intermediates. That such intermediates are feasible is shown by the fact that the anion of 1,3-naphthalenediol exists entirely as a ketone–enolate.[8] In intermediates postulated for the exchangeable protons, the aromaticity of one ring is retained in at least one of the resonance hybrids (e.g., XIV); the failure of the other *ortho* protons to exchange can be attributed to loss of the benzenoid character of both rings (e.g., XV).[9]

XIV   XV
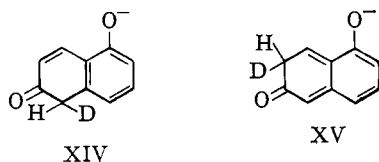
Regardless of mechanism, the exchange described above should be useful in structural elucidations of complex phenols and is, of course, suitable for the preparation of various deuterated aromatic compounds.

(8) E. S. Hand and R. M. Horowitz, unpublished results. It is of interest that H-2 and H-4 of 1,3-naphthalenediol exchange rapidly in deuterium oxide solution even in the absence of base.

(9) The fact that 5-nitro-1-naphthol has a pK_a not very different from that of 1-naphthol itself has been rationalized in similar terms: K. C. Schreiber and M. C. Kennedy, J. Am. Chem. Soc., **78**, 153 (1956).

(10) Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213.

FRUIT AND VEGETABLE CHEMISTRY   ELLI SMAKULA HAND[10]
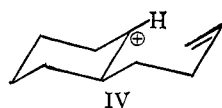   LABORATORY   ROBERT M. HOROWITZ
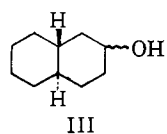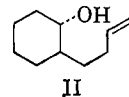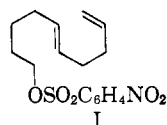WESTERN UTILIZATION RESEARCH
   AND DEVELOPMENT DIVISION
AGRICULTURAL RESEARCH SERVICE
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Cationic Cyclizations Involving Olefinic Bonds. V.[1] Solvolysis of *cis*-5,9-Decadienyl *p*-Nitrobenzenesulfonate

Sir:

In the formolysis of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate (I),[2] the processes resulting in the formation of cyclic products were highly stereoselective, possibly stereospecific. Thus (after cleavage of formate esters) *trans*-2-(Δ^3-butenyl)cyclohexanol (II) was formed to the exclusion of the *cis* isomer, while the decalols were exclusively those with *trans*-fused rings (III). It was not possible to decide whether this stereochemical consequence was the result of a synchronous process or of a stereoselective equatorial attack of nucleophile on a cationic intermediate like IV.[3] We now wish to present evidence which supports the former mechanism.

I   II

III   IV

(1) Paper IV of this series: W. S. Johnson, W. H. Lunn, and K. Fitzi, J. Am. Chem. Soc., **86**, 1972 (1964).

(2) W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jacques, and J. K. Crandall, ibid., **86**, 1959 (1964).

(3) W. S. Johnson, S. L. Gray, J. K. Crandall, and D. M. Bailey, ibid., **86**, 1966 (1964).

The formolysis of *cis*-5,9-decadienyl *p*-nitrobenzenesulfonate (V) has now been examined. If this reaction, as well as that of the *trans* isomer, were to proceed by a stepwise mechanism involving the intermediacy of a common cation like IV, both isomeric substrates would yield the same cyclic products.

5,9-Decadiynol[2] was selectively hydrogenated over Lindlar catalyst to yield *cis*-5,9-decadienol which was purified by preparative vapor phase chromatography, $n^{20}D$ 1.4637. *Anal.* Found: C, 77.9; H, 11.8. The *p*-nitrobenzenesulfonate V, m.p. 26.5–27° (*Anal.* Found: C, 56.5; H, 6.4; N, 4.4), was solvolyzed by heating a 0.02 M solution in anhydrous formic acid containing pyridine (0.04 M) for 1 hr. at 75°. The formate esters were reductively cleaved by treatment with lithium aluminum hydride, and the resulting product was analyzed by vapor phase chromatography.[2] The products were identified by peak enhancement experiments and by infrared spectral comparison with authentic specimens.[2] Since the solvolysis of the *trans* sulfonate ester had not been carried out previously under these conditions, it was re-examined for direct comparison with the *cis* isomer. The relative proportions of alcohols from the *trans* sulfonate ester were as follows: 3% of 1-(Δ^3-butenyl)cyclohexanol, 10% of Δ^3-butenylcyclopentylcarbinol, 57% of *trans*-2-(Δ^3-butenyl)cyclohexanol (II), 8% of *trans*-5,9-decadienol, 5% of *trans-anti*-2-decalol, 14% of *trans-syn*-2-decalol, and 3% total of several unidentified components. *There was no detectable amount of the cis monocyclic alcohol VI or the cis decalols VII among the products.* These results are quite comparable to those obtained with 80% formic acid.[2] Formolysis of the *cis* sulfonate ester V gave the following relative proportions of alcohols: 3% of 1-(Δ^3-butenyl)cyclohexanol, 8% of Δ^3-butenylcyclopentylcarbinol, 56% of *cis*-2-(Δ^3-butenyl)-cyclohexanol (VI), 16% of *cis*-5,9-decadienol, 13% of an inseparable mixture of *cis-syn*- and *cis-anti*-2-decalol, and 4% total of several unidentified components. *There was no detectable amount of the trans monocyclic alcohol II or of the trans decalols III among the products.* *cis*-2-(Δ^3-Butenyl)cyclohexanol (VI) was identified by comparison with an authentic specimen, $n^{20}D$ 1.4770 (*Anal.* Found: C, 77.8; H, 11.75), which was prepared by reduction of the corresponding ketone with lithium tri-*t*-butoxyaluminum hydride followed by preparative vapor phase chromatographic separation from the predominant *trans* isomer II.

OSO$_2$C$_6$H$_4$NO$_2$ VI   VII
V
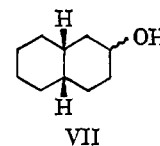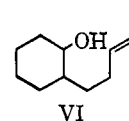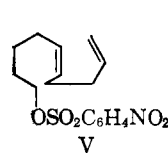
Since the cyclizations of I and V proceed stereochemically in exactly the opposite sense, a common cationic intermediate IV cannot possibly be involved. If the solvolyses of both I and V proceed by the same basic mechanism—an assumption which is reasonable, particularly in view of the strikingly similar type of product distribution—then it follows that the cyclizations must either be concerted processes or involve cationic intermediates (e.g., bridged carbonium ions) which retain the stereochemical integrity of the respective substrates. A decision between these latter two

mechanisms is not yet possible. We are in the process of examining the solvolysis of the 5-methyl-5,9-decadienyl p-nitrobenzenesulfonates in order to determine if this system behaves like the present case or whether the relative stability of the potential tertiary cation IV (CH$_3$ in place of H) will result in a changeover to a common carbonium ion process. This study may have a bearing on the mechanism of cyclizations in the biosynthesis of polycycloisoprenoids.

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Novel Ring Expansion and Carbon Insertion Reactions of Isatogens

Sir:

Recently, 2-phenylisatogen[1] (Ia) was reported to undergo two types of ring expansion reactions involving nitrogen insertion, resulting in a 4-cinnolinol 1-oxide derivative from ammonia and a 3,4-dihydro-4-quinazolinone derivative from tetracyanoethylene (II).[2] It has now been found that the reaction of the latter type, of Ia with II, goes even better with another negatively substituted nitrile, trichloroacetonitrile (III). Thus, reaction of Ia (0.0143 mole) with III (0.070 mole) in refluxing xylene (40 ml.) for 5 hr. gave 2-phenyl-3,4-dihydro-4-quinazolinone (IV) in 88% yield (in contrast to 30–39% yields with II[2]), m.p. 240.5–241°, identical, as shown by mixture melting point, 239–240°, and infrared comparison in Nujol, with a sample prepared[2] from II.

We report now two types of ring expansion reactions of Ia with acetylenes, which involve carbon insertion. Refluxing a solution of Ia (0.0224 mole) with phenylacetylene (V, 0.091 mole) and propionic acid (0.107 mole) in xylene (100 ml.) for 13 hr. gave a crystalline precipitate, which increased in amount upon cooling. Filtration removed pale straw-colored crystals (VIa, 42%), m.p. 254–256°. Concentration of the filtrate gave an oil, which was taken up in ether and extracted with sodium bicarbonate. Acidification of the bicarbonate extract and extraction with ether gave benzoic acid (VII, 44%, m.p. 113°; recrystallization from water gave a sample, m.p. 119–123°, identified by mixture melting point, 119–123°, with an authentic sample). Concentration of the ether which had been extracted with bicarbonate gave additional VIa (5%; total 47%). Recrystallization of the combined VIa from ethanol gave a sample, m.p. 261.5–262°,[3] identical with the known[4] 3-phenyl-4-quinolinol as shown by mixture melting point, ultraviolet, and infrared comparison in Nujol with a sample of m.p. 259.5–260.5°[3] prepared[4] by the Conrad–Limpach method[5] from aniline and ethyl phenylmalonaldehyde; λ_{max} mμ (log ϵ) in 95%

(1) (a) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951)
(b) F. Kröhnke and I. Vogt, *ibid.*, **85**, 376 (1952).
(2) W. E. Noland and D. A. Jones, *J. Org. Chem.*, **27**, 341 (1962).
(3) These melting points were determined in capillary tubes; all others were determined on calibrated Fisher–Johns hot stages.
(4) (a) W. J. Adams and D. H. Hey, *J. Chem. Soc.*, 3254 (1950); (b) R. C. Elderfield and J. B. Wright, *J. Am. Chem. Soc.*, **68**, 1276 (1946).
(5) (a) M. Conrad and L. Limpach, *Chem. Ber.*, **20**, 944 (1887); (b) *ibid.*, **21**, 521 (1888); (c) L. Limpach, *ibid.*, **64B**, 969, 970 (1931).

ethanol: 263 (4.42), 309 (3.99), 329 (4.01), and 334 (infl, 4.00). The mixture melting point with a sample of the isomeric 2-phenyl-4-quinolinol[6] (m.p. 258.5–261.5°[3]) was depressed, 213.5–254.5°,[3] and the infrared spectra in Nujol and halocarbon oil were different. Replacement of propionic acid with acetic acid in the reaction of Ia with V also gave VIa (40%).
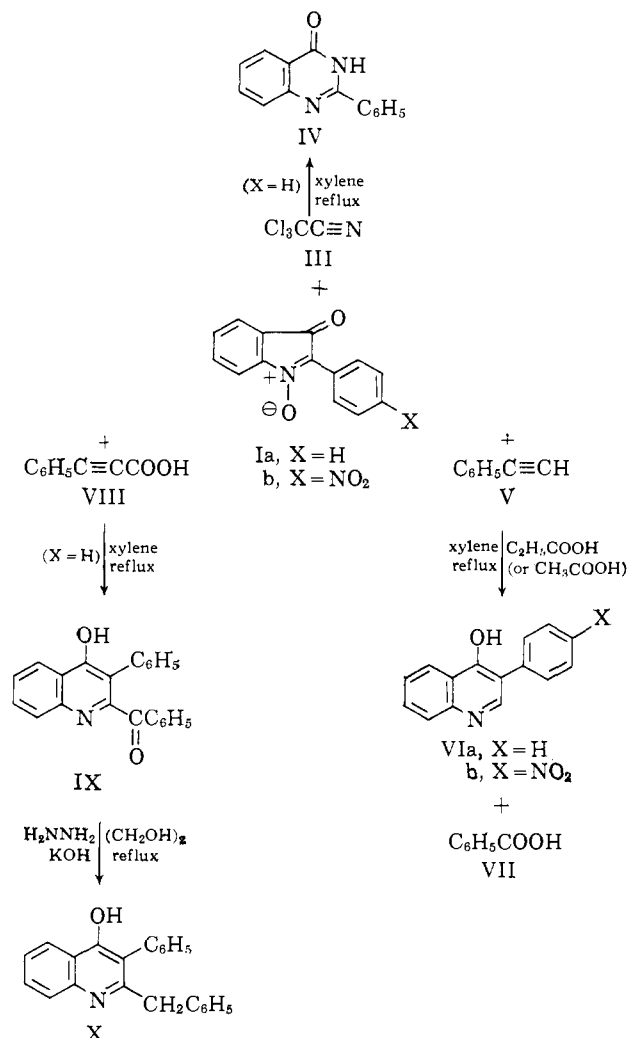
Addition of Ia to V is assumed to proceed through normal orientation of addition[7] by the cyclic nitrone system, followed by a hydrolytic rearrangement and ring expansion to VIa. That the phenyl substituent retained in VIa is derived from Ia (and not from V) is shown by the analogous reaction of 2-(4-nitrophenyl)-isatogen[1a] (Ib, 0.0073 mole) with V (0.072 mole) and propionic acid (0.080 mole) in refluxing xylene (60 ml.) for 3 hr. The products were VII (45%, m.p. 120–122°) and 3-(4-nitrophenyl)-4-quinolinol (VIb, 95%), yellow solid, m.p. 368–369° dec.[3] (from ethanol); λ_{max} mμ (log ϵ) in 95% ethanol: 238 (4.41), 290 (3.85), 328 (infl, 4.26), 336 (4.28), and 353 (infl, 4.15); ν_{NO_2} cm.$^{-1}$ in KBr: 1516 (vs), 1343 (vs).

Anal. Calcd. for $C_{15}H_{10}N_2O_3$ (mol. wt. 266.25): C, 67.66; H, 3.79; N, 10.52. Found: C, 67.50; H, 3.95; N, 10.27.

Location of the 4-nitrophenyl substituent in the hydroxyl-conjugated 3-position (analogous to VIa) is

(6) C. E. Kaslow and W. R. Lawton, *J. Am. Chem. Soc.*, **72**, 1723 (1950).
(7) (a) W. E. Noland and D. A. Jones, *Chem. Ind.* (London), 363 (1962);
(b) G. R. Delpierre and M. Lamchen, *J. Chem. Soc.*, 4693 (1963); (c) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 588 (1963).