	,, 13.24%

Bis-p-*toluenesulfonyl-hydrazone of* syn-*bis-homo*-p-*quinone* (**2**). By the same procedure as described in the preceeding experiment 0.168 g (1.24 mmol) *syn*-bis-homo-*p*-quinone (**2**), m.p. 98–100° [6] was reacted with 0.464 g (2.5 mmol) *p*-toluenesulfonyl-hydrazide to yield 0.504 g of the highly insoluble syn-*bis-homo*-p-*quinone-bis*-p-*toluenesulfonyl-hydrazone* (**4**), which showed decomposition on heating similar to the corresponding *anti*-isomer; yield 87%. – IR. (KBr): 3230 m; 1600 w; 1400 m; 1340 s; 1165 s. – ^{1}H-NMR. (60 MHz, CF_3COOH): δ = 7.80/*d* (*J* = 8), 4 pr (aromatic H's); 7.40/*d* (*J* = 8), 4 pr (aromatic H's); 2.8–3.4/*m*, 4 pr; 2.50/*s*, 6 pr (2 × CH_3); 2.1–2.7/*m*, 2 pr; 1.3–2.0/*m*, 4 pr; the non-interpreted signals could not be assigned reliably.

Decomposition of bis-*p*-toluenesulfonyl-hydrazones of the two bis-homo-*p*-quinones (3 and 4). 4,5-Homo-1,7a-diaza-indene (5, 1,10-diaza-tricyclo[5.3.0.0^{4,6}]deca-2,7,9-triene). - a) *From* anti-*bis-homo-p-quinone-bis*-p-*toluene-sulfonylhydrazone* (**3**). A mixture of 1.00 g (2.11 mmol) bis-*p*-toluenesulfonyl-hydrazone of *anti*-bis-homo-*p*-quinone (**3**) and 15 ml diglyme

was heated with 0.30 g (5.56 mmol) anhydrous sodium methoxide under reflux (oil bath 190°) for 16 hours. After cooling, 200 ml water was added and the product was extracted with ether. The extracts were washed well with water, dried and evaporated to give an oily residue which was purified by preparative TLC (silica gel, ether/hexane 1:3) and distillation to give 0.17 g (60%) of *4,5-homo-1,7a-diaza-indene* (**5**) as a colourless oil, b.p. 128–130°/5.6 Torr, which solidified at –20°. – IR. (Film): 3110 w; 3010 w; 1655 s; 1560 m; 1425 s; 1360 s; 935 m; 870 m; 765 s; 730 s. – MS. (70 ev): 132 (100, M^+), 131 (36), 105 (13), 104 (27), 79 (11), 78 (22), 77 (17), 66 (7), 65 (10), 63 (8), 52 (18), 51 (26), 50 (16), 39 (24), 38 (10). – UV. (EtOH): 255 (8.740); no change on addition of CF_3CO_2H, $HClO_4$, HCl or NaOH even after standing for 96 hours. – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 7.48/*d* (J = 2), 1 pr (H—C(2)); 6.92/*d* (J = 8), 1 pr (H—C(7)); 6.21/*d* (J = 2), 1 pr (H—C(3)); 5.67/*d*×*d* (J = 8 & 5), 1 pr (H—C(6)); 2.46/*d*×*d*×*d* (J = 5 & 8 & 9), 1 pr (H—C(4)); 1.88/*d*×*d*×*d*×*d* (J = 5 & 5 & 8 & 9), 1 pr (H—C(5)); 1.49/*d*×*d*×*d* (J = 4 & 9 & 9), 1 pr (*exo*-H—C(8)); 0.06/*d*×*d*×*d* (J = 4 & 5 & 5), 1pr(*endo*-H—C(8)). – Spin decoupling experiments: Irradiation at δ = 7.48 (H—C(2)) converted the signal at δ = 6.21 (H—C(3)) to *s*; irradiation at δ = 6.92 (H—C(7)) converted the signal at δ = 5.67 (H—C(6)) to *d* (J = 5); irradiation at δ = 1.88 (H—C(5)) converted the signal at δ = 5.67 (H—C(6)) to *d* (J = 8); irradiation at δ = 5.67 (H—C(6)) removed the long range coupling (J = 0.5) at δ = 2.46 (H—C(4)). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): δ = 140.0/*d* (C(2)); 136.8/*s* (C(3a)); 123.5/*d* (C(7)); 111.2/*d* (C(6)); 103.4/*d* (C(3)); 13.85/*d* (C(4) or C(5)); 13.05/*d* (C(5) or C(4)); 9.76/*q* (C(8)). – GC.: 5% SE-30 5^1/$_8$ column at 130°, detector temperature 250°, injector temperature 190°, retention time 1.75 min (100%).

$C_8H_8N_2$ (132.157) Calc. C 72.69 H 6.1 N 21.18% Found C 72.90 H 6.7 N 20.35%

The same product was obtained in 54% yield when sodium hydride was used as the base under the same conditions.

b) *From* syn-*bis-homo-p-quinone-bis*-p-*toluenesulfonyl-hydrazone* (**4**). The procedure reported in the preceeding experiment was carried out using the bis-*p*-toluenesulfonyl-hydrazone of *syn*-bis-homo-*p*-quinone (**4**). The product, obtained in 40% yield, was shown by b.p. and its IR.- and ^{1}H-NMR. spectra to be identical with the sample of 4,5-homo-1,7a-diaza-indene (1,10-diaza-tricyclo[5.3.0.0^{4,6}]deca-2,7,9-triene) (**5**) reported under a) above.

Treatment of 4,5-homo-1,7a-diaza-indene (**5**) *with 70% perchloric acid.* 0.02 g 4,5-Homo-1,7a-diaza-indene (**5**) in 2 ml ether/ethanol 1:1 was treated with 70% perchloric acid until the solution was acid to congo red paper. The solution was allowed to stand at room temperature for 8 h after which time TLC. showed no unreacted starting material. Removal of the solvent under reduced pressure gave a brown oil which blackened on standing. – IR. (Film): 3500 s (broad),; 3150 s; 1410 m; 1110 s (broad). – ^{1}H-NMR. (60 MHz, d_6-acetone): δ = 8.44/*d* (J = 3), 1 pr (H—C(2)); 7.35/*d* (J = 8), 1 pr (H—C(7)); 7.02/*d* (J = 3), 1 pr (H—C(3)); 6.48/*d*×*d* (J = 8 & 5), 1 pr (H—C(6)); 2.95/*d*×*d*×*d* (J = 5 & 8 & 9), 1 pr (H—C(4)); 2.35/*d*×*d*×*d*×*d* (J = 5 & 5 & 8 & 9), 1 pr (H—C(5)); 0.34/*d*×*d*×*d* (J = 4 & 5 & 5), 1 pr (*endo*-H—C(8)). The signal corresponding to *exo*-H—C(8) is not visible; it could possibly be masked by the solvent absorption at δ = 2.1.

Bromination of 4,5-homo-1,7a-diaza-indene (**5**). To a stirred solution of 0.05 g (0.38 mmol) 4,5-homo-1,7a-diaza-indene (**5**) in 2 ml ethanol was added dropwise an aqueous solution of 0.122 g (0.76 mmol) bromine. During the addition nitrogen gas was bubbled slowly through the solution. After stirring at room temperature for 2 h, the yellow-brown reaction mixture was made alkaline (~pH 11) with aqueous sodium hydroxide. Dilution with water and extraction with chloroform followed by drying of the combined extracts and evaporation of the solvent gave 0.094 g of a brown viscous oil. Purification by preparative TLC. on silica gel with ether/hexane 1:1 and distillation at 82–85°/0.02 Torr gave 0.056 g (45%) of *3,6α-dibromo-7β-ethoxy-4,5-homo-1,7a-diaza-indene* (**11**) as an orange-brown viscous oil. – IR. ($CHCl_3$): 1570 w; 1340 m; 1295 m; 1080 s. – MS. (70eV): 338/336/334 (7/14/7, M^+), 293/291/289 (2/4/3, M^+ – C_2H_5O), 257/255 (4/4, M^+ – Br), 212/210 (100/96, M^+ – C_2H_5O – Br), 199 (6), 131 (7, M^+ – 2× Br – C_2H_5O), 119 (9), 118 (11), 104 (8), 102 (7). – UV. (EtOH): 233 (5,400). – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 7.46/*s*, 1 pr (H—C(2)); 5.62/*d*×*d* (J = 1 & 2), 1 pr (H—C(7)); 4.82/*d*×*d* (J = 2 & 2), 1 pr (H—C(6)); 3.68/*q* (J = 8), 2 pr (OCH_2Me); 2.46/*d*×*d*×*d* (J = 5 & 8 & 8), 1 pr (H-C(4)); 2.12/*d*×*d*×*d*×*d*×*d* (J = 1 & 2 & 5 & 8 & 9), 1 pr (H—C(5)); 1.54/*d*×*d*×*d* (J = 5 & 5 & 5), 1 pr *endo*-H—C(8)); 1.34/*d*×*d*×*d* (J = 5 & 8 & 9), 1 pr (*exo*-H—C(8)); 1.00/*t* (J = 8), 3 pr (CH_3). – Spin decoupling experiments: Irradiation at δ = 5.62 (H—C(7)) converted the signal at δ = 4.82 (H—C(6)) to *d* (J = 2) and the signal at

$\delta = 2.12$ (H—C(5)) to $d \times d \times d \times d$ ($J = 2$ & 5 & 8 & 9); irradiation at $\delta = 4.82$ (H—C(6)) converted the signal at $\delta = 5.62$ (H—C(7)) to d ($J = 1$) and the signal at $\delta = 2.12$ (H—C(5)) to $d \times d \times d \times d$ ($J = 1$ & 5 & 8 & 9); irradiation at $\delta = 2.12$ (H—C(5)) converted the signal at $\delta = 5.62$ (H—C(7)) to d ($J = 2$).

$C_{10}H_{12}Br_2N_2O$ (336.042) Calc. C 35.74 H 3.60 Br 47.55 N 8.35%
Found ,, 35.63 ,, 3.72 ,, 46.44 ,, 8.45%

Catalytic hydrogenation of 4,5-homo-1,7a-diaza-indene (**5**). A solution of 0.110 g (0.83 mmol) 4,5-homo-1,7a-diaza-indene (**5**) in 4 ml ethanol was shaken with 0.015 g 5% Pd/C at room temperature under 4 atm. of hydrogen for 6 h. After filtration, the solvent was removed under vacuum and the residue was purified by preparative TLC. on silica gel with ether/hexane 1:1 and distillation at 98–102°/9 Torr to give 0.081 g (73%) of *6,7-dihydro-4,5-homo-1,7a-diaza-indene* (**12**) as a colourless oil. – IR. (Film): 3110 w; 3090 w; 1560 s; 1495 s; 1420 s; 1365 s; 1340 s; 1215 s; 940 s; 835 s; 775 s; 755 s. – MS. (70 eV): 134 (100, M^+), 133 (47), 132 (8), 120 (5), 119 (53), 118 (7), 107 (9), 106 (22), 105 (8), 104 (8), 92 (18), 89 (20), 85 (5), 83 (8), 79 (13), 78 (13), 77 (8), 66 (6), 65 (7), 63 (9), 59 (75), 58 (35). – UV. (EtOH): 222 (7,350). – ^{1}H-NMR. (100 MHz, $CDCl_3$): $\delta = 7.33/d$ ($J = 2$), 1 pr (H—C(2)); 6.10/d ($J = 2$), 1 pr (H—C(3)); 4.27/$d \times d \times d \times d$ ($J = 0.5$ & 4 & 5 & 13), 1 pr (Hα—C(7)); 3.65/$d \times d \times d$ ($J = 7$ & 10 & 13), 1 pr (Hβ—C(7)); 2.0–2.3/m, 3 pr (2 × H—C(6), H—C(4)); 1.63/$d \times d \times d \times d \times d \times d$ ($J = 0.5$ & 3 & 3 & 6 & 6 & 10), 1 pr (H—C(5)); 1.02/$d \times d \times d$ ($J = 6$ & 8 & 9), 1 pr (*exo*-H—C(8)); 0.87/$d \times d \times d$ ($J = 6$ & 6 & 6), 1 pr (*endo*-H—C(8)). – Spin decoupling experiments: Irradiation at $\delta = 7.33$ (H—C(2)) converted the signal at $\delta = 6.10$ (H—C(3)) to s; irradiation at $\delta = 1.63$ (H—C(5)) converted the signal at $\delta = 4.27$ (H—C(7)) to $d \times d \times d$ ($J = 4$ & 5 & 13).

$C_8H_{10}N_2$ (134.174) Calc. C 71.61 H 7.51 N 20.88% Found C 70.26 H 7.67 N 19.59%

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101. Oxydative Kupplung von Indolinen und 1,2,3,4-Tetrahydrochinolinen mit Kaliumpermanganat

153. Mitteilung über Alkaloide [1])

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(18. II. 74)

Summary. It is shown that treatment of indolines like 4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (**1**) and even indoline-alkaloids like **5** or **6** (*cf. scheme 1*) with $KMnO_4$ in boiling acetone solution leads to the indolenines **10**, **29** and **33**, respectively, and, in relatively high yields, to N,N'- or C,N-coupling products (*cf. schemes 2* and *5*). The results of the oxidation of 6- or 8-methoxy-indolines are shown in *schemes 3* and *4*, respectively. Analogous 'dimeric' dehydrogenation products are observed when tetrahydroquinolines (**8** and **9**, resp.) are treated with $KMnO_4$ (*cf. schemes 7* and *8*, resp.).

The formation of the bis-compounds is almost certainly due to the coupling of two intermediate indolenyl or tetrahydroquinolyl radicals.

The cleavage of the hydrazine derivatives **11** or **17** (*scheme 9*) also leads to 'dimeric' C,N-coupling products.

By heating the hydrazine derivative **17** with aqueous HCl, a complete cleavage into indoline **2** and the indolenines **16** and **20** is observed. The reaction is rationalized in *scheme 10*.

So far no naturally occurring alkaloids related to the above mentioned C,N-coupling products have been found.

1. Einleitung. – Die oxydative Kupplung von Phenolen spielt eine grosse Rolle bei der Biosynthese einer Vielzahl von Pflanzeninhaltsstoffen (vgl. [2]). Im Zusammenhang mit dem natürlichen Auftreten von Bis-indolalkaloiden (vgl. [3]) wurde die oxydative Kupplung der Indoline 4a-Methyl-1,2,3,4,4a,9a-hexahydrocarbazol (**1**), seines 6-Methoxy- (**2**), seines 8-Methoxy- (**3**) sowie des 7,8-Dimethoxy-Derivates **4** untersucht. Bei den Alkaloiden waren es (+)-N-Desacetyl-aspidospermin (**5**) [4] und (+)-O-Methyl-N-depropionyl-aspidolimin (**6**) [5]. Des weiteren wurden in die Untersuchungen auch 2-Methoxy-N-methylanilin (**7**), 1,2,3,4-Tetrahydrochinolin (**8**) sowie sein 8-Methoxyderivat **9** mit einbezogen (*Schema 1*).

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