Tetrahedron Letters No.60, pp. 5239-5242, 1969. Pergamon Press. Printed in Great Britain.

N-CARBETHOXYLAZONIN; THERMAL AND PHOTOCHEMICAL BOND RELOCATION

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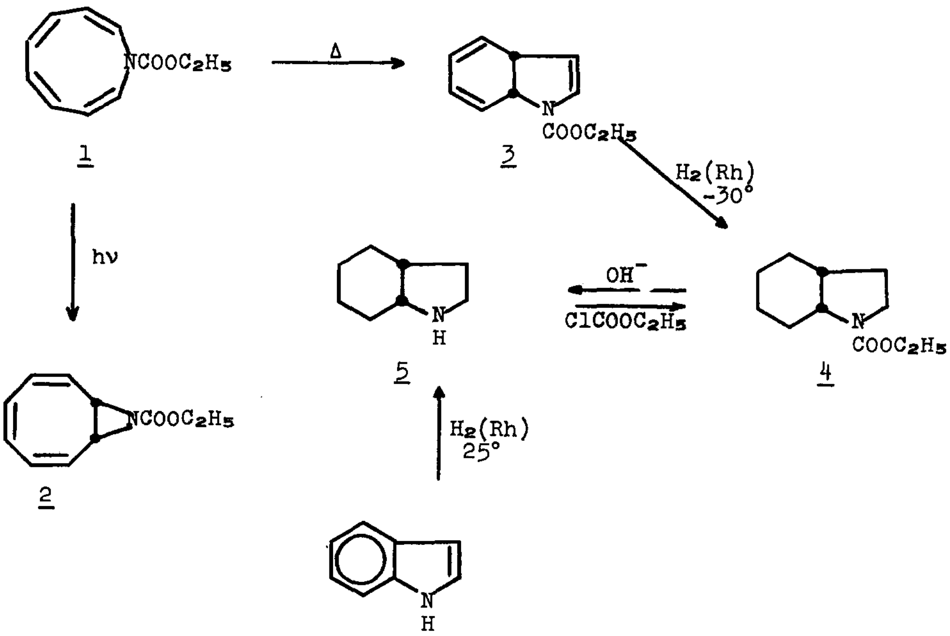
(Received in the USA 10 November 1969; received in the UK for publication 1 December 1969)

Recently we described the synthesis and isolation of N-carbethoxylazonin (1) (1). We presently relate additional information regarding this 10 π-electron heteromonocycle including a detailed description of both its thermally and photochemically induced skeletal rearrangement.

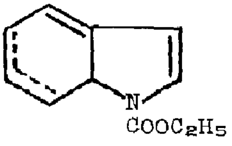
As we previously pointed out (1) the azonin, 1, is readily accessible through sensitized low temperature photolysis of its valence tautomer 2. Careful column chromatography of the resulting crude photolysate on neutral aluminum oxide at *ca.* -15° furnishes pure 1 as a colorless mobile liquid. This substance is characterized by the uniquely consistent nmr signals we already recorded (1) and displays u.v. absorption at $\lambda_{max}^{C_6H_{14}}$ 220 nm (ε 9000), 270 (sh) (2200).

At ambient temperature 1 suffers specific and irreversible bond relocation to N-carbethoxyl-8,9-dihydroindole, 3, which displays nmr signals ($CDCl_3$) centered at τ 3.33 (1 H multiplet), 4.20 (4 H multiplet), 4.95 (1 H doublet, J ~ 15 cps), 5.07 (1 H multiplet), 6.07 (1 H broad doublet, J ~ 15 cps) as well as quantitatively consistent ethyl absorption. Upon monitoring the thermal rearrangement of 1 quantitatively (2), we obtained $\Delta H^{\ddagger} = 22.0 \pm 1$ kcal/mole; $\Delta S^{\ddagger} = -4.9$ eu. Comparing these activation parameters to those associated with the analogous thermal reorganization of all-*cis* cyclonona-1,3,5,7-tetraene (all-*cis* CNT) (3,4) and of oxonin (5,6), we conclude that 1 is slightly *less* thermally stable than the former but decidedly more resistant to heat than the latter. Specifically, we estimate k (oxonin):k (1):k (CNT) ~ 14:1.2:1 at 20°.



In terms of stereochemistry, the most revealing feature in the nmr spectrum of 3 is the degree of splitting within each of the two doublets centered at τ 4.95 and τ 6.07 which undoubtedly arise from the tertiary protons bound to C_8 and C_9 respectively. The coupling constant in question is quite substantial (~ 15 cps) and obviously is more in keeping with a *trans* than with a *cis* disposition of the two key protons. Nevertheless, careful catalytic (Rh/C) hydrogenation of 3 at *ca.* -30° produced, in *ca.* 90% yield, a perhydro derivative 4 unquestionably identical (gc, ir, nmr) with an authentic sample prepared from reaction of *cis*-8,9-octahydroindole, 5 (7), with ethyl chloroformate. Additionally, basic hydrolysis of 4 obtained from 3 led exclusively to *cis*-8,9-octahydroindole positively characterized through its known (7) picrate and picrolonate derivatives (mp, mmp). Also, admixture of the picrate of 4 with that derived from *trans*-8,9-octahydroindole (8) produced the reported (7) melting point depression.

Finally, in order to securely infer the stereochemical features of 3 from those of its fully hydrogenated counterpart (4) it was necessary to demonstrate that stereochemistry is indeed preserved in the course of the hydrogenation. Obviously, stereochemical detail will be lost in part or in full in the event 3 rearranges to 6, 7 or 8 either prior to or during hydrogenation. The possibility that 3 isomerizes prior to treatment with molecular hydrogen was dismissed upon quantitative recovery of this material after being stirred in ether for several hours in the presence of substantial amounts of the catalyst employed for the reduction. In addition, strong suggestive evidence that 3 does not, in all likelihood isomerize during hydrogenation derives from reduction of this substrate with D_2 instead of hydrogen. This led to the quantitative incorporation of six deuterons into the molecule (parent ion at m/e = 203). Nmr analysis of this $C_{11}H_{13}D_6NO_2$ substance established the presence of exactly two protons α to nitrogen. This key feature of hexadeutero-4 is entirely consistent with the notion that reduction of 3 occurs without rearrangement (9). Therefore, our inference of the stereochemical features of 3 from those of 4 appears to be justified.



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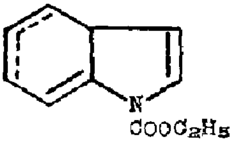

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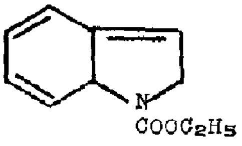

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Contrasting the thermal rearrangement, direct illumination of a cold (*ca.* 0°) ethereal solution of 1 produces 2.

In brief conclusion we point that both structural reorganizations of N-carbethoxylazonin described herein occur entirely as predicted (10) by the

Woodward-Hoffmann symmetry rules.

Acknowledgement. We are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work. We also thank Badische Anilin und Soda-Fabrik for a generous gift of cyclooctatetraene.

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2. The rearrangement was monitored by nmr spectroscopy in $CDCl_3$ solvent. Three first order rate constants were evaluated in the temperature range of 23.5° to 42°.
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8. We thank Dr. Harold Booth for a sample of the picrate of *trans*-8,9-octahydroindole.
9. To be sure, the result of the deuteronation experiment is also consistent with reduction of **3** by way of a. **6**, b. an equimolar mixture of **7** and **8**, c. an equimolar mixture of **6**, **7** and **8**. Neither of these alternatives appears attractive to us, for there is no compelling reason as to why **3** should isomerize to a single substance (case a) or if a variety of isomers are indeed produced why should these be present in equimolar quantities (cases b and c).
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