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(18) The relative basicity of **9** and **10** may be complicated by some tendency of **10** to protonate at the β-carbon atom.[16] Since the $C_\beta$-protonated structure cannot undergo the sigmatropic rearrangement,[16] clearly the formation of the N-protonated structure **13** must occur to an extent sufficient to permit the rearrangement to take place at a reasonable rate.
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# *Notes*

## Fischer Indole Synthesis from *cis*- and *trans*-9-Methyl-3-decalone

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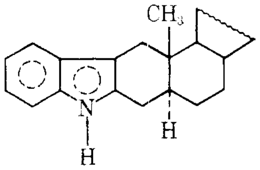
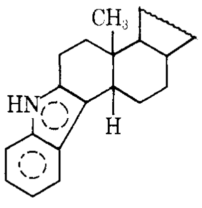
In the Fischer indole synthesis with the phenylhydrazone of an unsymmetrical ketone the direction of cyclization is governed in part by the relative stability of the two possible enehydrazines.[2] This regioselectivity has been well established[3] in the 3-keto steroid system in which 5α-cholestanone yields the linear indole 1 and the 5β isomer forms the angular product **2.** The same directions of enolization are observed in the bromination of the respective 3-ketones[4] in which relief of strain is maximized by enolization of the trans isomer parallel to the ring fusion and of the cis isomer toward the ring fusion.[5] In contrast, Stork and Dolfini[6] observed a linear product from both the cis and trans isomers of the bicyclic azadecalin system **3.** This behavior is analogous to the formation of the 2-bromo derivative from both *cis*- and *trans*-9-methyl-3-decalone (**4**).[7]



1



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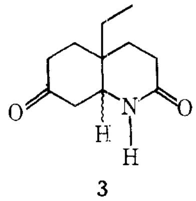

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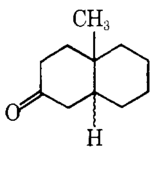
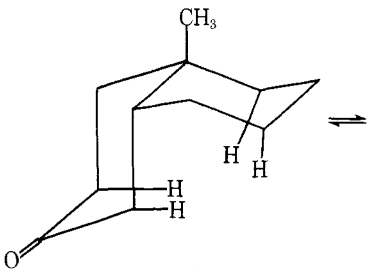
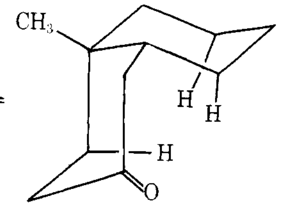


**4a** (cis)
**4b** (trans)

Unlike the more rigid cis steroid, the cis isomer of the bicyclic system can exist in two chair–chair conformations,[8] **5** and **6.** In the more stable of these two conformers, **6,** greater relief of strain results through enolization toward position 2 than toward position 4.

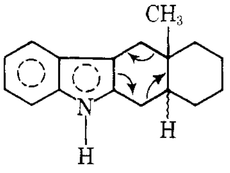


5

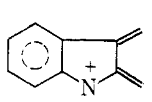


6

To confirm the course of cyclization in the Fischer indole synthesis with the decalin system, cyclization of the phenylhydrazones of both *cis*- and *trans*-**4** was carried out. That the product in each case was the linear indole **7** was determined from the mass spectral fragmentation to the *m/e* 143 ion (**8**), a fragmentation not available to the angular structure. The mass spectra of **7a** and **7b** are quite similar, showing only slight intensity differences. Between the parent peak (*m/e* 239) and the base peak (*m/e* 143), the greatest difference lies in the presence of the *m/e* 224 (P − 15) peak in the trans isomer **7b,** reflecting a greater tendency of this isomer to lose the angular methyl group. In the mass region below the base peak, the spectra are both very similar to the mass spectrum of 1,2,3,4-tetrahydrocarbazole because of fragmentation of the common ion 8 and are typical of the spectra of alkylindoles.[9]



**7a** (cis)
**7b** (trans)



8 (*m/e* 143)

### Experimental Section[10]

***cis*-9-Methyl-3-decalone (4a).** 9-Methyl-$\Delta^4$-3-octalone was prepared by the procedure of Yanagita and Yamaka,[7] bp 93–96 °C (1.5 mm) [lit.[7] bp 102–110 °C (2.5 mm)]. Hydrogenation of the unsaturated ketone using 10% palladium on carbon at atmospheric pressure[7] afforded the cis saturated ketone **4a**: mp 46–47 °C (lit.[7] mp 47 °C); NMR $\delta$ 1.33 ($CH_3$).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.52; H, 10.84. Found: C, 79.38; H, 10.67.

***trans*-9-Methyl-3-decalone (4b).** Reduction of the unsaturated ketone with Li in liquid $NH_3$[11] furnished the trans isomer: bp 98–101 °C (5 mm) [lit.[11] bp 95–112 °C (7 mm)]; NMR $\delta$ 1.15 ($CH_3$).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.52; H, 10.84. Found: C, 79.34; H, 10.79.

**Phenylhydrazones.** Equimolar quantities of the above ketones and phenylhydrazine were stirred at room temperature for 24 h. The mixture was taken up in ether and dried over $Na_2SO_4$. The ether was removed under vacuum and the phenylhydrazone distilled under vacuum.

***cis*-9-Methyl-3-decalone Phenylhydrazone:** bp 174–178 °C (1 mm); NMR $\delta$ 1.35 ($CH_3$).

Anal. Calcd for $C_{17}H_{24}N_2$: C, 79.69; H, 9.38; N, 10.94. Found: C, 79.56; H, 9.16; N, 10.23.

***trans*-9-Methyl-3-decalone Phenylhydrazone:** bp 180–185 °C

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**Indolization of the Phenylhydrazones.** A solution of 4.0 g of the phenylhydrazone and 26 g of anhydrous $ZnCl_2$ in absolute ethanol was refluxed for 5 h. Water was added, and the mixture was made alkaline with sufficient sodium hydroxide to dissolve the $Zn(OH)_2$ precipitate and extracted with ether. The ether extracts were washed with 1.0 N HCl, water, and 10% $NaHCO_3$ and dried over $Na_2SO_4$. The ether was evaporated, and the indole was purified by vacuum distillation. *cis*-6a,10a-10a-Methyl-6,6a,7,8,9,10,10a,11-octahydro-5*H*-benzo[*b*]carbazole (**7a**): bp 180–184 °C (1 mm); mp 44–46.5 °C; yield, 44%; UV max 229 nm (log ε 4.43), 284 (3.79), 291 (3.74); NMR δ 1.05 ($CH_3$); mass spectrum, *m/e* (relative intensity) 239 (30), 238 (4), 183 (9), 182 (15), 180 (10), 170 (4), 168 (16), 167 (18), 144 (20), 143 (100), 129 (10), 127 (8), 117 (5), 116 (4), 115 (12), 77 (14), 76 (4), 65 (6), 63 (5), 51 (8), 50 (3), 39 (23).

Anal. Calcd for $C_{17}H_{21}N$: C, 85.35; H, 8.75; N, 5.86. Found: C, 85.43; H, 8.53; N, 5.44.

The same product was obtained by heating the phenylhydrazone in glacial acetic acid at 80 °C for 5 h (yield, 36%).

*trans*-6a,10a-10a-Methyl-6,6a,7,8,9,10,10a,11-octahydro-5*H*-benzo[*b*]carbazole (**7b**): bp 189–194 °C (1 mm); yield, 41%; UV max 228 nm (log ε 4.45), 284 (3.78), 291 (3.74); NMR δ 0.88 ($CH_3$); mass spectrum, *m/e* (relative intensity) 239 (69), 238 (10), 224 (7), 183 (8), 182 (13), 180 (9), 170 (7), 168 (12), 167 (12), 144 (32), 143 (100), 129 (12), 127 (6), 117 (3), 116 (3), 115 (7), 77 (7), 76 (2), 65 (3), 63 (4), 51 (4), 50 (1), 39 (3).

Anal. Calcd for $C_{17}H_{21}N$: C, 85.35; H, 8.79; N, 5.86. Found: C, 84.96; H, 8.38; N, 5.46.

The same product was obtained by heating the phenylhydrazone in glacial acetic acid at 80 °C for 5 h (yield, 31%).

**Mass Spectrum of 1,2,3,4-Tetrahydrocarbazole:**[12] MS *m/e* (relative intensity) 171 (24), 170 (12), 114 (14), 143 (100), 129 (6), 127 (7), 117 (4), 116 (5), 115 (18), 77 (10), 76 (6), 65 (5), 63 (10), 51 (10), 50 (6), 39 (12).

**Registry No.**—**4a,** 938-06-7; **4a** phenylhydrazone, 66674-97-3; **4b,** 938-07-8; **4b** phenylhydrazone, 66674-98-4; **7a,** 66674-99-5; **7b,** 66675-00-1; 9-methyl-$\Delta^4$-3-octalone, 826-56-2; phenylhydrazine, 100-63-0; 1,2,3,4-tetrahydrocarbazole, 942-01-8.

## References and Notes

(1) From the Ph.D. Thesis of R.A.L., Northern Illinois University, 1977.
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(7) M. Yanagita and K. Yamaka, *J. Org. Chem.,* **22,** 291 (1957).
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(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, p 611.
(10) Melting points were taken on a Buchi melting point apparatus and are uncorrected. UV spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer in 95% ethanol solution. NMR spectra were determined in $CCl_4$ or $CDCl_3$ solution using internal $Me_4Si$ on a Varian A60-A spectrometer. Mass spectra were measured with a Hitachi Perkin-Elmer RMU-6 instrument at 70 eV. Elemental analyses were performed by Mr. Jerry Darby using a Perkin-Elmer 240 analyzer.
(11) M. Yanagita, K. Yamakawa, A. Tahara, and H. Ogura, *J. Org. Chem.,* **20,** 1967 (1955).
(12) C. U. Rogers and B. B. Corson, "Organic Syntheses", Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N.Y., 1963, p 884.

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# Reaction of Picryl Chloride with 3,5-Dinitrotriazole: Formation of 1-Picryl-3-nitro-5-chloro-1,2,4-triazole and 1-Picryl-3-nitro-1,2,4-triazol-5-one

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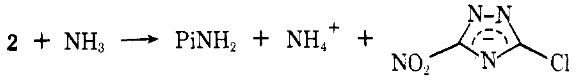
The reaction of picryl chloride with 3,5-dinitrotriazole salts ($K^+$, $Li^+$) in dry acetonitrile results in a complex mixture of products which include 1-picryl-3-nitro-5-chloro-1,2,4-triazole (**2**), 1-picryl-3-nitro-1,2,4-triazol-5-one (**4**), 2,4,6-trinitrophenol (picric acid), and oxides of nitrogen. The products (**2** and **4**) were identified by mass spectroscopy (parent ions), IR (characteristic bands for aromatic H; NH and C=O for **4**), NMR (singlets for picryl H; broad singlet (NH) for **4**), and elemental analysis. Additional evidence for the structure of **2** was its reaction with ammonia to give 2,4,6-trinitroaniline and ammonium chloronitrotriazole. Further support for the structures of **2** and **4** is that the formation of these products can be rationalized via the expected primary reaction intermediate, 1-picryl-3,5-dinitro-1,2,4-triazole (**1**) (see Scheme I).



Positional isomers for the intermediate **1** and compounds **2** and **4** are possible and the structures assigned to these species are the most likely ones based on previous structure

### Scheme I