caffeic acid in methanol or acetic acid was irradiated[3] at 2537 or 3500 A under nitrogen no other product was detected by thin layer chromatography over polyamide (in methanol–acetic acid–water, 8:2:1) or Avicel[4] cellulose (in 15% acetic acid). When the irradiation was performed in the presence of oxygen bubbled through the solution, a third compound was formed which was easily detected by tlc because of its bright fluorescence. Its mobility was intermediate between those of the two caffeic acid isomers.

As an example, after 14-hr irradiation at 2537 A in presence of oxygen, a solution of 440 mg of caffeic acid in 120 ml of glacial acetic acid was taken to dryness under vacuum. The residue was dissolved in ethyl acetate and the caffeic acids were extracted with the minimum amount of saturated sodium bicarbonate solution. The organic phase was dried and concentrated, yielding 44 mg of a solid. This product was recrystallized from dilute methanol and was found identical in all respects with an authentic sample of esculetin (6,7-dihydroxycoumarin).[5] The same reaction was observed in dilute acetic acid or in methanol. It also took place, but more slowly, at 3500 A.

Earlier workers had noted the presence of traces of esculetin during paper chromatography of caffeic acid solutions when it was performed in the presence of light or after short ultraviolet irradiation[2,6] and its absence when the chromatography was performed in the dark.[2] The primary effect was correctly ascribed to the partial isomerization of the caffeic acid to its *cis* isomer. It was further suggested that the *cis* isomer had undergone a metal ion catalyzed air oxidation to yield esculetin. We have now observed that mixtures of the *cis*- and *trans*-caffeic acid isomers are stable and can be analyzed by thin-layer or paper chromatography in the dark without formation of the coumarin. Furthermore, no esculetin was formed when a mixture of these isomers was neutralized with sodium bicarbonate and the latter mixture was reacidified. It must therefore be concluded that the formation of esculetin from *cis*-caffeic acid is also a photochemical process.

Coumarins are widely distributed in plants, but their biosynthesis has not been firmly established. Cinnamic acids are generally considered to be precursors, undergoing a combination of *cis* isomerization, *ortho* hydroxylation and/or glucosylation, followed by lactonization.[7]

G. W. Kenner, *et al.*, have already described oxidative cyclization reactions leading from cinnamic acids to coumarins through carboxylate cations or free radicals,[8,9] but these authors suggested that it was unlikely that such reactions would compete with enzymatic processes in plants.[9]

The results herein reported strongly suggest that a photochemically induced oxidative cyclization, so easily accomplished *in vitro*, could account, at least in part, for the synthesis of coumarins from cinnamic acids *in vivo*.

Work is in progress designed to elucidate the mechanism of the reaction and to determine its relevance to the biosynthesis of coumarins.

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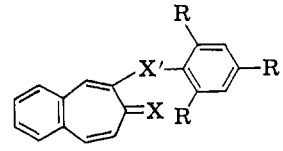
Electron Impact Induced 1,4-Phenyl Migration

Sir:

The study of electron impact induced rearrangements of substituents other than hydrogen is particularly important, not only for their contribution to mass spectral theory, but also practically for the possible limitations these rearrangements might impose on Biemann's elegant element-mapping technique.[1,2] The ejection of stable neutral molecules from the interior portion of some linear molecules with rebonding of the termini constitutes the most common type of rearrangement.[3] The other type, of which only two documented examples have been reported,[4] is the intrinsically more interesting 1,2 migration of an alkyl substituent. We now wish to describe the 1,4 transfer of an aryl group from one oxygen atom to another in a process which competes efficiently with fragmentation even at the lowest electron energies at which fragmentation occurs.

The mass spectrum of 2-phenoxy-4,5-benztropone (I, $M^+ = 248$; 100%) shows two fragment ions of substantial interest at *m/e* 231 (M − 17; 26%) and 220 (M − 28; 60%). The *m/e* 231 ion is due to the loss of –OH and the *m/e* 220 ion is due to the loss of carbon monoxide. Separate examination of carbonyl-^{18}O-labeled (II) and ether-^{18}O-labeled (III) benztropones (containing 29 and 18% of ^{18}O, respectively) shows



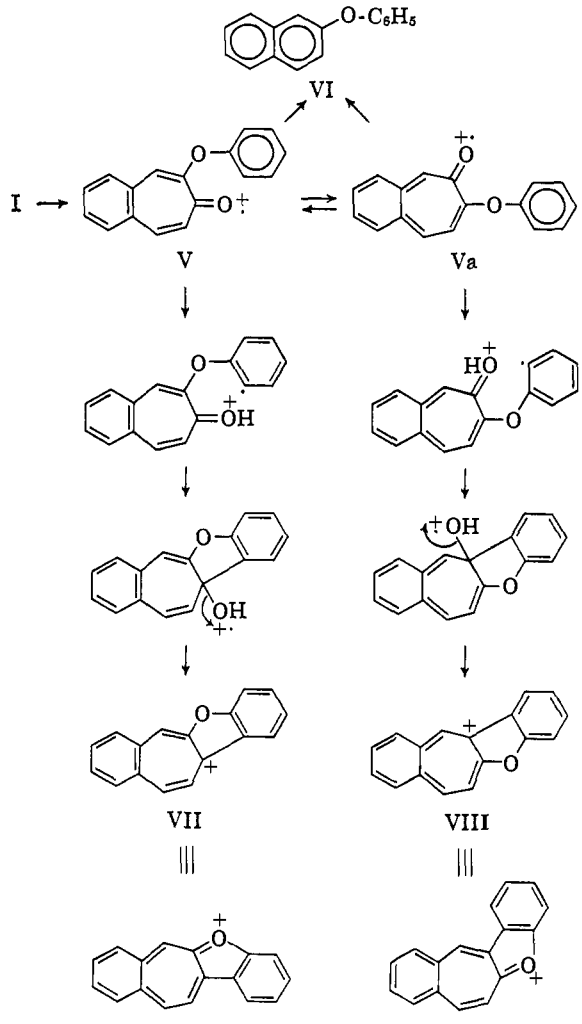
I, R = H; X = X′ = ^{16}O
II, R = H; X = ^{18}O; X′ = ^{16}O
III, R = H; X = ^{16}O; X′ = ^{18}O
IV, R = D; X = X′ = ^{16}O

(1) K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).
(2) H. Achenbach and K. Biemann, *J. Am. Chem. Soc.*, 87, 4944 (1965).
(3) (a) A. Bhati, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.*, 358 (1966); (b) J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Commun.*, 403 (1965); (c) J. O. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie, and D. H. Williams, *Tetrahedron Letters*, 4377 (1965); (d) P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S.-O. Lawesson, *J. Am. Chem. Soc.*, 87, 4559 (1965).
(4) (a) F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *ibid.*, 87, 1398 (1965); (b) C. Djerassi, A. M. Duffield, F. Komitsky, Jr., and L. Tokes, *ibid.*, **88**, 860 (1966).

(3) A Rayonet photochemical reactor from the Southern New England Ultraviolet Co., Middletown, Conn., was used in this work.
(4) (a) American Viscose Co., Newark, Del.; (b) M. L. Wolfrom, *Chem. Ind.* (London), 1065 (1964).
(5) We wish to thank Professor T. J. Mabry, Department of Botany, The University of Texas, who kindly provided this sample.
(6) C. F. van Sumere, F. Parmentier, and M. van Poucke, *Naturwiss.*, 46, 668 (1959).
(7) References to the earlier studies may be found in: (a) D. J. Austin and M. B. Meyers, *Phytochemistry*, 4, 255 (1965); (b) S. A. Brown, G. H. N. Towers, and D. Chen, *ibid.*, 3, 469 (1964); (c) T. Kosuge in "Proceedings of Symposium, Plant Phenolics Group of North America," V. C. Runeckeles, Ed., Imperial Tobacco Co., Montreal, Canada, 1964, p 83.
(8) G. W. Kenner, M. A. Murray, and C. M. B. Tylor, *Tetrahedron*, 1, 259 (1957).
(9) C. A. Bunton, G. W. Kenner, M. J. T. Robinson, and B. R. Webster, *ibid.*, 1001 (1963).

conclusively that loss of –OH *and* loss of CO involve *both* oxygen atoms. The oxygen of the –OH is derived about equally from the carbonyl and ether oxygens while the loss of carbon monoxide involves the ether

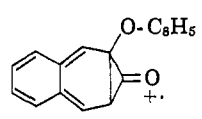
Scheme I



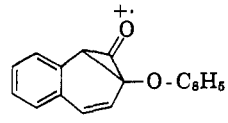
oxygen 80% of the time. The sole origin of the hydrogen atom of the –OH has been proven to be an *ortho* hydrogen from the phenyl ring by the shift of the *m/e* 231 ion to *m/e* 233 (loss of –OD) in the trideuteriophenoxy derivative IV. It is clear from these results that the phenyl group migrates from one oxygen to the other prior to fragmentation of the molecule ion. Furthermore, this rearrangement is important at reduced electron energies since the percentages of label retention cited above remain essentially unchanged at approximately 10–11 ev.[5]

The observation of 1,4 migration of the phenyl group at such low ionizing voltages implies that rearrangement occurs *via* the lowest energy ion which can be produced from I.[6] Ionization should involve the high-energy nonbonding pair on the carbonyl oxygen. Phenyl migration to n,π* excited carbonyl groups has been observed.[7] A mechanism consistent with all the above data is shown in Scheme I.

Further fragmentation of the stabilized ions VII and VIII is not important. The loss of CO[8] which occurs in a ratio of 1:4 from the isomeric ions V and Va (or a single bridged ion intermediate) is reasonable if CO is lost from the valence tautomers IX and X. Tautomer X retains the stability of the benzene ring.



IX



X

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(5) Investigation of the importance of previously cited[3,4] rearrangements at reduced electron energies will be of considerable interest.

(6) Thermal 1,4-phenyl migration is not observed in this system.

(7) (a) O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *J. Am. Chem. Soc.*, **85**, 2031 (1963); (b) H. Schmidt, H. Hochweber, and H. von Halban, *Helv. Chim. Acta*, **30**, 1135 (1947), and references cited therein; (c) G. W. Griffin and E. J. O'Connel, *J. Am. Chem. Soc.*, **84**, 4148 (1962); (d) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962).

(8) In principle, loss of CO from I might involve the ether portion of the molecule rather than the carbonyl group. This is most unlikely because of the observed efficiency of the loss of CO at low ionizing voltages. The loss of CO from diphenyl ether has an appearance potential of 12.56 ev,[9] in sharp contrast to the efficient loss of CO from I at 11 ev.

(9) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2943 (1965).

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