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THE CHEMISTRY OF 2-HYDROXY-2,4,6-CYCLOOCTATRIENONE
(1,7-π-HOMOTROPOLONE)

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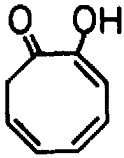
It is of interest to which the chemical properties of 2-hydroxy-2,4,6-cyclooctatrienone (1,7-π-homotropolone) 1[1] have likeness, 2,4,6-cyclooctatrienone 2 or tropolone 3. The photochemical behavior of 1 resembles 3.[2] We wish here to report the chemistry of 1.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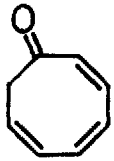
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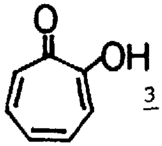
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Halogenations: We have already described the reaction of 1 with N-bromosuccinimide which affords 3-bromo derivative 5 via the diketo bromide 4.[1] On addition of molecular bromine to 1 (CH_2Cl_2, 0°C), the reaction mixture immediately began to liberate hydrogen bromide, and passing the mixture after a few minutes through a short Florisil column gave 5 in 66% yield. However, when the reaction mixture was treated as above after one day at room temperature, 5 was not obtained at all but was obtained 7-bromo-3,5-cyclooctadien-1,2-dione 6 (ν=1720, 1650 cm^{-1}) in 85% yield.[3] Since treatment of 5 with anhydrous hydrogen bromide at the same condition yielded 6, the reaction must be thermodynamically controlled by the acid catalyst (HBr) effecting the regeneration of 1 and bromonium ion via 4. Such acid catalyzed bromine shift in α-bromo ketones are well known particularly in steroidal compounds.[4] The diketo bromide 6 exclusively exists in the keto-form as does 3,5-cyclooctadien-1,2-dione.[5]

O-Alkylations: Compound 1 slowly reacts with diazomethane to afford the methyl ether 7. Action of triethyloxonium tetrafluoroborate, allyl bromide, and methyl chloroformate on 1 using t-BuOK as a base (THF, r.t.) exclusively gave O-alkylation product, 8 (50%), 9 (43%), and 10 (60%), respectively.

C-Alkylations: Reaction of 1 with 1.1 equivalent of tropylium ion (the tetrafluoroborate, NEt_3, CH_2Cl_2, r.t.) afforded 3-tropyl derivative 11 (33%) and 3,8-ditropyl derivative 12 (44%, m.p. 114-116°C). When two equivalent of the ion

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† Deceased, Feb. 4th, 1976.

was used, 12 was obtained in 88% yield. Similarly, diphenylcyclopropenylium ion gave 3,8-disubstituted compound 13 (m.p. 165.5-166.5°C) in 89% yield.

Grignard Reactions: Reaction of 1 with methylmagnesium iodide in ether gave rise to 2-hydroxy-2-methyl-4,6-cyclooctadienone 15 (ν=3480, 1710 cm^{-1}) in 27% yield. Phenylmagnesium bromide afforded the similar product 16 (39%). The reactions can be rationalized by the intermediacy of the double salt 14 which prevents the second alkylation.

Reactions with Amines:

Primary Amines: Heating to reflux of 1 with cyclohexylamine in toluene afforded 2-(cyclohexylamino)-2,4,6-cyclooctatrienone 18 (ν=3380, 1650, 1588, 1522 cm^{-1}) in 33% yield probably via the enol-imine 17. The similar product 19 (28%) was obtained using aniline as an amine. In the ^{1}H-NMR spectra of these compounds at room temperature, the signals of the methylene protons appear as a doublet in each compound (δ=2.89 in 18, δ=2.97 in 19) with somewhat larger half-width than that of 2,4,6-cyclooctatrienone 2. The observations suggest that the activation energies of the ring inversion of 18 and 19 are larger than 2[1], but smaller than 1[6].

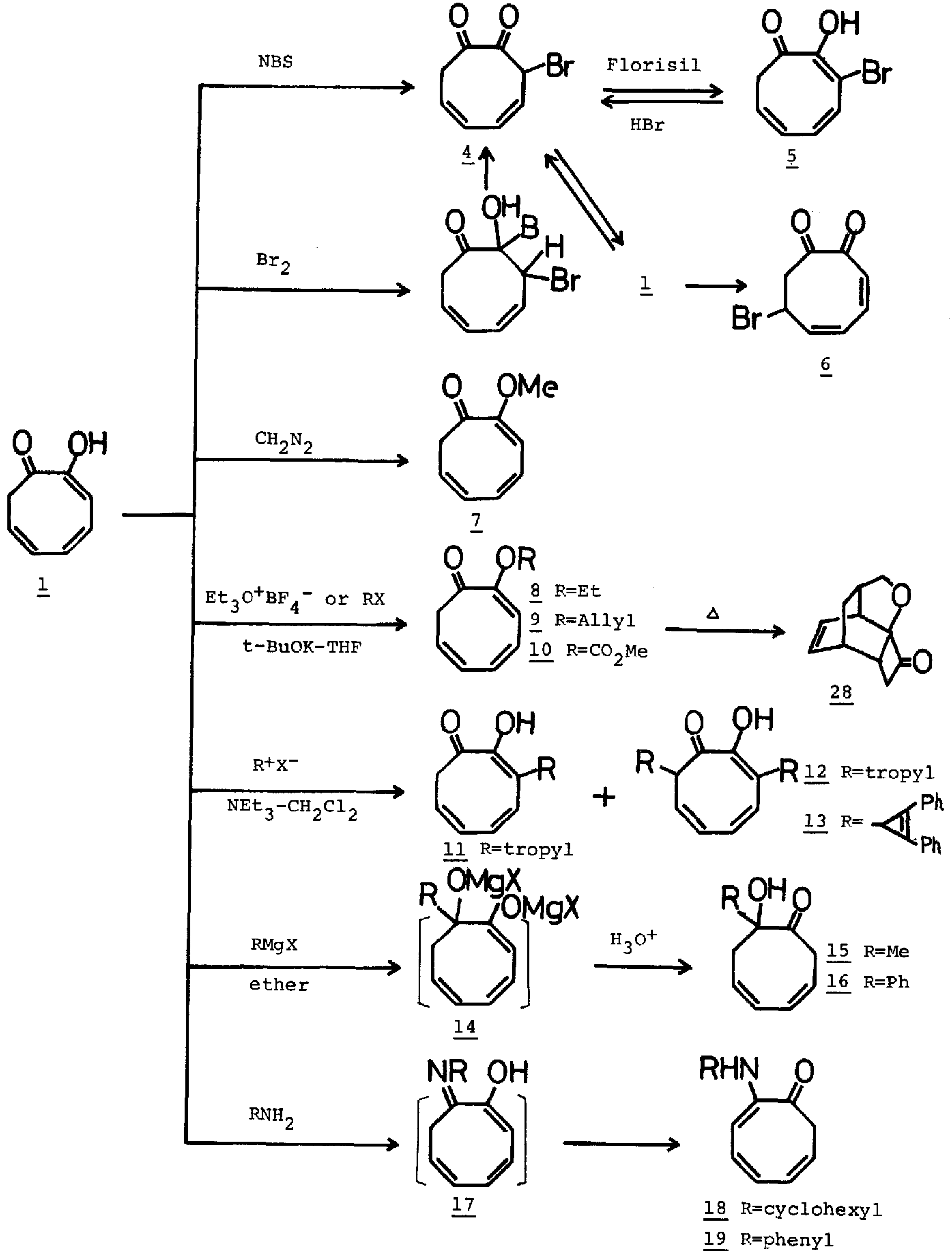
Secondary Amines: Reaction of 1 with pyrrolidine in refluxing benzene afforded the bicyclic ketone 21 (ν=1700, 1580 cm^{-1}) in 30% yield. Morpholine resulted similarly giving 22 (34%). The cyclization may have proceeded via the immonium cation 20. Compound 2 has been reported to undergo ring opening by the reactions with secondary amines.[7]

Reaction with Thionyl Chloride: Heating to reflux of 1 with thionyl chloride in methylene chloride afforded benzocyclobutenone 25 in 75% yield, probably by the spontaneous dehydrochlorination from 2-chloro-2,4,6-cyclooctatrienone 23 via the valence isomer 24.

Diels-Alder Reactions: When heated with N-phenylmaleimide in toluene to reflux, 1 gave the Diels-Alder adduct 26 (m.p. 217-218°C, ν=3430, 1780, 1720 cm^{-1}) in 73% yield. The result is similar to that of 2 and indicates that 1 valence-isomerizes to the bicyclic hydroxy ketone 27 at least at the transition state of the reaction, though 27 has not been detected spectroscopically (IR and ^{1}H-NMR) at the temperature range of -50 to +80°C (^{1}H-NMR)[1]. Attempted Claisen rearrangement of the allyl ether 9 at 195°C in diphenyl ether resulted in an intramolecular Diels-Alder reaction giving the tetracyclic ketone 28 (m.p. 77-78°C, ν=1770 cm^{-1}) in 74% yield.

Pyrolysis: Pyrolysis of 1 at 450°C in vacuum yielded phenol 29 (26%) presumably by the elimination of ketene from 27.

As a conclusion, the presence of the enol group in 1 made its chemical properties considerably different from those of 2,4,6-cyclooctatrienone 2 and did rather similar to tropolone 3.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9 R=Allyl
10 R=CO2Me
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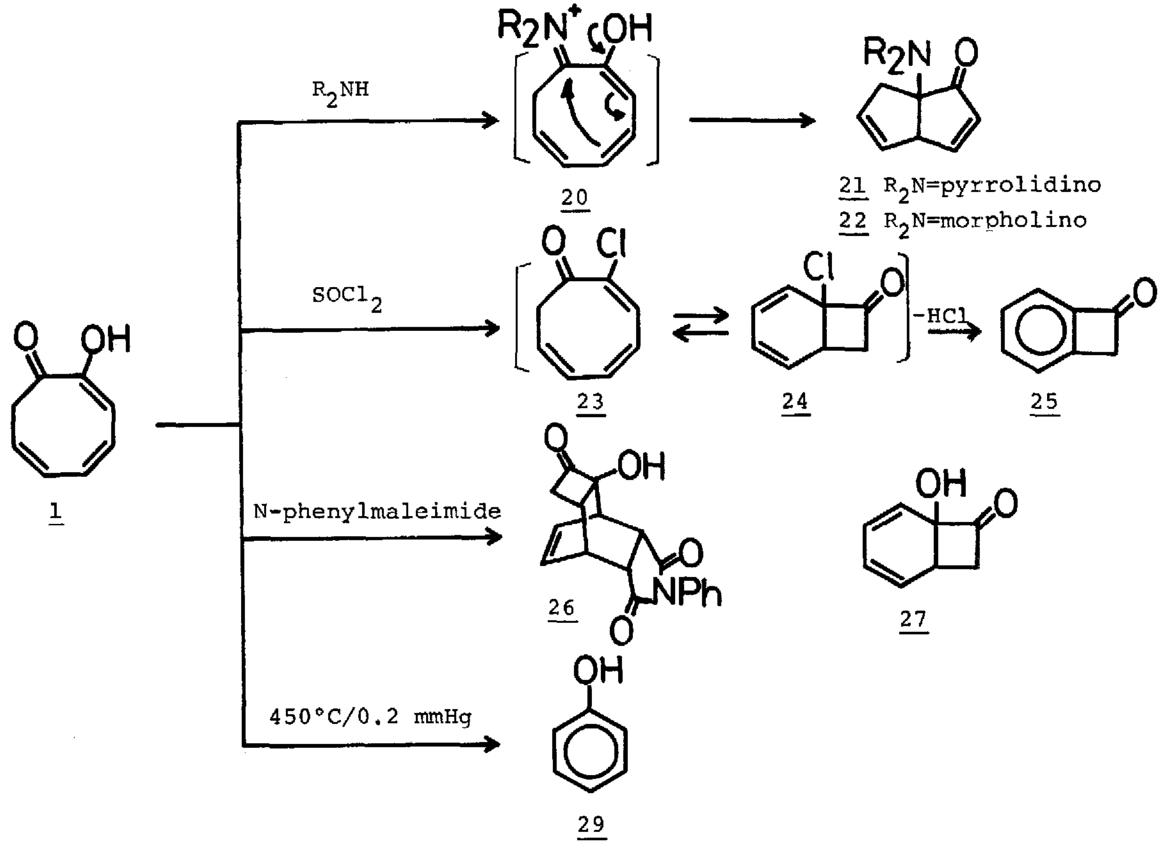
18 R=cyclohexyl
19 R=phenyl



REFERENCES AND NOTES

* To whom all correspondences should be addressed.

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3) Reasonable spectroscopic data other than partially given in this paper were obtained for all the new compounds here described.

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