

The Question of *quasi*-Enamine Reactivity of Aminocyclopropanes. Rearrangement of Isomeric 1-(Morpholino)-7-chloro-7-phenylbicyclo[4,1,0]heptanes

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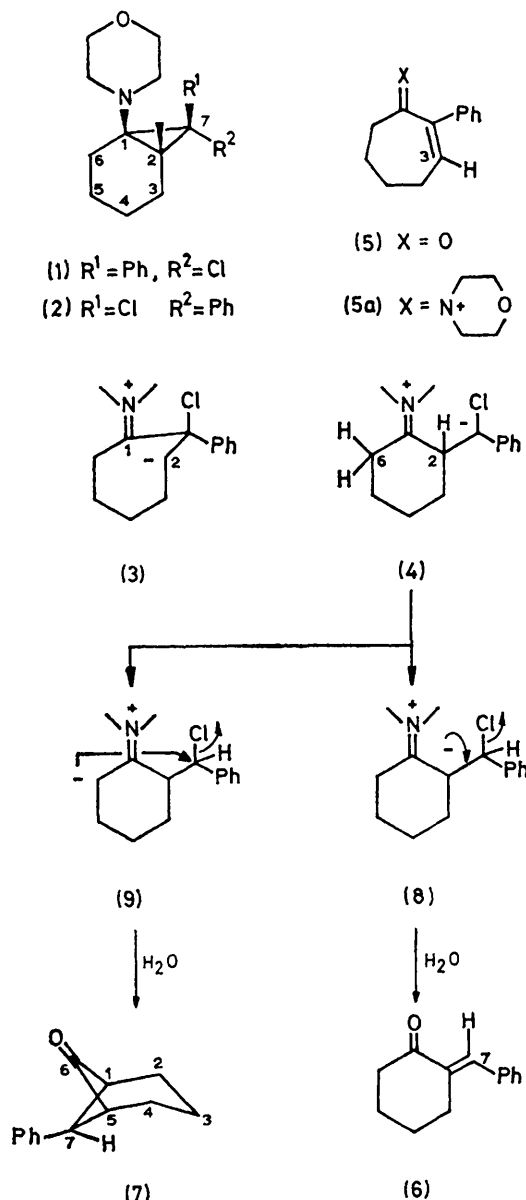
Summary Comparison of the course of thermal rearrangement of isomeric chlorobicycloheptanes (1) and (2) reveals that the formation of products from (2) can be interpreted in terms of "*quasi*-enamine" reactivity.

In the light of the known *quasi*-double bond character of the cyclopropane ring it is an interesting question whether suitable aminocyclopropanes can display a "*quasi*-enamine" reactivity. An essential feature of such reactivity would be the involvement of the nitrogen electron-pair in initiating the ring opening of the cyclopropyl system. The thermal ring-opening of cyclopropanes, comprising a cyclopropyl $\rightarrow$ allylic-cation transformation, constitutes a disrotatory electrocyclic process, permitted by the orbital-symmetry rules.¹ The course of thermal rearrangement of stereo-isomeric 1-(morpholino)-7-chloro-7-phenylbicyclo[4,1,0]heptanes (1) and (2) would be expected to provide information on the subject of *quasi*-enamine character of aminocyclopropanes. If the ring-opening reaction is initiated by a nucleophilic relay of the nitrogen *p*-electrons, to result in the formation of dipolar intermediates (3) or (4), little or no difference would be anticipated between the behaviour of the two isomers. On the other hand, rearrangement based upon the orbital-symmetry conservation principle should allow ring-opening in the case of *endo*-isomer (1), but not in that of *exo*-isomer (2).

The bicycloheptanes (1) and (2) were obtained as crystalline products by addition of phenylchlorocarbene to 1-(morpholino)cyclohexene. *endo*-Chloro isomer (1) exhibits considerable shielding of the morpholine methylene protons [δ (CDCl₃) 2.37, m, $-\text{CH}_2-\text{N}-\text{CH}_2-$; 3.42 p.p.m., m, $-\text{CH}_2-\text{O}-\text{CH}_2-$] consistent with *cis*-stereochemistry of the benzene and morpholine rings. The morpholine protons of (2) resonate at normal δ values: 2.79, m, $-\text{CH}_2-\text{N}-\text{CH}_2-$; 3.75, t, $-\text{CH}_2-\text{O}-\text{CH}_2-$.

When a solution of (1) in pyridine was refluxed for 2 h, it was quantitatively converted (after hydrolysis) into 2-phenylcycloheptene-2-one. Under similar conditions isomer (2) was unaffected. The formation of (5) can be readily accounted for in terms of a disrotatory ring-opening of (1), leading to iminium ion (5a), which serves as a precursor of ketone (5). The fact that (2) remains entirely unchanged, implies the non-involvement of the nitrogen electron-pair, under the aforementioned conditions, in initiating the C(1)-C(2) bond cleavage.

When (2) was subjected to prolonged heating (refluxing pyridine, 45 h), the reaction mixture, after hydrolysis, was found to contain (6) (70%), (5) (20%), and (7) (10%) (g.l.c. and spectral analysis). The *exo*-phenyl configuration of (7) rests upon the chemical shifts of C(2)*H*₂ and C(4)*H*₂: δ 2.49 p.p.m., td, which, in analogy to a model bicyclo[4,1,0]heptane-6-one system,² do not exhibit a shielding influence by the phenyl group, expected for the *endo*-phenyl isomer. Furthermore, the C(7)*H* resonates at a field typical for a tertiary benzyl proton (δ 3.12 p.p.m., t), lacking the diamagnetic influence of the carbonyl function.



The formation of (5)–(7) from (2), is of considerable mechanistic interest. Since a pathway involving an electrocyclic ring opening is sterically prohibited to (2), the system, under forcing reaction conditions, invokes a *quasi*-enamine reactivity, resulting in a second mode of ring opening leading to dipolar intermediates (3) and (4). While (3) is the obvious precursor of (5), (4) leads to ketones (6) and (7) *via* loss of chloride ions from enamines (ionic structures) (8) and (9), respectively. It is noteworthy that the *quasi*-enamine ring opening of (2), reflected in the relative amounts

of (5) versus (6) and (7), is consistent with the preferred C(1)–C(7) bond cleavage leading to resonance stabilized intermediate (4).

The work was carried out in part under auspices of the

Netherlands Foundation for Chemical Research (SON) and with financial support from the Netherlands Organization for Advancement of Pure Research (ZWO).

(Received, 9th March 1972; Com. 391.)

¹ R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie GmbH, Weinheim, 1970, p. 56.

² G. Brieger, D. L. Hachey, and D. Ciaramitaro, *J. Org. Chem.*, 1969, **34**, 220.