C(CH$_3$)$_2$], 20.6 (q, CHCH$_3$), 52.8 (s, $-\overset{|}{\underset{|}{C}}-$), 59.6 (d, CH), 135.8 (s, C$_\alpha$), 128.4 (d, C$_{ortho}$),

128.8 (d, C$_{meta}$), 128.0 (d, C$_{para}$), and 154.1 ppm (s, C=N). Found, %: C 71.4; H 8.2; N 20.3. C$_{12}$H$_{17}$N$_3$. Calculated, %: C 71.0) H 8.4; N 20.7.

5,5-Dimethyl-6-phenyl-3-(p-chlorophenyl)-2,3,4,5-tetrahydro-1,2,4-triazine (X). This compound was obtained in 70% yield and had mp 94-95°C. IR spectrum: 1670 cm^{-1} (C=N). UV spectrum, λ_{max} (log ε): 217 (20200) and 271 nm (8200). ^{1}H NMR spectrum (CCl$_4$): δ 1.21 and 1.48 [s, 3H and 3H, C(CH$_3$)$_2$], 1.9 (s, 1H, NH), 4.87 (s, 1H, CH), 6.3 (s, 1H, NH), and 7.3 ppm (s, 5H, C$_6$H$_5$). ^{13}C NMR spectrum (CDCl$_3$): δ 30.2 and 28.0 [q, C(CH$_3$)$_2$], 54.3 (s,

$-\overset{|}{\underset{|}{C}}-$), 66.1 (d, CH), 154.6 (s, C=N), 139.0, 138.4, 135.0 (s), 128.0, 128.2, 128.8, 128.9, and

129.5 ppm (d, C$_{arom}$). Found, %: C 68.0; H 5.9; N 14.5. C$_{17}$H$_{18}$ClN$_3$. Calculated, %: C 68.1; H 6.0; N 14.0.

LITERATURE CITED

1. T. Nishiwaki and T. Saito, Chem. Commun., No. 22, 1479 (1970).
2. T. Nishiwaki and T. Saito, J. Chem. Soc., C, No. 15, 2648 (1971).
3. B. Singh and E. F. Ulmann, J. Am. Chem. Soc., 89, 6911 (1967).
4. N. I. Leonard, E. F. Muth, and V. Nair, J. Org. Chem., 33, 827 (1967).
5. B. V. Ioffe, O. V. Sverdlova, and L. M. Korzhikova, Teor. Éksp. Khim., 3, 119 (1967).
6. Yu. P. Kitaev and B. I. Buzykin, Hydrazones [in Russian], Nauka, Moscow (1974).
7. M. Busch, G. Friederberger, and W. Tischbin, Ber., 57, 1783 (1924).
8. R. F. Parcell, Chem. Ind., No. 33, 1396 (1963).

PYRROLES FROM KETOXIMES AND ACETYLENE

II.* EXHAUSTIVE HYDROGENATION OF 4,5,6,7-TETRAHYDROINDOLE

AND ITS N-VINYL DERIVATIVE

B. A. Trofimov, S. E. Korostova,   UDC 547.75:542.941.7
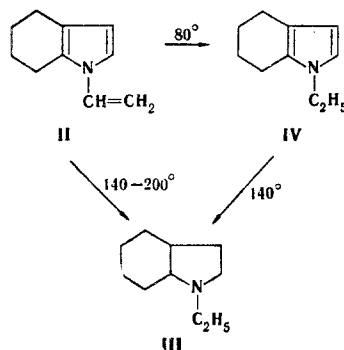L. N. Balabanova, A. I. Mikhaleva,
and A. N. Vasil'ev

The hydrogenation of 4,5,6,7-tetrahydroindole and 1-vinyl-4,5,6,7-tetrahydroindole (with H$_2$ at 150°C and 50-100 atm) in ethanol gives 1-ethyloctahydroindole in 89 and 96% yields, respectively. The hydrogenation of 4,5,6,7-tetrahydroindole in n-butanol is also accompanied by alkylation, and its hydrogenation in tetrahydrofuran proceeds with the primary formation (69%) of nitrogen-unsubstituted octahydroindole; the principal side product (21%) is 1-butyloctahydroindole.

4,5,6,7-Tetrahydroindole (I) and 1-vinyltetrahydroindole (II), which are now readily obtainable from cyclohexanone oxime and acetylene [1], may become a source of octahydroindole and 1-ethyloctahydroindole (III), which are becoming increasingly more difficult to obtain.
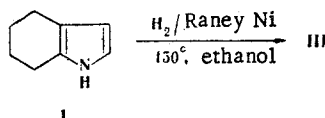
The catalytic hydrogenation of II over Raney Ni in ethanol at 50-80°C under hydrogen pressure (40-60 atm) proceeds selectively [2] to give 1-ethyltetrahydroindole (IV) in 90% yield. Continuing our research in this area, we found that when the reaction temperature is

---

*See [1] for communication I.

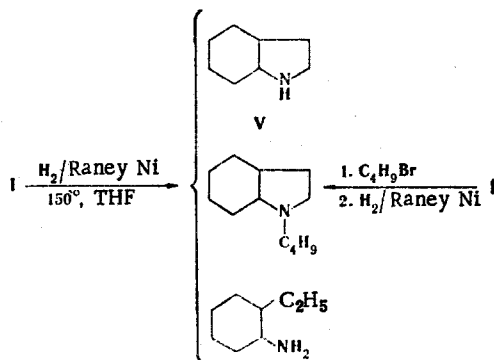raised to 140°C, the only product is octahydroindole III (in 96% yield).

Hydrogenation at 120°C gives a mixture of III and IV. Raising the temperature to 200°C at a hydrogen pressure of 50-60 atm does not give rise to any significant hydrogenolysis: Only traces of the cleavage product are present in the reaction mixture. Octahydroindole III (in 89% yield) was obtained instead of the expected unsubstituted octahydroindole (V) in the catalytic hydrogenation of nitrogen-unsubstituted I in ethanol, i.e., alkylation proceeds along with reduction.

The physicochemical constants of the III obtained in the latter reaction are in complete agreement with the values for III obtained from tetrahydroindole II. The results of thin-layer chromatography (TLC) and gas—liquid chromatography (GLC) confirm the identical character of the samples obtained by the two different methods. Instances of the alkylation of ammonia, aliphatic amines, and some aromatic amines by primary and secondary alcohols when they are heated under the conditions of hydrogenation on Raney Ni are known (for example, see [3, 4]. However, no information regarding alkylation of indole or pyrrole under similar conditions is available. We have shown that reductive alkylation may also be effected by other primary alcohols (for example, butanol), although in the latter case reduction proceeds with greater difficulty than in the case of ethanol: We were able to detect 1-butyloctahydroindole in the reaction mixture only by chromatography.

In the hope of preparing the difficult-to-obtain octahydroindole V [5, 6], free of III, we carried out the hydrogenation of tetrahydroindole I in tetrahydrofuran (THF). However, GLC analysis showed that the resulting reaction mixture contained 69% octahydroindole V and 21% 1-butyloctahydroindole and 10% ethylcyclohexylamine. 1-Butyloctahydroindole, which is formed as a result of alkylation of V with butanol — the product of hydrogenolysis of THF — was identified from its retention volume vis-a-vis the retention volume of an authentic sample synthesized by alternative synthesis (by alkylation of I with butyl bromide and subsequent hydrogenation).

Compound V was identified by chromatographic comparison with a sample obtained by hydrogenation of tetrahydroindole I over an Adams catalyst in glacial acetic acid by the

method in [7]. The reaction in this case is accompanied by polymerization of the starting compound.

The structures of all of the compounds obtained were confirmed by IR and PMR spectroscopic data. The problem regarding cis,trans fusion of the rings in the octahydro structures is under investigation.

The IR spectrum of III does not contain absorption bands of the stretching vibrations of an NH group or the characteristic absorption of the pyrrole ring [8]. Its PMR spectrum contains a triplet of the protons of the CH_3 group (δ 0.56 ppm), the multiplet of the proton attached to the angular carbon atom closest to the nitrogen atom (δ 3.08 ppm), and a broad multiplet of the remaining protons at δ 3.0 ppm.

The hydrogenation of 2-phenyl- and 3-alkyl-2-phenylpyrroles and their N-vinyl derivatives under the various conditions described above gives a complex mixture of products that is difficult to separate not only by means of vacuum fractionation but also by means of preparative chromatography.

EXPERIMENTAL

Samples of the synthesized octahydroindoles III and V were analyzed chromatographically with a Khrom-4 chromatograph (the detector was a catharometer, the column was 2.5-m long and had a diameter of 3 mm, the solid phase was Chromaton N-AW-DMCS, the liquid phase was 15% DS 550 silicone, the thermostat temperature was 170°C, and the carrier gas was helium) and in a thin layer [on Silufol in a heptane–ether system (1:2)]. The IR spectra of films were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-487B spectrometer (80 MHz); the internal standard for solutions in CCl_4 was hexamethyldisiloxane.

Hydrogenation of Vinyltetrahydroindole II in Ethanol. A 10-g (0.06 mole) sample of II was heated in 75 ml of ethanol at 160°C for 5 h under hydrogen pressure (50 atm) in the presence of 2 g of Raney Ni [9], after which the catalyst was removed by filtration, the ethanol was removed from the filtrate, and the residue was fractionated in vacuo to give 9.7 g (94%) of III with bp 68°C (5 mm), n_D^{20} 1.4739, and d_4^{20} 0.9008. IR spectrum: 630 w, 780, 837 w, 867 w, 984, 1022, 1047, 1088 w, 1120 w, 1128, 1238 w, 1256 w, 1282, 1310 w, 1340, 1360 w, 1375, 1450, 2660 w, 2720 w, 2790, 2860, and 2935 cm^{-1}. Found, %: C 78.4; H 12.4; N 9.6. $C_{10}H_{19}N$. Calculated, %: C 78.4; H 12.5; N 9.2%. The reaction product was 99.9% pure according to GLC.

At 140 and 200°C, all other conditions being equal, III was obtained in 96 and 64.5% yields, respectively; ∿1% of the hydrogenolysis product was present in the product (GLC).

Hydrogenation of Tetrahydroindole I in Ethanol. A 5-g (0.04 mole) sample of I was heated at 150°C for 5 h under hydrogen pressure (100 atm) in 50 ml of ethanol over Raney Ni (1.5 g). Standard workup gave 5.6 g (89%) of III with bp 78°C (8 mm) and n_D^{20} 1.4731; with respect to its retention volume (GLC) and IR and PMR spectra, the product was identical to the product obtained from II. Found, %: C 78.9; H 12.7; N 8.9.

Hydrogenation of Tetrahydroindole I in THF. A 5-g (0.04 mole) sample of I was heated at 150°C for 5 h under hydrogen pressure (100 atm) in 50 ml of THF over Raney Ni (1.5 g). Workup as above gave 4.7 g of a mixture containing 69% octahydroindole V, 21% 1-butylocta-hydroindole, and 10% ethylcyclohexylamine (according to GLC).

Hydrogenation of Tetrahydroindole I over an Adams Catalyst [9]. A 6-g (0.05 mole) sample of I was stirred in 60 ml of glacial acetic acid in the presence of 0.6 g of PtO_2 at room temperature for 6 h under hydrogen pressure (30 atm). The mixture was then made alkaline with dilute NaOH solution and extracted with ether. The ether extracts were washed with water and dried with $MgSO_4$. Vacuum fractionation gave 2.5 g (40%) of octahydroindole V with bp 41-42°C (2 mm) and n_D^{20} 1.4881.

LITERATURE CITED

1. B. A. Trofimov, A. S. Atavin, A. I. Mikhaleva, G. A. Kalabin, and E. G. Chebotareva, Zh. Org. Khim., 9, 2205 (1973).
2. B. A. Trofimov, S. E. Korostova, L. N. Balabanova, A. I. Mikhaleva, and A. N. Vasil'ev, Khim. Geterotsikl. Soedin., No. 2, 215 (1976).

3. R. G. Rice and E. J. Kohn, J. Am. Chem. Soc., 77, 4052 (1955).
4. R. G. Rice, E. J. Kohn, and L. W. Daasch, J. Org. Chem., 23, 1352 (1958).
5. H. Booth and F. E. King, J. Chem. Soc., No. 8, 2688 (1958).
6. M. Kojima and Y. Tomioka, Yakugaku Zasshi, 95, 889 (1975).
7. L. R. Kray and N. G. Reinecke, J. Org. Chem., 32, 225 (1967).
8. B. A. Trofimov, N. I. Golovanova, A. I. Mikhaleva, S. E. Korostova, A. N. Vasil'ev, and L. N. Balabanova, Khim. Geterotsikl. Soedin., No. 7, 915 (1977).
9. H. R. Billica and H. Adkins, J. Am. Chem. Soc., 70, 695 (1948).
10. B. A. Trofimov, A. I. Mikhaleva, A. N. Vasil'ev, and M. V. Sigalov, Khim. Geterotsikl. Soedin., No. 1, 54 (1978).

PYRROLES FROM KETOXIMES AND ACETYLENE

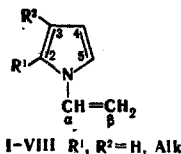## III.* CONJUGATION IN 2-ALKYL- AND 2,3-DIALKYL-1-VINYLPYRROLES AND THEIR ^{13}C NMR SPECTRA

B. A. Trofimov, M. V. Sigalov,
V. M. Bzhezovskii, G. A. Kalabin,
A. I. Mikhaleva, and A. N. Vasil'ev

UDC 541.67:547.741:543.422.25

The ^{13}C NMR spectra of eight 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles were studied. The ^{13}C chemical shifts of all of the carbon atoms of the ring and the vinyl group depend substantially on the position and structure of the alkyl substituent. As the branched character of the alkyl group in the 2 position increases, the signal of the β-carbon atom of the vinyl group is shifted to weak field due to weakening of the p–π conjugation in the N-vinyl group because of disruption of its coplanarity with the pyrrole ring. The conjugation between the double bond and the pyrrole π system involves competition for possession of the p electrons of the nitrogen atom.

Detailed information regarding the electronic and conformation structures of pyrroles is necessary for a better understanding and prediction of their chemical behavior and physicochemical properties. However, up until recently the accumulation of this sort of information was deterred by the fact that it was difficult to obtain sufficiently representative series of substituted pyrroles. Systematic studies in this direction became possible after the discovery of the reaction of ketoximes with acetylene [2, 3], which makes it possible to easily obtain variously substituted pyrroles, including the previously unknown 1-vinyl-pyrroles.

The chemical shifts (CS) in the ^{13}C NMR spectra can be used to estimate the total and π-charge densities on the carbon atoms and particularly changes in these values [4, 5]. In the present research we studied the dependence of the ^{13}C CS of 1-vinylpyrroles I-VIII on the position and structures of the alkyl substituents (R^1 and R^2) in the hope of achieving a more thorough analysis of the nature of the mutual effect of the double bond and the pyrrole ring, the character of the p–π conjugation in the N-vinyl group, the transmission of the substituent effects through the pyrrole nitrogen atom, and the relative orientation of the π systems.

I-VIII R^1, R^2= H, Alk

*See [16] for communication II.