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# REACTION OF 5-NITROSOTROPOLONE AND ITS ACETATE WITH CYCLOPENTADIENE

Ikuo SAITO, Kunio SAKAN, and Shô ITÔ*

Department of Chemistry, Tohoku University

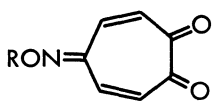
Sendai 980

The reaction of nitrosotropolone 1 with cyclopentadiene was found to proceed peri- and stereospecifically yielding unstable endo [4+2] adduct 6. Nitrosotropolone acetate 2 also reacts regio- and stereospecifically in benzene to give endo adduct 3. The structure of the products were determined on the basis of their spectra. Their quinoxaline derivatives were also prepared.

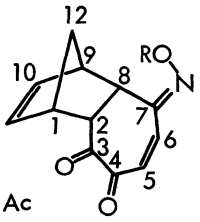
Tropone and its derivatives are known to undergo cycloaddition reactions both with mono-olefins ([4+2] type)[1,2] and with 1,3-dienes ([6+4], [4+2] and [2+4] types)[3] to form a variety of carbon skeletons. Tropolones, however, do not usually react with 1,3-dienes although they do with mono-olefins.[2c,2e] We describe here the cycloaddition reaction of cyclopentadiene and 5-nitrosotropolone, which is known to behave as p-tropoquinone oxime 1, and its acetate 2.[4]

When 5-nitrosotropolone acetate 2 was heated with cyclopentadiene at 60° for 3 hr in benzene, the hygroscopic adduct 3, colorless semisolid, was obtained in 70% yield as a sole product. Addition of methanol to the benzene solution of 3 afforded the corresponding hemiacetal 4, colorless liquid, which was also obtained in 75% yield by the cycloaddition reaction in methanol. For the structure determination, 3 or 4 was mixed with o-phenylenediamine and the quinoxaline derivative 5, pale yellow liquid, was obtained quantitatively.[5] While molecular composition was secured by the elemental analyses and mass spectrum, structure of 5 except the geometry of acetoxy imino group was disclosed by the detailed PMR analysis. All the proton signals were assigned as shown at the end of text with the aid of the deuterated compounds 5-2,5-$d_2$, prepared from 1-3,7-$d_2$. The magnitude of $J_{1,2}$ and $J_{8,9}$(=3 Hz) thus disclosed suggests the endo configuration.[6]

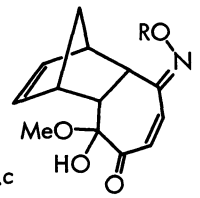
Information on the only ambiguous point in the structures of 3-5, geometry of acetoxyimino group, was obtained from the cycloaddition reaction of 1. When 5-nitrosotropolone 1 and cyclopentadiene were left in methanol at room temperature for 5 days, a colorless amorphous substance 6, mp 150-155°, was obtained in 35% yield.[5] Sparingly soluble in ordinary solvent, 6 is stable in air but easily reverted to 1 and cyclopentadiene when dissolved in methanol. Purification by recrystallization and spectral measurements in solution were therefore not possible. Thermal instability hampered the determination of molecular composition. 6 was consequently correlated with 5 in the following way. Condensation of o-phenylenediamine in methanol at room temperature afforded a 4:1 mixture of isomeric quinoxaline derivatives 7, yellow needles, mp 263°(dec.) and 8, yellow needles, mp 172-173° (dec.). Acetylation of these compounds (room temperature) afforded the acetate 5 and 9, pale yellow liquid, respectively. The spectral features of 7 and 8, and 5 and 9 are very similar to each other, respectively, suggesting them to have very similar structures. Judging from $J_{1,2}$ and



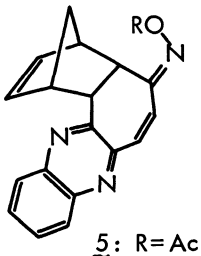
1: R=H
2: R=Ac



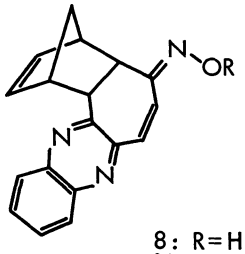
3: R=Ac
6a: R=H



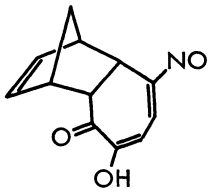
4: R=Ac
6b: R=H



5: R=Ac
7: R=H



8: R=H
9: R=Ac



6c

$J_{8,9}$ (=2.5~3), 8 and 9 also have endo configuration. Therefore, 7 and 5, and 8 and 9 are geometrically isomeric pairs with respect to the C=N bond. Observations that the chemical shift of $H_6$ is lower in 8 and 9 than in 7 and 5, respectively, and that reverse is true for $H_8$ suggest that OH or OAc are syn to $H_6$ in the formers and to $H_8$ in the latters.[7] Thus, the peri- and stereoselectivity in the reaction of 1 and regio- and stereoselectivity for 2 were demonstrated. This leaves the structure of 6 to be clarified.

Three structures are plausible for 6; quinonoid form 6a, its hemiacetal form 6b and its tautomeric nitroso form 6c. If the structure 6a or 6b represents correct structure, 6 is possible to exist as a mixture of the geometrical isomers. We prefer 6c on the basis of IR spectral evidence. IR spectrum of 6 exhibits bands at 1672 $cm^{-1}$ (v.s) and 1620 $cm^{-1}$ (m), which are similar to the carbonyl region of diosphenol,[8] and lacks a strong $\nu_{C=N}$ band at 1520-1570 $cm^{-1}$ which generally appears in the spectra of benzoquinone oximes.[9] Formation of 7 and 8 from 6 can be rationalized by the initial tautomerism of 6c to 6a and subsequent condensation.

Thus, high peri- and stereoselectivity of 1 and high regio- and stereoselectivity of 2 in the cycloaddition reaction was revealed.

## Spectroscopic Data

3: PMR: $\delta_1,\delta_9$ 3.17 (br.s), 3.40 (br.s), $\delta_2$ 4.41 (dd, J=9, 3.5), $\delta_5$ 6.39 (d, J=13), $\delta_6$ 7.09 (br.d, J=13), $\delta_8$ 3.61 (dd, J=9, 3), $\delta_{10},\delta_{11}$ 6.15 (t, J=4), $\delta_{12}$ 1.65 (2H, t, J=3), $\delta_{CH_3}$ 2.35.

4: UV ($\lambda$max): 222 (10600), 243 (9100 sh), 285 (3800 sh), 430 nm (550 sh). IR ($\nu$): 3450, 1780, 1680. PMR: $\delta_1,\delta_9$ ~3.1 (2H, m), $\delta_2$ 3.23 (dd, J=9.5, 2.8), $\delta_5$ 6.30 (d, J=13), $\delta_6$ 7.00 (dd, J=13, 0.3), $\delta_8$ 4.33 (ddd, J=9.5, 3.0, 0.3), $\delta_{10},\delta_{11}$ 5.78, 5.98 (both ddd, J=5, 2.5, 1), $\delta_{12}$ 1.51 (2H, m), $\delta_{CH_3}$ 2.29 (3H, s), $\delta_{MeO}$ 3.00 (3H, s).

5: MS (m/e): 331 ($M^+$), 265, 223, 178, 83 (base peak), 66. UV ($\lambda$max): 239 (14100), 243 (13500 sh), 259 (12200), 285 (7500 sh), 310 (6900 sh), 320 (7400), 354 (5100), 368 (4100 sh), 406 nm (320). IR ($\nu$): 1770,

1490, 1370, 1320, 760 $cm^{-1}$. PMR: $\delta_1,\delta_9$ 3.29 (br.s), 3.42 (br.s), $\delta_2$ 4.21 (dd, J=10, 3), $\delta_5$ 6.94 (d, J=13), $\delta_6$ 6.49 (dd, J=13, 0.3), $\delta_8$ 4.56 (dd, J=10, 3), $\delta_{10},\delta_{11}$ 5.88, 6.13 (both dd, J=6, 3), $\delta_{12}$ 1.54 (dt, J=8.5, 1.5), 1.77 (br.d, J=8.5), $\delta_{CH_3}$ 2.30 (s), $\delta_{Bz}$ 7.68, 7.94 (4H, complex).

6: IR (ν): 3400 (v.s), 2940 (m), 1672 (v.s), 1620 (m), 1550 (w), 1400 (w), 1342 (m), 1310 (m), 1295 (w), 1253 (m), 1191 (m), 1150 (m), 1116 (w), 1090 (m), 1056 (m), 1020 (w), 955 (br.s), 890 (m), 845 (m), 833 (m), 795 (m), 780 (m), 760 (w), 736 (m), 680 (w).

7: MS (m/e): 289 ($M^+$), 223 (base peak), 180, 66. UV (λmax): 224 (ε 17500 sh), 236 (15800 sh), 256 (20400), 280 (11500 sh), 318 (9400), 362 nm (10100). IR (ν): 3200, 1637, 1566, 985, 760 $cm^{-1}$. PMR (Py-$d_5$): $\delta_1,\delta_9$ 3.30 (br.s), 3.74 (br.s), $\delta_2$ 4.26 (dd, J=10, 3.3), $\delta_5$ 6.88 (d, J=13), $\delta_6$ 6.74 (br.d, J=13), $\delta_8$ 4.82 (dd, J=10, 3), $\delta_{10},\delta_{11}$ 5.81, 6.14 (both dd, J=5.7, 2.8), $\delta_{12}$ 1.43, 1.71 (both br.d, J=8), $\delta_{Bz}$ 7.60, 8.05 (4H, complex).

8: MS (m/e): 289 ($M^+$), 223 (base peak), 180, 79, 66. UV (λmax): 221 (ε 15700 sh), 254 (18000), 275 (9800 sh), 323 (8000), 335 (7800), 348 (7700). IR (ν): 3200, 1630, 1560, 970, 930, 760 $cm^{-1}$. PMR (Py-$d_5$): $\delta_1,\delta_9$ 3.30 (br.s), 3.56 (br.s), $\delta_2$ 4.07 (dd, J=10, 2.5), $\delta_5$ 6.96 (d, J=13), $\delta_6$ 7.24 (br.d, J=13), $\delta_8$ 4.13 (dd, J=10, 2.5), $\delta_{10},\delta_{11}$ 6.12, 6.32 (both dd, J=5.5, 2.8), $\delta_{12}$ 1.54 (2H, br.s), $\delta_{Bz}$ 7.60, 8.05 (4H, complex).

9: MS (m/e): 331 ($M^+$), 289, 265, 223 (base peak), 193, 180, 66. UV (λmax): 221 (ε 13300 sh), 247 (16700 sh), 253 (17800), 320 (6400), 332 (5900 sh), 347 (5200 sh), 364 (3100 sh), 446 nm (130). IR (ν): 1770, 1480, 1370, 1350, 760 $cm^{-1}$. PMR: $\delta_1,\delta_9$ 3.32 (br.s), 3.43 (br.s), $\delta_2$ 4.11 (dd, J=10, 2.5), $\delta_5$ 6.72 (br.d, J=13), $\delta_6$ 6.89 (d, J=13), $\delta_8$ 4.29 (dd, J=10, 3), $\delta_{10},\delta_{11}$ 5.96 (dd, J=6, 3), 6.24 (dd, J=6, 2.5), $\delta_{12}$ 1.64 (2H, br.s), $\delta_{CH_3}$ 2.13 (s), $\delta_{Bz}$ 7.68, 7.95 (4H, complex).

## References and Notes


* To whom all the correspondences should be addressed.

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5) All the crystalline compounds described in this paper except 6 gave the correct elemental analyses. Spectral data are referred to the following conditions unless otherwise stated. UV (λmax): methanol, IR (ν): KBr, PMR (δ): $CDCl_3$.

6) Cf. A.P. Marchand and J.E. Rose, J. Am. Chem. Soc., 90, 3274 (1968).

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