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# REARRANGEMENTS OF AZIDOQUINONES. IX. PYROLYSIS OF 2,3-DIAZIDO-1,4-NAPHTHOQUINONE-DIBENZENESULFONIMIDE

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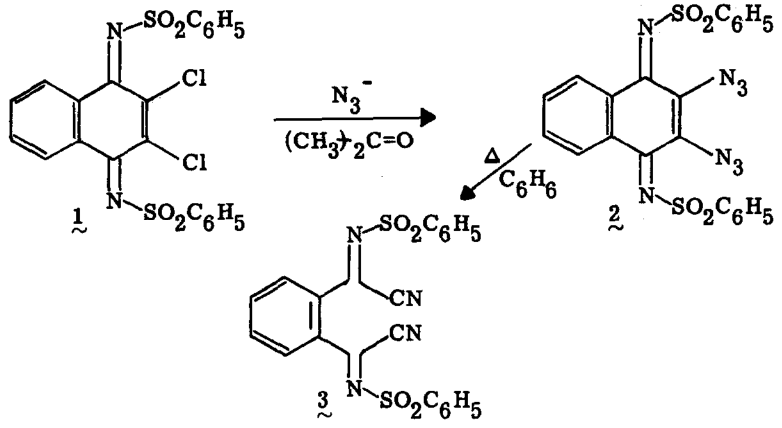
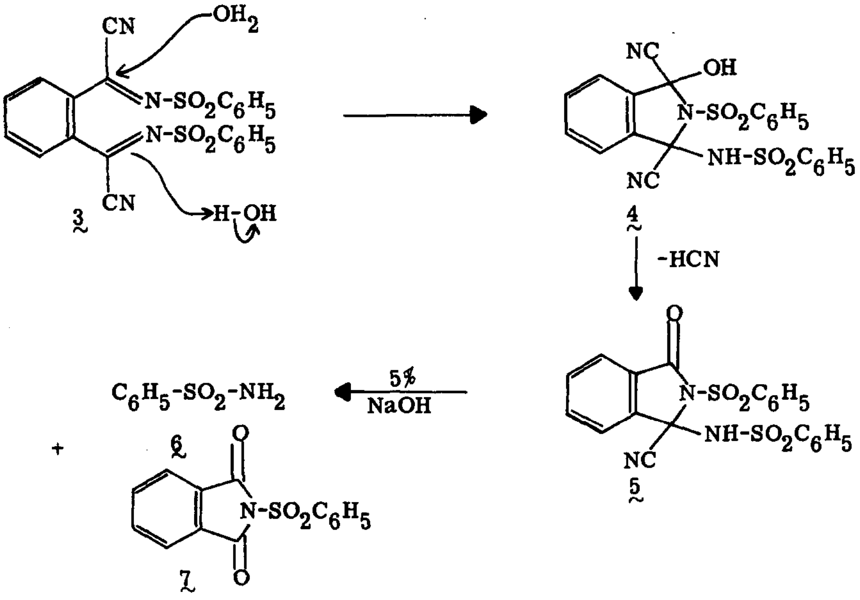
Azidoquinones have been shown to be very versatile synthetic intermediates. γ-cyanoalkylidine-$\Delta^{\alpha,\beta}$-butenolides,[1] 2-cyano-1,3-cyclopentenediones,[2] cyanoketenes,[3] azapinediones,[4] aminoquinones[5] and acylcyanides[6] can be prepared from azidoquinones by employing the appropriate reaction conditions. The synthetic utility of this class of compounds suggested an investigation of certain azidoquinone derivatives to see if analogous transformations could be accomplished. Reported here is a study of the thermal decomposition of 2,3-diazido-1,4-naphthoquinone-dibenzenesulfonimide, **2**. This vicinal diazide cleaves pyrolytically in refluxing benzene to give phthaloyl cyanide-dibenzenesulfonimide, **3**. Compound **3** undergoes subsequent hydrolytic ring closure upon reaction with alcohols to 1,3-substituted isoindolines and phthalimidine-benzenesulfonimides.

The purple crystalline diazide, **2**, was prepared in nearly quantitative yield from 2,3-dichloro-1,4-naphthoquinone-dibenzenesulfonimide,[7] **1**, upon reaction with excess sodium azide. A solution of 2.1 m mol of **1** in 40 ml of acetone was reacted with 6.1 m mol of sodium azide in 5 ml of water at 0-5°. The reaction solution immediately turned from yellow to purple upon addition of the azide. Water (20 ml) was added to the reaction solution which induced the precipitation of the diazide, **2**.

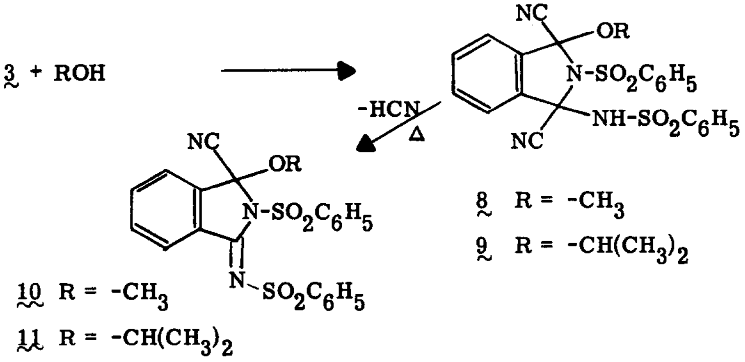
Phthaloyl cyanide-dibenzenesulfonimide, **3**, was obtained by refluxing a suspension of 725 mg (1.4 m mol) of **2** in 7 ml of anhydrous benzene for 6 hrs. A small amount (40 mg) of an unidentified insoluble precipitate was collected by filtration and the solvent removed *in vacuo* to give **3** as a brownish oil. The structure of **3** is in complete agreement with its spectral data (Table I) and its chemical properties. The thermal cleavage, **2** ⟶ **3**, has good precedent; 2,3-diazido-1,4-naphthoquinone loses nitrogen in refluxing toluene and forms phthaloyl cyanide,[6] and *o*-diazidobenzene thermally fragments to *cis*-1,4-dicyanobutadiene.[8]



The α-cyanobenzenesulfonimide moieties in **3** are very reactive toward hydroxylic reagents. Compound **3** reacts readily with water to give the substituted N-benzenesulfonyllactam, **5**, in 85% yield. The formation of **5** is envisaged as arising via the isoindoline, **4**, which then eliminates hydrogen cyanide. Hydrolysis of the lactam **5** with 5% NaOH converted it to benzenesulfonamide, **6**, and N-benzenesulfonylphthalimide, **7**,[9] which were identified by comparison (ir and mixed mp) with authentic samples.



The hydrolytic ring closure of 3 could also be accomplished with alcohols. Methanol and isopropanol react with 3 to give respectively the 1, 3-substituted isoindolines, 8 and 9. These compounds are heat labile and lose hydrogen cyanide upon attempted recrystallization from acetone-diethyl ether to give respectively the substituted N-benzenesulfonylphthalimidine-benzenesulfonimides, 10 and 11. The spectral data (Table I) for compounds 8 -11 are in complete accord with their proposed structures. Of particular utility in the structural assignments is the nmr spectrum of 11 which shows nonequivalent methyl absorptions (δ, 1.38 and 1.10) for the isopropyl group. This is consistent with structure 11 which has the isopropoxide moiety directly substituted to an asymmetric center.



8 R = $-CH_3$

9 R = $-CH(CH_3)_2$

10 R = $-CH_3$

11 R = $-CH(CH_3)_2$

TABLE I

Spectral Data of New Compounds[10]

| Compound | Yield | mp <br> °C | ir(Nujol) <br> $cm^{-1}$ | | nmr ($CDCl_3$) <br> ppm |
|---|---|---|---|---|---|
| 2 | >95% | 126-28° | 2137<br>2105 | $N_3$ | 8.83-7.26 m |
| | | | 1558 | C=N- | |
| 3 | | oil | 2208 | -C≡N | |
| | | | 1585 | C=N- | |
| 5 | 85% | 158-60 | 3247 | >NH | 7.90-6.40 m |
| | | | 1754 | C=O | |
| 8 | 72% | 175-185 dec | 3205 | >NH | |
| 9 | 74% | 165-185 dec | 3200 | >NH | |
| 10 | | 187-89 | 1621 | C=N- | 3.29 s(3) $OCH_3$ |
| | | | | | 8.20-7.30 m (14) |
| 11 | | 166-68 | 1630 | C=N | 1.10 d(3) $CH_3$ |
| | | | | | 1.38 d(3) $CH_3$ |
| | | | | | 4.08 m(1) CH |
| | | | | | 8.00-7.08 m (14) |

Adams and coworkers[10] have published an extensive investigation concerning the synthesis and chemistry of variously substituted quinonedimides. The availability of the corresponding azidoquinonedimides *via* standard routes gives a class of previously unexplored azides. The chemistry of these compounds as compared to that of the corresponding azidoquinones is currently under study.

## ACKNOWLEDGEMENT

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