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CONTRAST OF PHOTOCHEMICAL AND PYROLYTIC MODELS FOR MASS SPECTRAL FRAGMENTATION. DEALKYLATION OF N-ALKYL-2,4-DIPHENYLPYRROLES.

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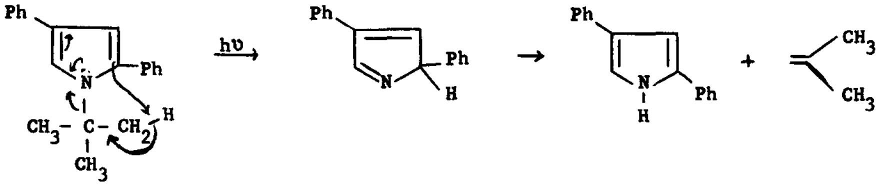
Recent studies have shown that useful empirical correlations exist between the unimolecular reactions induced by electron impact and the thermal or photochemical decompositions of organic molecules.[1-6] In order to explore further the potentiality of using the mass spectrum of a compound as a basis for predicting its thermal and photochemical behavior, we have undertaken a comparative study using N-alkyl-2,4-diphenylpyrroles as model systems.

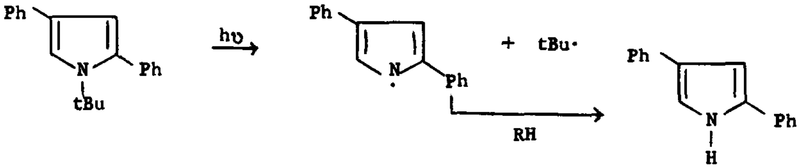
The mass spectrum of N-t-butyl-2,4-diphenylpyrrole(I),[7] recorded at a probe temperature of 50°, shows that the major process in the decomposition of the molecular ion is the loss of a C_4H_8 fragment. The loss of a methyl group, which by analogy to the α-cleavage reported for other N-alkylpyrroles should be the cause of an intense ion[8,9], is insignificant. Furthermore, the loss of a C_4H_8 fragment produces an ion that is similar in structure to the molecular ion of 2,4-diphenylpyrrole itself; the intensities of the ions at lower mass bear the same proportions to the height of this peak and the ratios of metastable intensities[10] are very close.

Irradiation of N-t-butyl-2,4-diphenylpyrrole(I) in dilute alcohol solution with a low pressure mercury arc (2537 A° output) for one hour leads to 2,4-diphenylpyrrole(II) (95%) as the exclusive photoproduct. Solutions became light yellow on extended irradiation and a solid, intractable precipitate was formed upon removel of the solvent. The complete disappearance of 2,4-diphenylpyrrole upon prolonged exposure may be due to the further photooxidation of the pyrrole ring.[11] Independent of the nature of the excited state(s) involved, two fundamentally different types of pathway which might be invoked to rationalize this transformation are given in equations 1 and 2.

(1)



(2)



The first of these involves a concerted hydrogen atom migration from the beta carbon of the alkyl substituent, while the second involves homolytic fission of the nitrogen-carbon bond followed by hydrogen abstraction from solvent. In order to test the hypothesis that the hydrogen atom rearrangement (pathway 1) might be required for the observed dealkylation, two substituted 2,4-diphenylpyrroles, for which such a mechanism should occur, were prepared and studied.[7] Experimentally, prolonged irradiation (24 hr.) of N-cyclohexyl (III) or N-phenethyl-(IV)-2,4-diphenylpyrrole afforded only recovered starting material. This observation is not compatible with scheme 1 and instead adds credence to reaction scheme 2. Additional evidence in support of sequence 2 is obtained from the irradiation of N-benzyl-2,4-diphenylpyrrole (V). When a solution of V was irradiated with 2537 A° light for 30 min. an 80% yield of II was obtained. The ease of bond cleavage in pyrroles I and V and the photostability of pyrroles III and IV are in accord with known trends in radical reactions based on the stabilities of the respective radicals formed. Pyrolysis of I at 310° gave II and isobutylene in high yield. The other pyrroles were inert under comparable reaction conditions.

Since both the photolysis and pyrolysis of I give II and isobutylene, it is tempting to hypothesize that a relationship exists between the unimolecular reactions of ions in the mass spectrometer and the photochemical and thermal behavior in solution. This analogy should be viewed cautiously, however, for even though there appear to be similarities between the fragmentation patterns in the mass spectrum and in solution, the observations described above seriously weaken hopes for establishing general quantitative correlations of broad predictive value. In the first place, the loss of the C_4H_8 fragment on electron impact cannot be explained by loss of C_4H_9 followed by a gain of hydrogen atom, since mass spectral decompositions are unimolecular. Even if one choses to view the mass spectral reaction as an abstraction of hydrogen from C_4H_9 in concert with its departure, there is still a great deal of difficulty in reconciling the mass spectral behavior of the other N-alkyl compounds with their photochemical and thermal stability.

It is clear that the reactivities of a related set of pyrroles are poorly correlated by either of these models and that quantitative correlations with model systems are of little value in this series. This is in contrast to other well-established systems where good correlation with solution chemistry is observed.[12] Apparently, the reactivities of these systems involve an interplay of radical stability and steric demand. No useful comparisons exist between solution and electron impact chemistry for the evaluation of effective steric requirements; such studies are currently in progress in our laboratory. In this respect it is of interest to note the low voltage fragmentation patterns of these compounds. The loss of cyclohexene becomes progressively less important relative to the loss of isobutylene in III and I as the voltage is reduced, and the appearance potential of the m/e 219 peak is some two volts greater in III than in I. Thus the pyrolytic analogy is more secure at low voltage than at normal ionizing voltages. The deviation from correspondence at high voltage suggests that for alkyl groups effective steric requirements are a function of ionizing voltage. This may be rationalized in terms of the amount of energy transferred into vibrational modes of the molecular ion.

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References

1. N.J. Turro, D.S. Weiss, W.F. Haddon, F.W. McLafferty, J. Am. Chem. Soc., 89, 3371 (1967).
2. N.J. Turro, D.C. Neckers, P.A. Leermakers, D. Seldner, and P. D'angelo, ibid., 87, 4097 (1965).
3. M.M. Bursey, L.R. Dusold, and A. Padwa, Tetrahedron Letters, 2649 (1967).
4. D.C. DeJongh, R.Y. VanFossen, and C.F. Bourgeois, ibid., 271 (1967).
5. E.K. Fields and S. Meyerson, J. Am. Chem. Soc., 88, 2836 (1966).
6. R.F.C. Brown, D.V. Gardner, J.F. McOmie, and R.K. Solly, Aust. J. Chem., 20, 139 (1967).
7. A. Padwa, R. Gruber, and D. Pashayan, J. Org. Chem., 33, 454 (1968).
8. H. Budzikiewicz, C. Djerassi, A.H. Jackson, G.W. Kenner, D.J. Newman, and J.M. Wilson, J. Chem. Soc., 1494 (1964).
9. A.M. Duffield, R. Beugelmans, H. Budzikiewicz, D.A. Lightner, D.H. Williams, and C. Djerassi, J. Am. Chem. Soc., 87, 805 (1965).
10. T.W. Shannon and F.W. McLafferty, ibid., 88, 5021 (1966).
11. H.H. Wasserman and A. Liberles, ibid., 82, 2086 (1960).
12. M.M. Bursey and F.W. McLafferty, J. Am. Chem. Soc., 88, 529 (1966).