

1-H AZONIN

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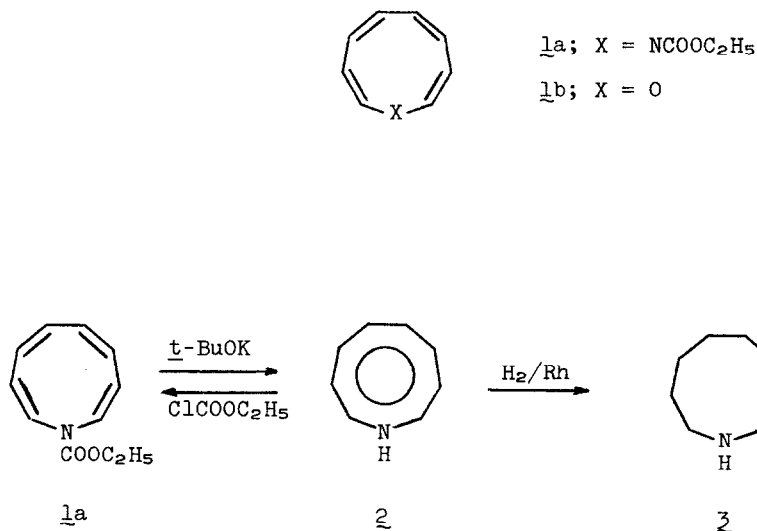
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RECENTLY, we reported the first synthesis of N-carbethoxylazonin¹ (1a) and of oxonin² (1b). We now describe the synthesis and certain key characteristics of parent azonin (2).

The title compound was prepared on brief low-temperature contact of 1a with potassium t-butoxide in tetrahydrofuran. This treatment leads to the quantitative consumption of the urethane (1a) and the formation of a new substance which was isolated in essentially pure form upon removal of all volatile constituents³ at -20° and 0.025 mm. The nmr spectrum (CDCl₃; +10°) of this product remains unchanged within the temperature range⁴ of -50° to +35° and consists of a doublet of doublets centered at τ 2.85 (2H; J = 8 Hz, 10 Hz); a narrow multiplet centered at τ 3.27 (4 H) and a broad multiplet extending from τ 3.92 to τ 4.25 (2 H). Catalytic hydrogenation (1 atm., Rh/C; 0°) of the substance in question produced azacyclononane (3) entirely identical (ir; mass spectrum)⁵ with an authentic sample. In addition, treatment of the initial alcoholysis product with ethyl chloroformate at ca. -15° led to the exclusive regeneration of N-carbethoxylazonin, identified by its nmr spectrum⁴ determined at -45° and +10°. Clearly, the combined spectral and chemical information serves to identify the product under consideration as the parent azonin (2).

A very central question with regards to the heteronins and one which primarily motivated our successful synthesis of certain choice members of the

family concerns their potential aromatic character. We already commented on 1a^{1,6} and 1b^{2,7} in this connection and stressed that these substances are best regarded as classical polyenes. Presently, we furnish pertinent evidence which serves to effectively classify azonin (2) as "aromatic".



First, we note that all resonances in the nmr spectrum of 2 appear at considerably lower field² than their counterparts in the spectrum of either 1a or 1b. Specifically, we calculate the following downfield shifts on going from N-carbethoxylazonin to azonin: $\Delta\delta(\alpha) = 43$ Hz, $\Delta\delta(\beta) = 30$ Hz and $\Delta\delta(\gamma\delta) = 49$ Hz. No doubt, the overall displacement of the nmr spectrum of 2 to lower field results from the presence of a fairly sizeable diamagnetic ring current within this molecule.⁸ A second necessary condition for aromaticity is, of course, thermodynamic stability. We note in this context that, while extremely reactive⁹, azonin is quite stable thermally when stored in an inert environment. For example, the nmr spectrum of a rigorously purged (He) solution of 2 in acetone-d₆ undergoes no detectable qualitative or quantitative changes on heating for 2 hr at 34° followed by 1 hr at 50°. In striking contrast, 1a and 1b thermally

reorganize quite rapidly at ambient temperature.^{6,7}

Finally, in brief summary, we stress that all presently available information requires that azonin be termed "aromatic". Not unexpectedly, the relative stability of our three heteronins increases with decreasing effective electronegativity of the hetero atom. We are actively pursuing work in this area.

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REFERENCES AND REMARKS

- (1) A. G. Anastassiou and J. H. Gebrian, J. Am. Chem. Soc., **91**, 4011 (1969).
- (2) A. G. Anastassiou and R. P. Cellura, Chem. Comm., 903 (1969).
- (3) Significantly, the volatile portion consisted entirely of di-*t*-butyl carbonate (ir., nmr., mass spectrum).
- (4) The nmr spectrum of 1a undergoes radical and characteristic changes at temperatures below ca. -10°; A. G. Anastassiou, R. P. Cellura and J. H. Gebrian, Chem. Comm., in press.
- (5) Collected gas-chromatographically. G. c analysis also served to establish the absence of the urethane of 3 which would have been formed had any unreacted 1a been present in the initial reaction mixture.
- (6) A. G. Anastassiou and J. H. Gebrian, Tetrahedron Letters, in press.
- (7) A. G. Anastassiou and R. P. Cellura, Chem. Comm., 1521 (1969).
- (8) The effect of this induced ring diamagnetism becomes all the more striking when one considers that 2 contains the most effective electron-donor of the three hetero-atoms. It follows that this molecule should possess the most electron rich π frame and consequently, that its protons ought to resonate at higher field than those of either 1a or 1b. The observed downfield shift thus attests to the "aromatic" character of 2.
- (9) The molecule immediately decomposes on exposure to air.