Tetrahedron Letters No.16, pp. 1243-1246, 1969. Pergamon Press. Printed in Great Britain.

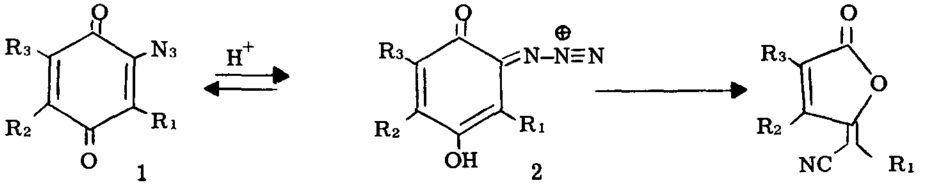
REARRANGEMENT OF AZIDOQUINONES IV.
RING EXPANSION OF 4-AZIDO-1, 2-NAPHTHOQUINONE

Harold W. Moore, H. Raymond Shelden and Walter Weyler Jr.

Department of Chemistry
University of California
Irvine, California 92664

(Received in USA 13 January 1969; received in UK for publication 3 March 1969)

In a previous communication[1] it was shown that azido-1, 4-benzo- and 1, 4-naphthoquinones (1) undergo a highly stereoselective ring contraction to γ-cyanoalkylidene- or γ-cyanoarylidene-$\Delta^{\alpha,\beta}$-butenolides (3) in concentrated sulfuric acid (Scheme I).

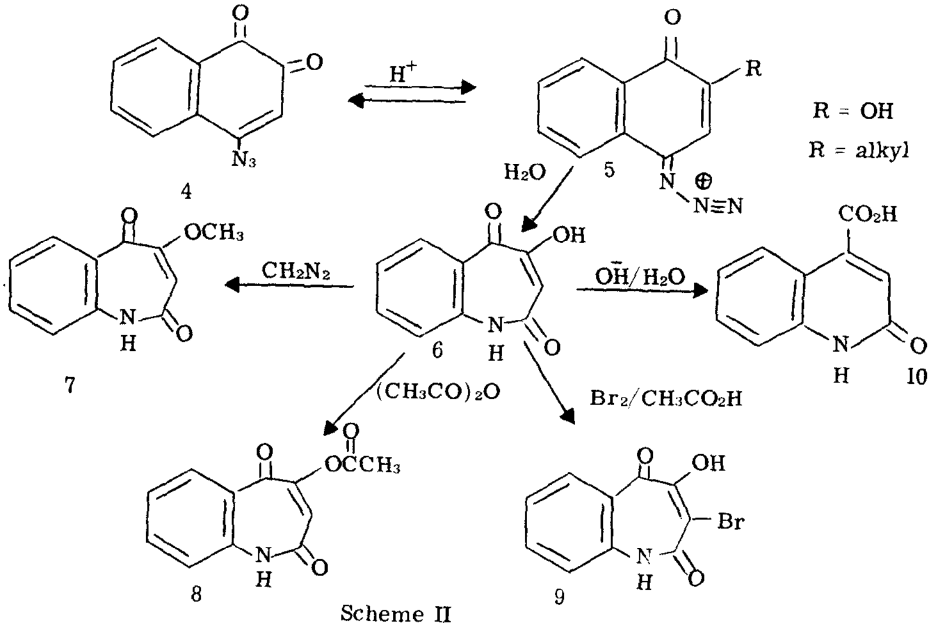


1 2 3

Scheme I

Reported here[2] is the first example of an acid-catalyzed rearrangement of an ortho-azidoquinone, 4-azido-1, 2-naphthoquinone (4), which results in ring expansion to 2, 5-H-4-hydroxy-benzoazepine-2, 5-dione (6). This reaction provides a convenient, high yield (82 %) synthesis of an hydroxyazepinedione, a member of a class of compounds which may be useful synthetic precursors to the illusive azatropolone ring system. The mechanism of this transformation is also significant in regards to the observed reactions[3-7] of alkyl- and hydroxy-1, 4-quinones with sodium azide in concentrated sulfuric acid.

4-Azido-1, 2-naphthoquinone (4) was prepared in 52% yield by the reaction of sodium azide with an aqueous solution of 1, 2-naphthoquinone-4-sulfonic acid, sodium salt. The azidoquinone (4) shows the following characteristic spectral properties; ir (nujol): 2120(N_3), 1665 cm^{-1}(C=O); nmr ($CDCl_3$): δ, 6.32 s(1) = CH, 7.50 - 8.30, m(4)ArH. Reaction of (4) with concentrated sulfuric acid at ambient temperature until nitrogen evolution ceased gave the yellow azepinedione (6) in 82% isolated yield[8], mp, 260° dec. The ir spectrum (nujol) of (6) is very similar to the only other reported member of this series, 2, 5-H-4-hydroxy-7, 8-dimethyl-benzoazepine-2, 5-dione,[9] showing characteristic absorptions at 3300 (NH), 3110 (OH), 1670, 1635 (C=O) and 1600 cm^{-1} (C=C). The nmr spectrum (DMSO-d_6) of (6) shows the amide proton as a broad singlet at δ, 11.0, the four aromatic protons as a multiplet between δ, 7.15 and 8.20 and the vinyl proton as a doublet (J = 1.5 cps) at δ, 6.25. The amide proton absorption disappears and the vinyl proton collapses to a sharp singlet when a drop of D_2O is added to the above sample.[10] The uv spectrum of an ethanolic solution of (6) shows λ_{max} at 237 mμ (24,800) and 277 mμ (15,900).



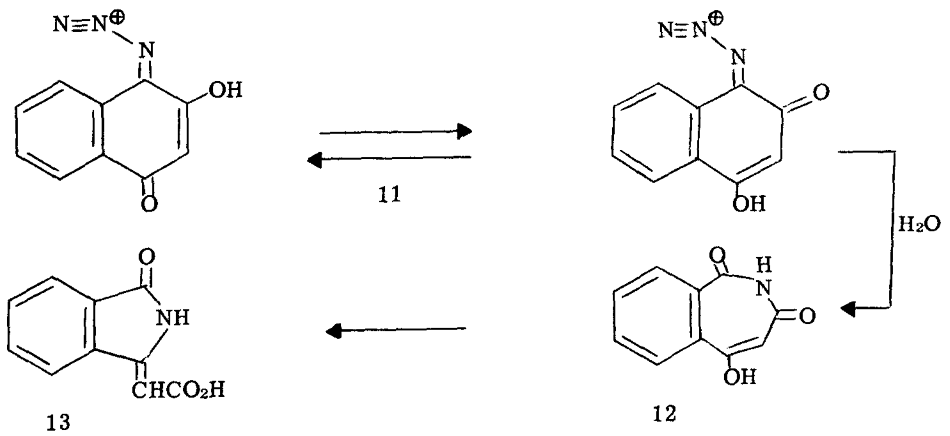
Scheme II

Treatment of the azepinedione (6) with hot strong aqueous sodium hydroxide resulted in ring contraction to the known quinoline derivative (10) in 80% yield.[11] This rearrangement is analogous to the reaction reported by Rees[9] for 2, 5-H-4-hydroxy-7, 8-dimethylbenzoazepine-2, 5-dione, and the result assign the position of the nitrogen atom in (6).

The azepinedione (6) undergoes characteristic transformations to give a methyl ether (7) (92%) and acetate ester (8) (75%) and the bromo derivative (9)(85%) by respectively treating (6) with diazomethane. acetic anhydride and bromine in acetic acid. The spectral properties for these new compounds follow; Compound (7): ir (nujol), 3300 (NH), 1670, 1660 (C=O), and 1610 cm^{-1} (C=C); nmr (DMSO-d_6), δ, 10.95 b (1)NH, 7.11-8.00 m(4)ArH, 6.18 d (1) = CH (J = 1.8 cps), 3.85 s (3) OCH_3; Compound (8): ir (nujol), 3210 (NH), 1775, 1685, 1640 (C=O), 1615 cm^{-1} (C=C); nmr (DMSO-d_6), δ, 11.18 b (1)NH, 7.15-8.05 m (4)ArH, 6.82 d (1) = CH (J = 1.7 cps) 2.31 s (3)CH_3; Compound 9: ir (nujol), 3200 (NH), 1680 (C=O), 1612 cm^{-1} (C=C); nmr (DMSO-d_6), δ, 11.18 b (1)NH, 7.12-8.12 m (4)ArH. It is interesting to note that the above three compounds (7) (8) (9) are all soluble in dilute (10%) sodium hydroxide, indicating an unusually high acidity of the amide protons. On the basis of the above spectral and chemical data the structure of (6) appears well documented.

The most reasonable mechanism for the formation of (6) is one involving the protonated azidoquinone (5) (R = OH). Aryl migration followed by solvolysis would give the ring expanded product. This reaction provides a chemical analogy for the observed ring expansion of alkyl-1,4-benzo and 1,4-naphthoquinones to 2,5-azepinediones under Schmidt reaction conditions.[3,4,6,7] Such rearrangements undoubtedly involve intermediates such as (5) (R = alkyl) which are formed by addition of hydrazoic acid to one of the carbonyl groups followed by protonation of the resulting hydroxyl group and loss of water.

2-Hydroxy-1,4-naphthoquinone provides an interesting example of a compound which could conceivably give three different azido intermediates when reacted with hydrazoic acid in strong acid medium, i.e., reaction at C-2 to give (2) (R_1 = H, R_2 = R_3 = –CH=CH–CH=CH–), reaction at C-4 to give (5) (R = OH) and/or reaction at C-1 to give (11). We have previously shown[5] that the γ-lactam (13) is the product obtained when 2-hydroxy-1,4-naphthoquinone is reacted with hydrazoic acid in concentrated sulfuric acid. This product (13) can only be explained as arising from (11) since as shown in the present communication (5) leads to (6) and as shown previously[1] (2) (R_1 = H, R_2=R_3 = – CH=CH–CH=CH–) leads to (3) (R_1 = H, R_2 = R_3 = – CH=CH–CH=CH–) in concentrated sulfuric acid. Also, compounds (3) and (6) show no rearrangement to (13) under the reaction conditions.[12]



ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for partial support of this work from Grant G. P. 8706.

REFERENCES

1. H. W. Moore and H. R. Shelden, Tetrahedron Letters, No. 52, 5431 (1968).
2. C, H-Analysis for all new compounds are consistent with their proposed formulations.
3. D. Misiti, H. W. Moore and K. Folkers, Tetrahedron, **22**, No. 4, 1201 (1966).
4. D. Misiti, H. W. Moore and K. Folkers, Tetrahedron Letters, No. **16**, 1071 (1965).
5. H. W. Moore and H. R. Shelden, J. Org. Chem., **32**, 3603 (1967).
6. R. W. Richards and R. M. Smith, Tetrahedron Letters, No. 22, 2361 (1966).
7. G. R. Bedford, G. Jones and B. R. Webster, ibid., No. 22, 2367 (1966).
8. On a one gram scale this reaction takes approximately 1-1/2 hours and the product precipitates in high purity when the reaction solution is poured into ice water.
9. A. H. Rees, J. Chem. Soc., 3111 (1959).
10. Coupling ($J = 1 \sim 2$ cps) between the amide proton and the vinyl proton adjacent to the carbonyl has previously been observed (see ref. 3, 4, 6, 7).
11. J. A. Aeschliman, J. Chem. Soc., 2902 (1926). Comparison of (10) with an authentic sample of 2-oxo-1, 2-dihydroquinoline-4-carboxylic acid, prepared according to the above reference showed the compounds to be identical.
12. These results are contrary to those previously proposed for the formation of (13) where C–2 in 2-hydroxy-1, 4-naphthoquinone was assumed to be the reactive position (see ref. 5).