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THE ISOMERIZATION OF HYDROGENATED ADDUCTS OBTAINED FROM 1,4-PHTHALAZINEDIONE

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The hydrogenated adducts obtained from 1,4-phthalazinedione with 1-vinylcyclohexene I and 1-vinylcyclopentene III, are isomerized with concentrated sulfuric acid to give the spiro-compounds II and IV respectively by contraction of ring C.

This ring contraction also takes place in the hydrogenated adducts X, XII, XIV and XVI corresponding to 1,3-pentadiene, 2-methyl-1,3-pentadiene and 2,4-hexadiene derivatives and it does not occur in the hydrogenated adducts of isoprene and 2,3-dimethylbutadiene derivatives XVIII and XIX.

In all the cases we have studied, the isomerization takes place when of the two carbon atoms involved in the ring contraction, the adjacent to the nitrogen atom is substituted, being not necessary any substitution on the other carbon atom.

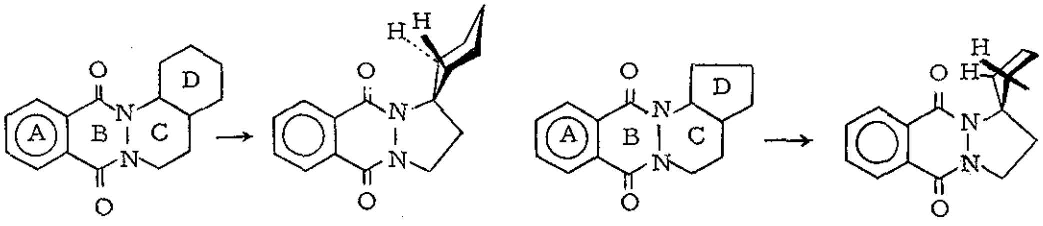
The mechanism of the reaction is discussed.

In previous papers[1,2] we have described the synthesis of compounds I and III by means of catalytic hydrogenation of the adducts obtained from 1,4-phthalazinedione with 1-vinylcyclohexene and 1-vinylcyclopentene, respectively.

Now, we wish to report on the isomerization of these compounds.

Treatment of I with concentrated sulfuric acid at 100° C for a half hour, affords a spiro compound II, in 90 % yield, m.p. 160-161° C (from cyclohexene), m/e 270 (M^+).

In a similar way, compound III led to IV in 50 % yield, m.p. 110-111° C (from cyclohexene), m/e 256 (M^+).



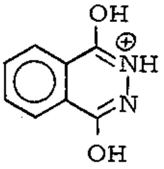
I II III IV

The structures of the new spiro compounds II and IV were ascertained[3] on the basis of the ^{1}H nmr and mass spectra. The nmr spectrum of II shows two multiplets at 7.6 - 8.3 ppm and 1.0 - 2.1 ppm corresponding to aromatic protons and eight protons of the cyclohexane ring, respectively.

The most characteristic features of the structure II are as follows. The presence of two triplets corresponding to the methylenic group of the pyrazolidine ring is observed at 4.1 and 2.3 ppm. The coupling constant between these methylenic groups shows to be ≃7 Hz. On the other hand, it is observed a deshielding of the axial protons of the cyclohexane nearest to the spiranic carbon compared with the rest of the protons of this ring. These two protons appear as a multiplet at 2.9 ppm. Two of the splittings of this signal must be due to a geminal coupling (J = 11.9 Hz) and an axial-axial coupling (J = 8.9 Hz).

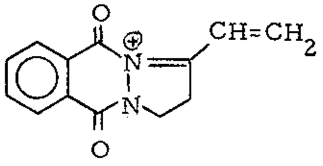
Similarly, the nmr spectrum of IV shows the two characteristic triplets corresponding to the two methylenic groups of the pyrazolidine ring at 4.25 and 2.32 ppm (J = 7 Hz), and a multiplet at 2.7 ppm due to two of the axial protons nearest to the spiranic carbon, which are deshielded in comparison with the other six protons of the cyclopentane ring (broad multiplet at 1.4 – 2.5 ppm).

In the mass spectra of II and IV the base peak at m/e = 163 (V) as well as the peak at m/e = 227 (VI) are common in both spectra. The latter peak can be explained from the corresponding molecular ions, m/e = 270 and m/e = 256 by loss of a propyl and an ethyl radical, respectively.



m/e = 163

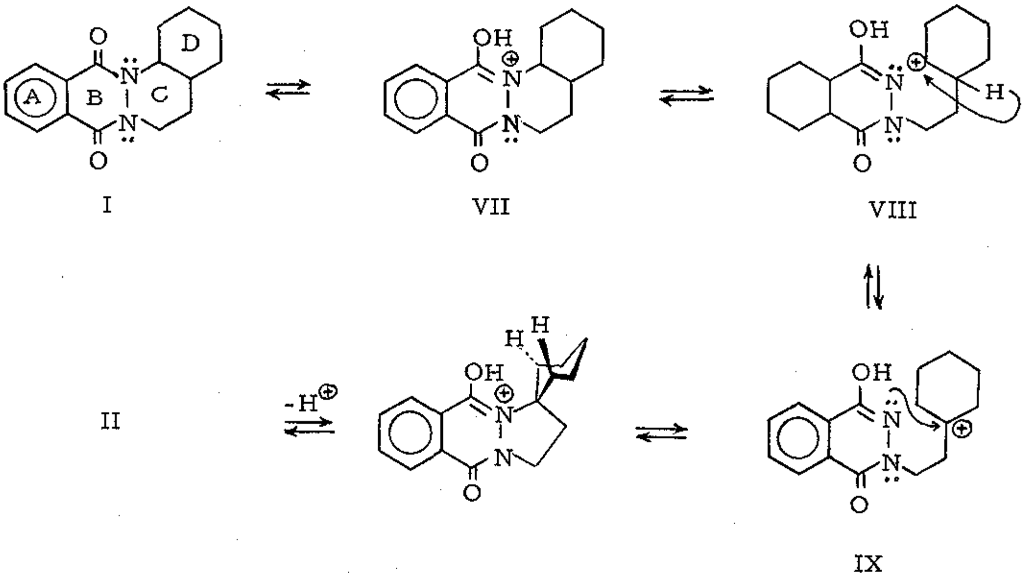
V



m/e = 227

VI

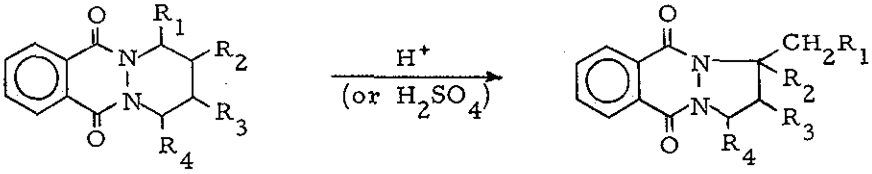
The isomerization with sulfuric acid can be explained by means of an ionic mechanism through the following equilibria.



Protonation of I led to the secondary carbonium ion VIII which is isomerized to the more stable tertiary carbonium ion IX. Cyclization of IX led to the spiranic structure II.

The same mechanism as above explains the formation of IV from III.

This kind of contractions has also been observed in the hydrogenated adducts[4] (X, XII, XIV and XVI), which after treatment with sulfuric acid yield the 1,2-phthaloyl-3-ethylpyrazoline derivatives: XI, m.p. 112-114° C, m/e = 244 (M^+), in 98 % yield; XIII, m.p. 98-100° C, m/e = 230 (M^+) in 65 % yield; XV, m.p. 92-94° C, m/e = 244 (M^+), in 45 % yield, and XVII, m.p. 102-104° C, m/e = 244 (M^+), in 98 % yield.



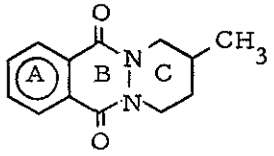
X and XI: $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
XII and XIII: $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
XIV and XV: $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
XVI and XVII: $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$

It should be noted that, in a similar way to the cases indicated above, the rearrangement of compound X implies the formation of a tertiary carbonium ion from a secondary one. However, the rearrangement of compounds XII, XIV and XVI must occur through secondary carbonium ions.

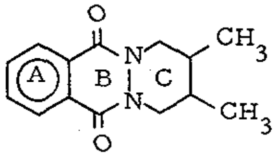
The more noticeable feature of the nmr spectra of compounds XI, XIII, XV and XVII is the presence of signals corresponding to the ethyl group.

On the other hand, the presence of the ethyl group is clearly confirmed from the mass spectra of these compounds, since in all the cases the base peaks m/e 201 from XIII and m/e 215 from XI, XV and XVII are originated by loss of an ethyl radical (M-29).

Finally, when the compounds XVIII and XIX were treated with concentrated sulfuric acid under the same conditions as before, no isomerization could be observed and the starting material was recovered.



XVIII



XIX

From all these experiments we can deduce that the required condition for the rearrangement is that, of the two carbon atoms involved in the ring contraction, the adjacent to the nitrogen atom must be substituted.

REFERENCES

1. M. F. Braña, M. Lora-Tamayo, P. Navarro and J. L. Soto, Tetrahedron Letters, 1969, 20, 1523-1526.
2. M. F. Braña, M. Lora-Tamayo, P. Navarro and J. L. Soto, An. Quím., 1972, 68, 523.
3. Satisfactory elemental analyses were obtained for all the new compounds.
4. M. D. Romero, Doctoral Thesis, University of Madrid, 1975.

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