

CYCLOADDITION REACTION OF 5-ARYLAZOTROPOLONE DERIVATIVES WITH CYCLOPENTADIENE.  
CYCLOADDITION OF C=C-N=N LINKAGE

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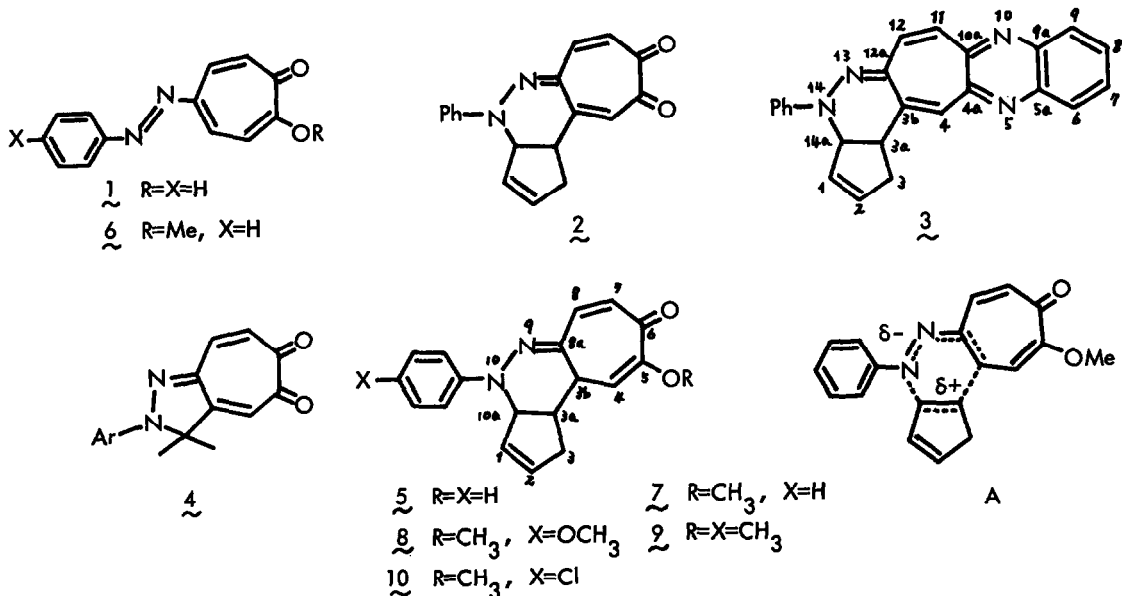
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(Received in Japan 29 January 1977; received in UK for publication 21 February 1977)

In the previous paper (1), we have studied the cycloaddition reaction of 5-nitrosotropolone with cyclopentadiene, first example of stable tropolone derivatives reacting as  $2\pi$  component in [4+2] cycloaddition (2). We have extended our study to 5-phenylazotropolone, which is known (3) to behave as its tautomeric diketo form and subsequently found that it cycloadds to cyclopentadiene utilizing its N=N=C=C linkage. Since this type of the reaction has some novelties (4), we have also carried out some kinetic study on the corresponding methyl ethers and established the nature of the reaction.

5-Phenylazotropolone **1** was stirred in methanol at room temperature for 1 week with excess cyclopentadiene to yield red oil **2** in 20% yield. **2**:  $\lambda_{\max}$  222 ( $\epsilon$  10100), 260 (5320), 280 (5320), 290 (5440), 319 (5700), 342 (4960), 390 (2900), 494 nm (10600),  $\nu$  1618, 1460  $\text{cm}^{-1}$ ,  $\delta$  ~2.80 (2H, br. d,  $J=7.5$ ), 3.65 (1H, br. q,  $J=7.5$ ), 5.23 (1H, br. d,  $J=7.5$ ), 5.90 (1H, br. d,  $J=8.0$ ), 6.18 (1H, br. d,  $J=8.0$ ), 6.50 (1H, d,  $J=13.0$ ), 6.50 (1H, d,  $J=1.0$ ), 7.30 (1H, d,  $J=13.0$ ), ~7.45 (5H, m) (5). On stirring with *o*-phenylenediamine in methanol at room temperature, **2** yielded the crystalline quinoxaline derivative **3**, red powder, m.p. 183-4° (decomp.), MS  $m/e$  362 ( $M^+$ ),  $\lambda_{\max}$  218 ( $\epsilon$  10680), 255 (19900), 277 (12600), 341 (9210), 498 nm (16300),  $\nu$  1620 (w), 1590, 1485, 1400  $\text{cm}^{-1}$ ,  $\delta$  2.72 ( $H_{3n}$ , br. d, d,  $J=17.5$ , 7.5), 2.91 ( $H_{3x}$ , br. d, d,  $J=17.5$ , 7.5), 3.42 ( $H_{3a}$ , br. q,  $J=7.5$ ), 4.95 ( $H_{14a}$ , br. d,  $J=7.5$ ), 5.93 ( $H_1$ ,  $H_2$ , m), 6.54 ( $H_{11}$ , d,  $J=13.0$ ), 6.60 ( $H_4$ , d,  $J=1.0$ ), 6.70 ( $H_{12}$ , d,  $J=13.0$ ), ~7.35 (5H, m), 7.70 (4H, center of AA'BB'). Structures of the compounds **2** and **3**, which were implied by the similarity of their spectra with those of hinopurpurins **4**, the oxidative cyclization products of arylazohinokitiols, and their derivatives (6) were established by the detailed NMR analysis. Thus, it is clear that **1** formed the 1:1 cyclo-



adduct  $\underset{\sim}{2}$  utilizing the azo linkage and the C=C bond conjugated to it in the tropolone ring, one of the rare heterodiene which undergoes cycloaddition reaction.

Since the formation of  $\underset{\sim}{2}$  from  $\underset{\sim}{1}$  apparently involves an oxidation of the primary adduct  $\underset{\sim}{5}$  (7) and therefore the yield remains always low, the reaction with 2-methoxy-5-phenylazotroponone  $\underset{\sim}{6}$ , which would afford the primary adduct without the oxidation was carried out. Upon the reaction with cyclopentadiene at room temperature for 2 days,  $\underset{\sim}{6}$  yielded the adduct  $\underset{\sim}{7}$ , brown oil, in 54% yield, and the structure of  $\underset{\sim}{7}$  was elucidated spectroscopically: MS  $m/e$  306 ( $M^+$ ),  $\lambda_{max}$  249 ( $\epsilon$  8800), 285 (5180), 315 (4320), 438 nm (7700),  $\nu^{oil}$  1630, 1600  $cm^{-1}$ ,  $\delta$  H<sub>1</sub> 5.87, H<sub>2</sub> 5.77, H<sub>3n</sub> 2.08, H<sub>3x</sub> 2.46, H<sub>3a</sub> ~ 3.6, H<sub>3b</sub> ~ 3.6, H<sub>4</sub> 5.44, H<sub>7</sub> 6.91, H<sub>8</sub> 6.24, H<sub>10a</sub> 5.34, CH<sub>3</sub>O 3.66, Ph ~ 7.30, J<sub>7,8</sub> 13.0, J<sub>3b,4</sub> 4.0, J<sub>3n,3a</sub> 6.2, J<sub>3x,3a</sub> 8.0, J<sub>3a,10a</sub> 10.0, J<sub>3n,3x</sub> 17.5, J<sub>1,2</sub> 6.0.

Since the primary product was thus obtained in good yield, we have studied the mechanism of the reaction, using 2-methoxy-5-phenylazotropones with a methoxyl, a methyl, or a chloro group at the para position of the benzene ring. All these tropone yielded the 1:1 cycloadducts,  $\underset{\sim}{8}$ ,  $\underset{\sim}{9}$ ,  $\underset{\sim}{10}$ , respectively, of the similar structure with  $\underset{\sim}{7}$  (8).

The kinetic study of the cycloaddition reaction in benzene at 40-50° revealed that they followed the pseudo 1st order rate equation and the relative reaction rate decreased in the order of Cl > H > CH<sub>3</sub> > OMe

( $k_{Cl}/k_{OMe}$  ( $40^\circ$ )=13.3). The activation parameters obtained for the formation of  $\underline{2}$  are  $E_a=17.1$  kcal/mole,  $\log A=7.36$ ,  $\Delta S^\ddagger=-24.9$  e. u.,  $\Delta H^\ddagger=16.5$  kcal/mole,  $\Delta G^\ddagger=24.3$  kcal/mole (all at  $40^\circ$ ) (9). Those parameters as well as the relative rate  $k_{Cl}/k_{OMe}$  indicate that all the reactions proceed through a highly-ordered non-ionic transition state as in typical Diels-Alder reactions (10). Solvent effect,  $k_{CH_3CN}/k_{Bz}=1.2-1.9$  ( $40^\circ$ ) for all cases, revealed that the transition state is slightly more polar than the cycloaddends. All of these kinetic data strongly indicate the concerted nature of the reaction (11). Furthermore, the relative reaction rate and, in more quantitative term, the Hammett correlation of these reaction [ $\log(k_R/k_H)$  =  $2.31\sigma_p - 0.22$  ( $r=0.96$ , in benzene) (12)] indicate that the arylazotropones reacted as the electron-deficient diene (Diels-Alder reaction with inverse electron demand). In fact, both  $\underline{1}$  and  $\underline{6}$  failed to react with maleic anhydride under various conditions. Thus the transition state can be depicted as A. This picture can also rationalize the regiospecificity.

Our thanks are due to Dr. Hermann Daum for his technical assistance.

#### References and Footnotes

- 1) I. Saito, K. Sakan and S. Itô, to be published.
- 2) Another known instance is the transient dehydrotropolone. T. Yamanami, M. Yasunami and K. Takase, Tetrahedron Letters, 1725 (1970).
- 3) T. Nozoe, S. Itô, S. Suzuki and K. Hiraga, Proceed. Japan Acad., 32, 344 (1956).
- 4) As far as we are aware, only a few example of this type of cycloadditions has been known between aliphatic azo compounds and maleic anhydride, etc. e.g. L. Caglioti, G. Rosini, P. Tundo and A. Vigevani, Tetrahedron Letters, 2349 (1970), K. N. Zerenin, et al., Zh. Org. Khim., 8, 1438 (1972), Khim. Geterostikl Soedin, 579 (1972), 124 (1973).
- 5) Spectra were measured in the following status unless otherwise stated: UV ( $\lambda$ ) in methanol, IR ( $\nu$ ) in chloroform, and NMR ( $\delta$ ) in  $CDCl_3$  at 100 MHz or 60 MHz.
- 6) T. Nozoe, E. Sebe and S. Ebine, Proceed. Japan Acad., 26, 24 (1950), T. Nozoe, T. Ikemi and T. Ozeki, ibid., 31, 455 (1955). Spectral data for phenylhinopurpurin:  $\lambda_{max}$  259 ( $\epsilon$  7950), 348 (5010), 505 nm (36300),  $\nu$  (KBr) 1615, 1585  $cm^{-1}$ ,  $\delta$  1.70 (6H, s), 6.50 (1H, s), 6.90 (1H, d,  $J=13.0$ ),  $\sim$ 7.30 (5H, m), 7.70 (1H, d,  $J=13.0$ ); those for its quinoxaline derivative:  $\lambda_{max}$  255 ( $\epsilon$  27600), 285 (12600), 345 (8700), 503 nm (22900),  $\nu$  1640 (w), 1595, 1490  $cm^{-1}$ ,  $\delta$  1.68 (6H, s), 6.17 (1H, s), 6.56 (1H, d,  $J=13.0$ ), 6.72 (1H, d,  $J=13.0$ ),  $\sim$ 7.30 (5H, m), 7.4-7.8 (4H, m).
- 7) In fact, when the reaction of  $\underline{1}$  and cyclopentadiene was carried out under  $N_2$ , a few colored products were detected by TLC along with a small amount of  $\underline{2}$ . Attempted separation of these products, however, always resulted in the isolation of  $\underline{1}$  and  $\underline{2}$ . One of them may be the primary product mentioned in the text. The other product could be the [2+4] adducts because this type of the adduct is known to revert to the original cycloaddend very easily (1).

- 8) The reaction conditions, yields and spectral properties of the cycloadducts are as follows: p-Methoxy-phenyl compound 8: brown oil, room temp., 3 days, 90% yield, MS m/e 336 ( $M^+$ ),  $\lambda_{\max}$  228 ( $\epsilon$  8770), 247 (9060), 302 (5550), 345 (2590 sh), 448 nm (7660):  $\nu^{\text{oil}}$  1620, 1510  $\text{cm}^{-1}$ :  $\delta_1$  5.84,  $\delta_2$  5.70,  $\delta_{3n}$  2.07,  $\delta_{3x}$  2.45,  $\delta_{3a} \sim 3.50$ ,  $\delta_{3b} \sim 3.62$ ,  $\delta_4$  5.42,  $\delta_7$  6.91,  $\delta_8$  6.19,  $\delta_{10a}$  5.24,  $\delta_{\text{OMe}}$  3.68, 3.80,  $\delta_{\text{Ph}}$  7.10 ( $A_2B_2$ ):  $J_{1,2}$  7.2,  $J_{3n,3x}$  18.0,  $J_{3n,3a}$  5.0,  $J_{3x,3a}$  8.0,  $J_{3b,4}$  4.0,  $J_{3a,10a}$  9.0,  $J_{7,8}$  13.0. p-Tolyl compound 9: brown oil, room temp., 2 days, 62% yield, MS m/e 320 ( $M^+$ ),  $\lambda_{\max}$  245 ( $\epsilon$  9800), 252 (10400), 255 (10700), 261 (10000), 285 (6700 sh), 318 (5820 sh), 442 nm (11250),  $\nu^{\text{oil}}$  1620, 1515  $\text{cm}^{-1}$ ,  $\delta_1$  5.84,  $\delta_2$  5.73,  $\delta_{3n}$  2.07,  $\delta_{3x}$  2.44,  $\delta_{3a} \sim 3.49$ ,  $\delta_{3b} \sim 3.60$ ,  $\delta_4$  5.41,  $\delta_7$  6.94,  $\delta_8$  6.20,  $\delta_{10a}$  5.26,  $\delta_{\text{OMe}}$  3.67,  $\delta_{\text{Ph}}$  7.20 ( $A_2B_2$ ),  $\delta_{\text{Me}}$  2.32,  $J_{1,2}$  6.0,  $J_{3n,3x}$  17.5,  $J_{3n,3a}$  4.0,  $J_{3x,3a}$  7.5,  $J_{3a,10a}$  9.0,  $J_{3b,4}$  4.0,  $J_{7,8}$  13.0. p-Chlorophenyl compound 10, brown oil, room temp., 1 day, 45% yield, MS m/e 340, 342 ( $M^+$ ),  $\lambda_{\max}$  257 ( $\epsilon$  7400), 270 (6020), 294 (4500), 427 nm (6940),  $\nu^{\text{oil}}$  1620, 1490  $\text{cm}^{-1}$ ,  $\delta_1$  5.84,  $\delta_2$  5.71,  $\delta_{3n}$  2.08,  $\delta_{3x}$  2.46,  $\delta_{3a} \sim 3.49$ ,  $\delta_{3b} \sim 3.60$ ,  $\delta_4$  5.42,  $\delta_7$  6.91,  $\delta_8$  6.19,  $\delta_{10a}$  5.27,  $\delta_{\text{OMe}}$  3.68,  $\delta_{\text{Ph}}$  7.29,  $J_{1,2}$  6.0,  $J_{3n,3x}$  17.5,  $J_{3n,3a}$  6.0,  $J_{3x,3a}$  8.0,  $J_{3a,10a}$  9.0,  $J_{3b,4}$  4.0,  $J_{7,8}$  13.0.
- 9) Those parameters fall in the following ranges for all cases:  $E_a = 15.7-17.5$  kcal/mole,  $\log A = 5.74-7.80$ ,  $\Delta S^\ddagger = -22.9 \sim -32.3$  e.u.  $\Delta H^\ddagger = 15.1-16.9$  kcal/mole,  $\Delta G^\ddagger = 24.0-25.7$  kcal/mole (at  $40^\circ$ ).
- 10) Cf. A. Wasserman, "Diels-Alder Reactions", Elsevier, New York, 1969.
- 11) Although the stereochemistry of the process is not clear unfortunately from the structures of products, it should be endo [4+2] cycloaddition from the concertedness of the reaction.
- 12) The  $\rho$  value obtained is rather large for the Diels-Alder reactions. However, it should be reasonable if the nature of heterodiene system is taken into account. The similar value (+2.50 at  $25^\circ$ ) was obtained in the reaction of nitrosobenzenes with 2,3-dimethylbutadiene (M. Ahmad and J. Hamer, J. Org. Chem., 31, 2829 (1966)).