

COMMUNICATIONS

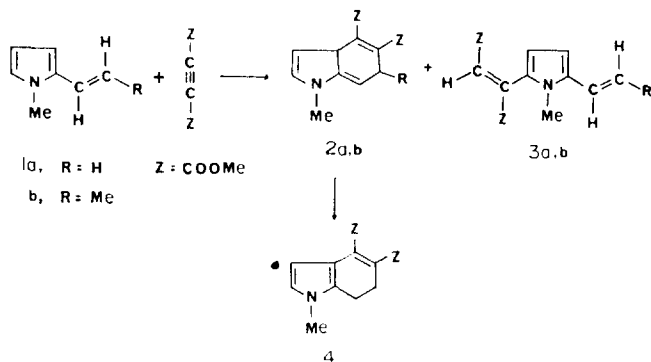
LETTERS

Preparation of a 3a,6-Dihydroindole from an Alkenylpyrrole

Chang Kiu Lee

Department of Chemistry, Kangweon National University, Chuncheon 200, Korea (Received September 24, 1983)

Vinylpyrrole has an interesting structural characteristics. Besides the fact that it is a heterocyclic aromatic compound it has two diene systems consisting of conjugated double bonds in the ring and of side chain and one of the ring double bonds. The latter diene system has been subjected to investigation if [4+2] addition with suitable dienophiles would give 3a,6-dihydroindoles (*e.g.* **2**) which would be converted to indole derivatives. An extensive investigation has been going on in this laboratory to prepare 3a,6-dihydroindole skeleton *via* [4+2] addition of vinylpyrroles with dimethyl acetylenedicarboxylate (DMAD).^{1,2} Though an example of isolation of a dihydroindole was reported with dimethyl 1-(2,6-dimethylphenyl)-2-pyrrolylmalate and DMAD,¹ compounds of this type usually undergo aromatization to indole derivatives.²⁻⁵ Jones and his coworkers reported that 2-ethenyl-1-methylpyrrole (**1a**) gave a 6,7-dihydroindole (**4**) when it was refluxed in CHCl₃ with DMAD at 80°C.³ But at room temperature a Michael-type adduct **3a** was formed.⁴ The formation of **4** can be explained by an [1,3] H-shift from **2a** to produce aromatization of pyrrole ring. Here we report the first example of a 3a,6-dihydroindole synthesis from a simple 2-(alkenyl)pyrrole and its structural establishment.



1-Methyl-2-(*E*-1-propenyl)pyrrole (**1b**) was prepared *via* Wittig reaction of 1-methyl-2-pyrrolicarboxaldehyde with ethyltriphenylphosphonium iodide. When **1b** and DMAD (1:2 by mole) were refluxed in ether for 38 h yellow viscous solution resulted. The solution was chromatographed on preparative TLC plates (silica gel; benzene) to separate two

products, **2b**⁸ (40 %, $R_f = 0.19$) and **3b**⁸ (37 %, $R_f = 0.39$) as yellow liquids. The NMR spectra (CDCl₃) of **2b** and **3b** are shown together with that of **4**⁶ in Figure 1.

The doublet at δ 1.88 in the spectrum of **2b** is a definite indication of a structure which should have 3a,6- or 6,7-dihydroindole moiety. In order to be the latter the pyrrole ring protons should show an AB pattern as shown in the spectrum of **4**. However, a much complexed splitting in the region of δ 5.8–6.5 with total of four protons appears to be consistent with the structure **2b**. Furthermore, UV spectrum showed a rising end absorption at 230 nm indicating the lack of conjugation.

The Michael-type adduct **3b** which was formed together with the Diels-Alder adduct **2b** also showed NMR spectrum consistent with the structure. The methyl protons in the propenyl group appeared as a double doublet at δ 1.88 with $J=7.0$ Hz for vicinal coupling and with $J=1.5$ Hz for *w* coupling. The *trans* proton peaks ($J=12.0$ Hz) splitted further by the methyl group which appeared in the region of δ 5.4–6.4. The chemical shifts of protons at C-3 and C-4 of pyrrole ring appeared at δ 6.22 as a singlet while that of fumarate proton appeared at δ 6.92.⁷ The extended conjugation seemed to be a clear cause to the bathochromic shift in the UV absorption from 271 nm for **1b** to 330 nm for **3b**.

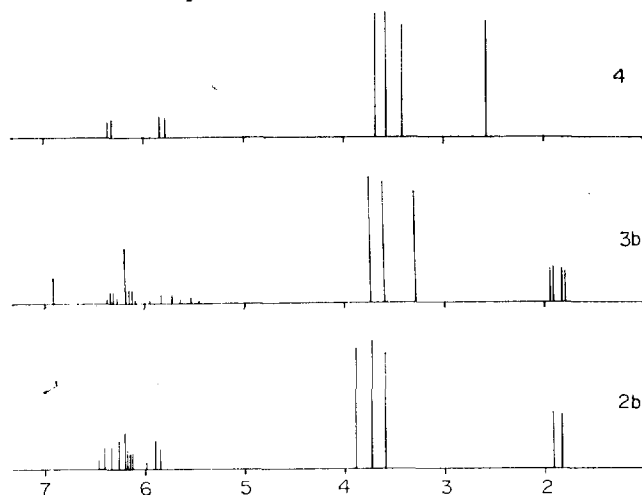


Figure 1. NMR spectra of **2b**, **3b**, and **4** in CDCl₃.

The structural requirement in vinylpyrroles and the reaction condition for the formation of 3a,6-dihydroindole compounds are currently under investigation in this laboratory.

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- (6) This compound was prepared independently in this laboratory and its spectra are consistent with values reported in the literature (reference 3).
- (7) W. E. Noland, C. K. Lee, *J. Org. Chem.*, **45**, 4573 (1980).
- (8) Other spectral data: **2b**; IR (neat) 3050 w, 2975 w, 2825 w, 1730 vs, 1620 m, 1445 ms, 1300 s, 1160 s, 1010 s, 820 ms cm^{-1} ; mass spectrum, m/e (%) 263 (5, M^+), 261 (12), 232 (20), 204 (52), 203 (100), 202 (98), 188 (24). **3b**; IR (neat) 3030 w, 2975 w, 2820 w, 1748 s, 1685 s, 1612 ms, 1450 ms, 1275 ms, 1035 m, 970 s, 800 ms cm^{-1} ; mass spectrum, m/e (%) 263 (24, M^+), 232 (96), 204 (100), 203 (94), 172 (21), 145 (15).

Sigmatropic Hydrogen Rearrangements in the Gas-Phase Decarboxylation and Isomerization of But-3-enoic Acid

Ikchoon Lee[†] and Jeoung Ki Cho

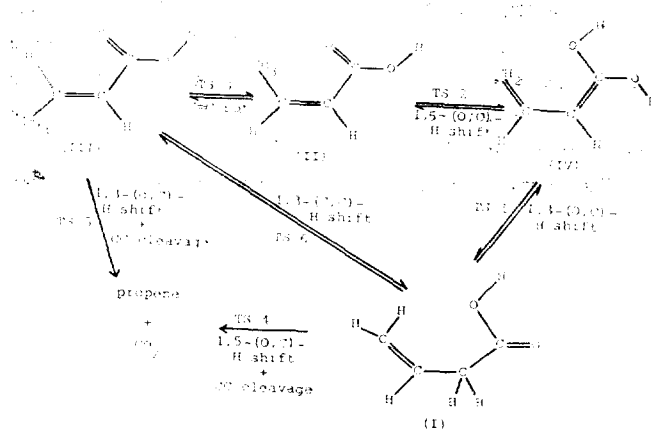
Department of Chemistry, Inha University, Incheon 190, Korea (Received June 25, 1983)

Sigmatropic rearrangements have attracted considerable interest in recent years, especially in connection with orbital symmetry rules.¹ A number of quantitative studies at both the semiempirical² and *ab initio*³ levels of MO calculations using simple model compounds have been reported. The calculated barriers for the rearrangements have shown that 1,3-hydrogen shifts are in general considerably higher than 1,5-H shifts⁴ in agreement with expectations based on orbital-symmetry considerations.

The gas-phase decarboxylation and isomerization of but-3-enoic acid (I) provide a very interesting and convenient example in which various types of such sigmatropic hydrogen rearrangements are involved. Experimental studies on these processes¹ have led to the following conclusions: (a) direct interconversion of the acid (I) and its isomer crotonic acid (III) is a negligibly slow process, proceeding only *via* the intermediacy of the enolic form (IV) and isocrotonic acid (II); (b) direct decarboxylation occurs only from (I).

In this work we report the MO theoretical thermodynamic energy profile obtained for the complex system, scheme 1, where the specific types of process involved in each transition state (TS) are shown.

All geometries were optimized and heats of formation were calculated using MINDO/3 RHF method.⁵ Transition state geometries were deduced by fixing the forming and breaking



Scheme 1.

bonds at the appropriate lengths varying in steps of 0.005 Å and minimizing the energy of the system with respect to the remaining variables. Smoothed plots were obtained by quadratic interpolation.

All the TS (1-6), except the TS3 where a double-bond rotation is involved, had some types of sigmatropic hydrogen rearrangements.

In view of the considerable barrier height differences involved according to the terminal atoms to which the moving hydrogen is simultaneously bonded,^{3d} introduction of a notation specifically designating the two atoms is convenient;