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# REARRANGEMENTS OF AZIDOQUINONES II. STEREOSELECTIVE ACID-CATALYZED REARRANGEMENT OF AZIDOQUINONES TO γ-ALKYLIDENE (ARYLIDENE)-$\Delta^{\alpha,\beta}$-BUTENOLIDES

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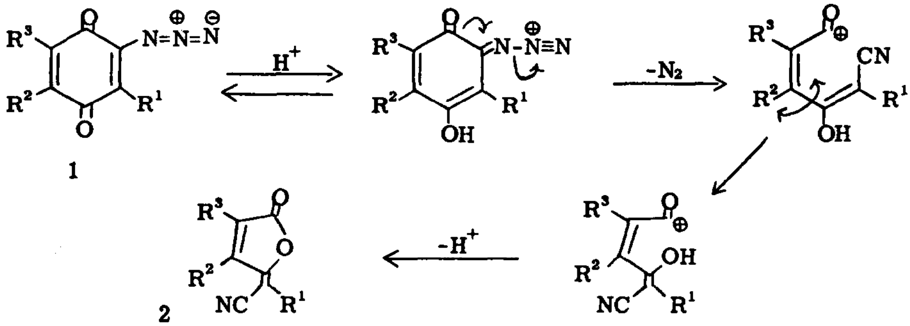
Azidoquinones undergo a stereoselective rearrangement in acidic media to give high yields of ring-contracted γ-alkylidene- (or arylidene)-$\Delta^{\alpha,\beta}$-butenolides. This rearrangement is of mechanistic significance in regards to certain reactions which have appeared in the literature,[1, 2, 3] and also finds synthetic utility in the preparation of pulvinic acid (4), a naturally occurring γ-arylidene-$\Delta^{\alpha,\beta}$-butenolide found in a variety of lichens.[4]

The general structures (1) and (2) illustrate the overall chemical transformation as indicated by the following possible mechanistic scheme:



| | $R_1$ | $R_2$ | $R_3$ | Yield |
|---|---|---|---|---|
| a | $CH_3$ | H | $(CH_3)_2C$ | 87 |
| b | $CH_3$ | $N_3$ | $CH_3$ | 83 |
| c | $C_6H_5$ | OH | $C_6H_5$ | 95 |
| d | H |  | | 60 |
| e | H | $C_6H_5$ | H | 80 |
| f | H | $(CH_3)_3C$ | H | 95 |

Scheme I

The azidoquinones, 1a-f, were prepared from the respective chloro-substituted quinones by direct nucleophilic displacement of the halogen by azide ion in ethanolic solution.[5] Reaction of these azidoquinones with cold concentrated sulfuric acid resulted in their facile rearrangement to the $\gamma$-alkylidene (or arylidene)-$\Delta^{\alpha,\beta}$-butenolides, 2a-f, in 60 to 95% yields. The structures of these butenolides are completely consistent with their spectral data which are presented in Table I. They all show characteristic absorptions for nitrile, carbon-carbon double bond and $\gamma$-lactone carbonyl groups in their ir spectra. Their nmr spectra show the correct proton count, coupling constants and chemical shifts, and the mass spectra show molecular ions and fragmentation patterns in accord with their formulations.

These rearrangements proceed in a highly stereoselective manner, giving a single detectable isomer as evidenced by spectral (ir and nmr) and gas chromatographic analysis of the crude product. The butenolides, 2e and 2f, lend themselves to direct stereochemical analysis by nmr spectroscopy which showed the vinyl protons in these two compounds to be in a trans-trans relationship to one another on the butadiene moiety. Bothner-By and Harris[6,7] have investigated long-range coupling in a number of butadienes and found that the 1,4-vinyl protons in the trans-trans configuration show coupling constants ranging from 1.3 to 1.9 cps. All other long-range couplings were found to be appreciably smaller. For example, coupling between the 1,4-vinyl protons in a cis-trans relationship (the other possible stereochemical configuration of the butenolides 2e and 2f) were found to range from 0 to 0.9 cps. The nmr spectra of the butenolides, 2e and 2f, showed an AB pattern for the vinyl protons with a coupling constant of 1.6 cps., in agreement with the proposed structures. The possibility that the stereoselectivity in the formation of 2e and 2f is a result of an acid-catalyzed equilibration of the exocyclic double bond subsequent to rearrangement is unlikely on the basis of steric considerations.

Chemical evidence for the stereochemistry of the butenolide, 2c, was obtained by its conversion to the natural product, pulvinic acid, 4, a compound of known configuration.[8] Reaction of 2-chloro-5-hydroxy-3,6-diphenyl-1,4-benzoquinone (3) with ethanolic sodium azide gave the azidoquinone, 1c, in 89% yield. Simply refluxing this azioquinone in chloroform for 10 minutes resulted in its rearrangement to the known[9] butenolide, 2c, in 95% yield. No external source of acid was necessary for this transformation, the hydroxyl group in 1c apparently being of sufficient acidity to initiate the reaction. Acid hydrolysis of the nitrile group in the butenolide, 2c, to a carboxylic acid gave the known natural product, pulvinic acid, 4, which was identical in all respects to an authentic sample.[8]

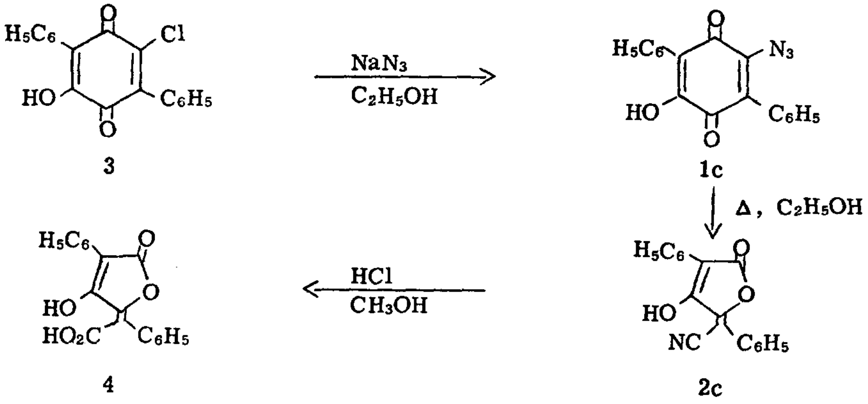


TABLE I

Physical Properties of $\gamma$-Arylidene (Alkylidene)-$\Delta^{\alpha,\beta}$-butenolides[10]

| Comp'd | mp | ir, $cm^{-1}$ (nujol) | nmr, ppm ($CDCl_3$) | Mass Spec |
|---|---|---|---|---|
| 2a | 38-40 | 2110, 1780<br>1645 | 1.26 d (6) J = 7cps;<br>2.12 (s) (3); 2.80 h (1)<br>J = 7cps; 7.30 d (1)<br>J = 1.7cps | 177 $M^+$ (100%); 162 (48%);<br>134 (52%); 96 (46%);<br>53 (51%); 39 (27%) |
| 2b | 115 | 2230, 2140,<br>1730, 1670 | 2.16 s (3); 2.07 s (3) | 190 $M^+$ (45%); 81 (100%);<br>53 (95%); 39 (7%) |

TABLE I (Continued)

| Comp'd | mp | ir, $cm^{-1}$ (nujol) | nmr, ppm ($CDCl_3$) | Mass Spec |
|---|---|---|---|---|
| 2c | 190-191 | 2260, 1820 1630 | 7.4-7.6 m(6); 7.8-8.0 m(4) | 289 $M^+$ (100%); 144 (85%); 118 (80%); 89 (80%); 39 (12%) |
| 2d | 170 | 2230, 1800, 1650 | 7.9-8.4 m(4); 5.9 s(1) | 171 $M^+$ (100%); 143 (22%); 104 (53%); 76 (43%); 39 (6%) |
| 2e | 136-137 | 2230, 1810, 1780, 1650, 1620 | 7.45 s(5); 6.4 d(1) J = 1.6cps; 5.55 d(1) J = 1.6cps | 197 $M^+$ (95%); 169 (15%); 141 (56%); 102 (100%); 39 (9%) |
| 2f | 89-90 | 2230, 1820, 1780 1640 | 6.33 d(1) J = 1.6cps<br>5.67 d(1) J = 1.6cps<br>1.48 s(9) | 177 $M^+$ (56%); 162 (62%); 134 (100%); 110 (30%); 39 (43%) |

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## REFERENCES

1. H. W. Moore and H. R. Shelden, *J. Org. Chem.*, **32**, 3603 (1967).
2. A. H. Rees, *Chem. and Ind.*, 931 (1964).
3. H. W. Moore and H. R. Shelden, *J. Org. Chem.*, in press.
4. O. P. Mittal and T. R. Seshadri, *Current Sci. (India)*, **26**, 4 (1957).
5. L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **57**, 1482 (1935).
6. A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445 (1965).
7. A. A. Bothner-By and R. K. Harris, *ibid.*, **87**, 3455 (1967).
8. R. L. Frank, G. R. Clark and J. N. Coker, *ibid.*, **72**, 1824 (1950).
9. J. Volhord and F. Henke, *Ann.*, **282**, 61 (1894).
10. C,H analysis of all compounds are in agreement with their formulations.