CYCLOHEXADIENONES. 3. PREPARATION AND THERMAL DECOMPOSITION OF 4-AZIDO-2,4,6-TRI-t-BUTYL-2,5-CYCLOHEXADIEN-1-ONE[1]

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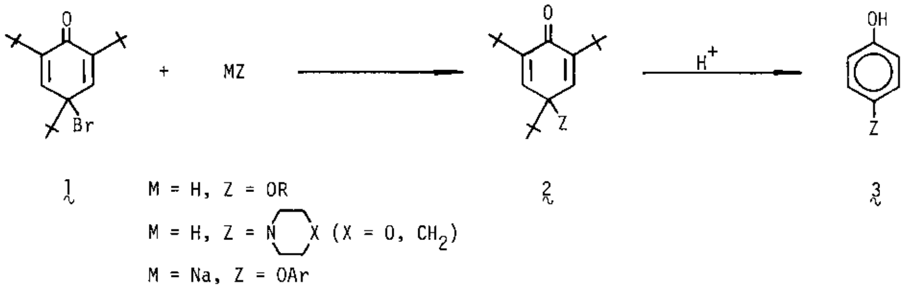
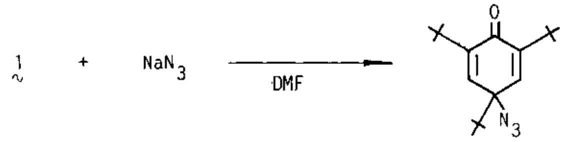
Abstract —— Reaction of 4-bromo-2,4,6-tri-tert-butyl-2,5-cyclohexadien-1-one (1) with sodium azide was carried out in DMF to afford 4-azido-2,4,6-tri-tert-butyl-2,5-cyclohexadien-1-one (4) in 85% yield. Thermal decomposition of 4 in boiling toluene gives 6-amino-2,4-di-tert-butylphenol (5), 2,4,6,8-tetra-tert-butylphenoxazin-1-one (7) and 2,4,6,8a-tetra-tert-butyl-7-cyano-8-oxo-5a,8a-dihydrocyclopenteno[2,3-b]benzoxazine (8). However, the thermal decomposition of 4 was carried out under highly diluted conditions to afford 5 and 2,4-di-tert-butyl-5-cyano-2,4-cyclopentadien-1-one (9) in 48 and 50% yields, respectively. It was also found that the thermal decomposition of 4 in boiling toluene in the presence of acetic anhydride afforded 6-acetoamido-2,4-di-tert-butylphenol (6) and 9 in 47 and 50% yields, respectively. The reaction pathways of the formation of 5, 8 and 9 were proposed in the present paper.

It has been previously reported that 4-bromo-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (1) reacted with alcohols,[2] sodium phenolates[3] and amines such as piperidine and morpholine[4] to afford the corresponding 4-substituted 2,4,6-tri-t-butyl-2,5-cyclohexadien-1-ones (2) which were easily leaded to p-substituted phenols (3) by the acid-catalyzed trans- or dealkylation.



Scheme 1

When **1** was treated with sodium azide in DMF at room temperature for 24 h, the expected 4-azido-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one[5] [**4**, mp. 41-42°, pale yellow prisms] was obtained in 85% yield.



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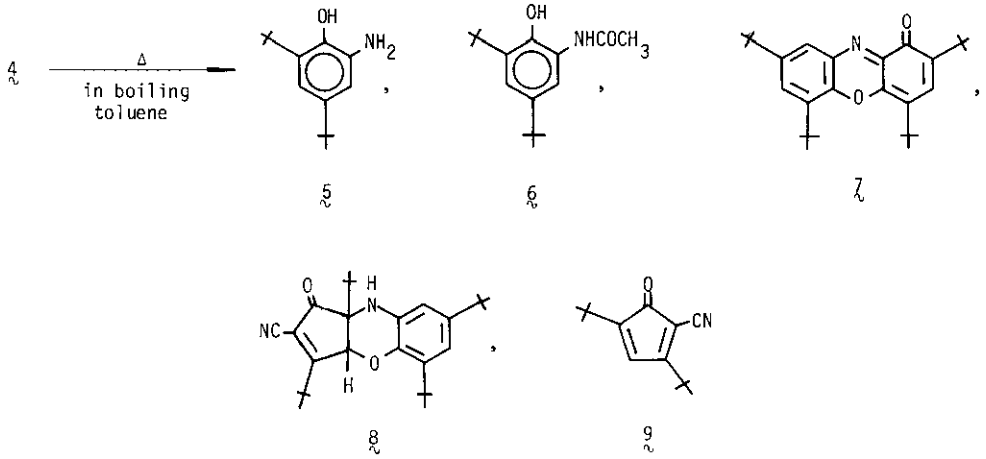
Thermal decomposition of **4** was carried out in boiling toluene and the results are summarized in Table 1 and Scheme 2.



Scheme 2

Table 1. Thermal Decomposition of **4** in Boiling Toluene[a)]

Run	Time (h)	Product (%)
1	1	**5** (15), **7** (15), **8** (50)
2[b)]	2	**5** (48), **9** (50)
3[c)]	1	**6** (47), **9** (50)

a) **4**/toluene : 1 g/50 ml b) Highly diluted condition

c) Acetic anhydride (Ac_2O/**4** : 1/1) was added into toluene solution before the reaction.

As is shown in Run 1, the thermal decomposition of **4** afforded 6-amino-2,4-di-t-butylphenol (**5**)[6], 2,4,6,8-tetra-t-butylphenoxazin-1-one [**7**, mp. 220-221°C, blue prisms, lit.,[7] mp. 208°C] and

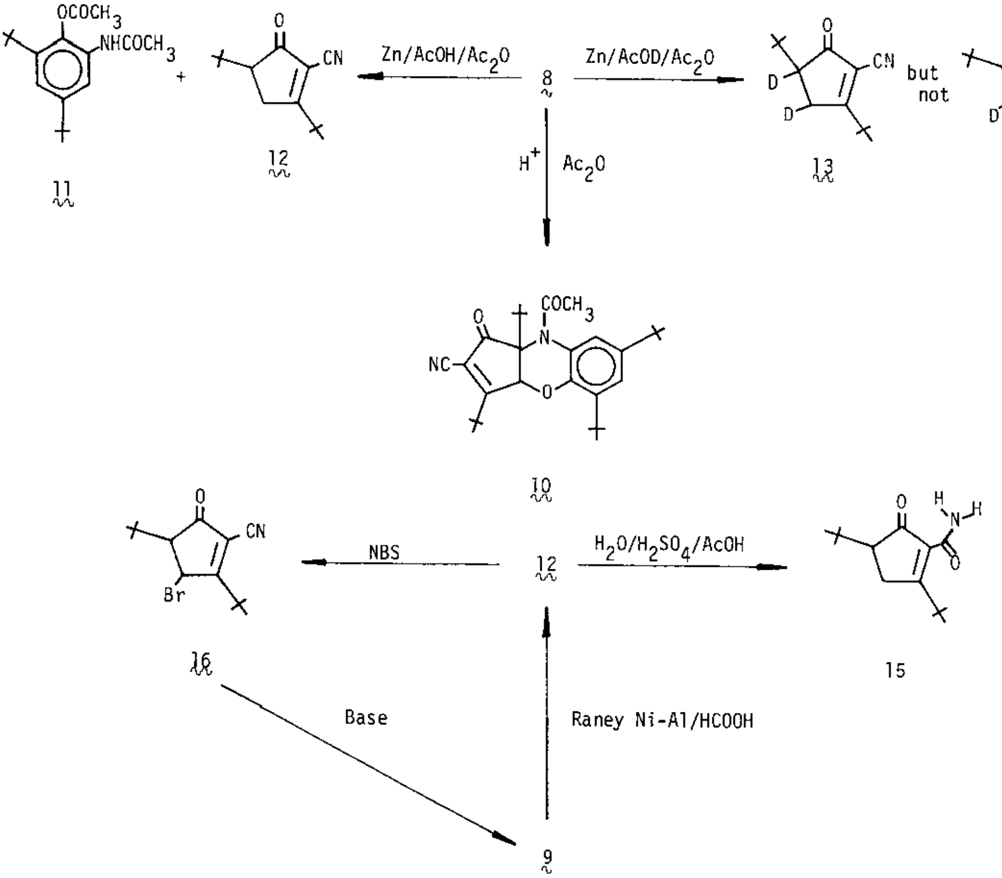
2,4,6,8a-tetra-t-butyl-7-cyano-8-oxo-5a,8a-dihydrocyclopenteno[2,3-b]benzoxazine[8][8, mp. 184-185 °C, orange yellow plates] in 15, 15 and 50% yields, respectively.

Although Stegmann and Scheffler[7] reported that the oxidation of 5 with air in pyridine afforded 7 of mp. 208 °C, the sample prepared by their method has melting point of 220-221 °C which is same as that of our sample.

$$5 \xrightarrow[\text{in pyridine}]{\text{air}} 7$$

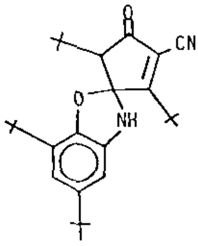
This finding suggests that the the compound 7 obtained by Stegmann and Scheffler must be impure.

The structure of 8 was confirmed by its elemental analysis and spectral data as well as chemical conversions shown in Scheme 3.



Scheme 3

When 8 was treated with acetic anhydride in the presence of sulfuric acid, N-acetylated compound[9] [10, mp. 189-190 °C, colorless prisms] was obtained. *The reduction of 8 with Zn powder in acetic* acid-acetic anhydride afforded 2-amino-4,6-di-t-butylphenol diacetated [11, mp. 201-202 °C, colorless needles] and 3,5-di-t-butyl-2-cyano-2-cyclopenten-1-one[10] [12, mp. 78-79 °C, colorless prisms] in 60 and 65% yields, respectively. When this reduction was carried out in CH_3COOD, 4,5-dideutero derivative 13[11] was obtained but not 4,4-dideutero derivative 14. This finding cancelled spiro structure 17 for compound 8. Hydrolysis of 12 afforded 2-carbamoyl-3,5-di-t-butyl-2-cyclopenten-1-one[12] [15, mp. 134-136.5 °C, colorless needles] in 29% yield. Bromination of 12 with NBS in CCl_4 gave 4-bromo-3,5-di-t-butyl-2-cyano-2-cyclopenten-1-one[13] [16, mp. 82-84 °C, pale yellow prisms] from which hydrogen bromide was readily eliminated by the treatment with a strong organic base such as DBU to afford 3,5-di-t-butyl-2-cyano-2,4-cyclopentadien-1-one[14] [9, mp. 130-131 °C, reddish yellow prisms]. Reduction of 9 with Raney Ni-Al alloy in HCOOH afforded 12 in 70% yield. The results mentioned above supported strongly the structure proposed to compound 8, however, its geometrical structure (8a or 8b) could not be confirmed by available data.



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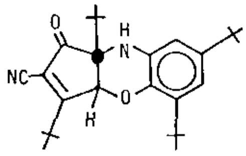

8a

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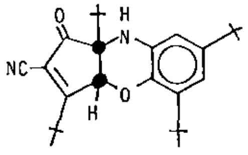
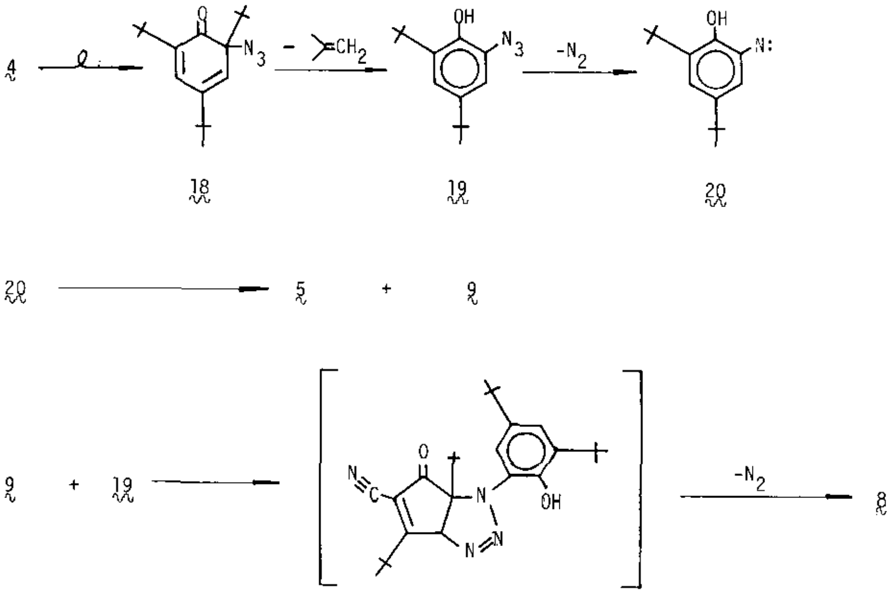


8b

The thermal decomposition of 4 under highly diluted conditions afforded 5 and 9 in 48 and 50% yields, respectively, but not 8. It was also found in the thermal decomposition of 4 in the presence *of acetic anhydride that 6 and 9 were obtained in 48 and 50% yields, respectively, though the thermo*lysis was not carried out under highly diluted conditions. From the above results, compounds 5 and 9 seem to be intermediates for the formation of 8. However, reaction of 5 with 9 in boiling toluene did not give any products but the starting compounds were recovered in almost quantitative yields.

$$5 \quad + \quad 9 \quad \xrightarrow{\Delta} \quad \text{no reaction}$$

Although detailed reaction mechanism of the thermal decomposition of 4 is still obscure, the reaction pathway of the formations of 5, 8 and 9 might be proposed as following Scheme 4. Under highly diluted conditions, the reaction of 9 with 19 might not progress because a chance of the collision between 9 and 19 should be very low. Addition of acetic anhydride might accelerate the decomposition of 19 affording nitrene intermediate 20, therefore, the reaction of 9 with 19 might not occur in this condition.



Scheme 4

REFERENCES AND NOTES

1. Part 2. G. Fukata, H. Yoshiya and M. Tashiro, submitted to J. Chem. Soc..
2. M. Tashiro, G. Fukata and H. Yoshiya, Synthesis, 1979, 988.
3. M. Tashiro, H. Yoshiya and T. Yamato, Synthesis, 1978, 399.
4. M. Tashiro and G. Fukata, Synthesis, 1979, 602.
5. IR (KBr): νmax = 2100, 1660, 1640 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ = 0.98 (9H, s), 1.27 (18H, s), 6.65 (2H, s); ^{13}C-nmr ($CDCl_3$): δ = 25.52 (q), 29.7 (q), 35.6 (s), 39.1 (s), 68.6 (s), 136.2 (d), 150.3 (s), 185.4 (s).
6. S. H. Schroeter, J. Org. Chem., 34, 4012 (1969).
7. H. B. Stegmann and H. Scheffler, Chem. Ber., 101, 262 (1968).
8. IR (KBr): νmax = 3340, 2240, 1735 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ = 0.95 (9H, S), 1.20 (9H, s), 1.40 (9H, s), 1.62 (9H, s), 4.28 (1H, s, disappeared with D_2O), 5.23 (1H, s), 6.63 (1H, d, J = 3 Hz), 6.78 (1H, d, J = 3Hz); ^{13}C-nmr ($CDCl_3$): δ = 26.1 (q), 29.4 (q), 30.3 (q), 31.6 (q), 34.4 (s), 34.7 (s), 36.9 (s), 38.2 (s), 67.4 (s), 79.2 (d), 110.8 (d), 112.3 (s), 114.5 (d), 117.6 (s), 133.9 (s), 137.9 (s), 140.0 (s), 145.7 (s), 191.7 (s), 200.4 (s).
9. ^{1}H-nmr ($CDCl_3$): δ = 0.79, 1.33, 1.44, 1.56 (each 9H, s), 1.97 (3H, s), 5.43 (1H, s), 7.26 (1H, d, J = 3 Hz), 7.32 (1H, d, J = 3 Hz).

10. IR (KBr): νmax = 2225, 1707, 1602 cm^{-1}. ^{1}H-nmr (CDCl$_3$): δ = 1.00 (9H, s), 1.40 (9H, s), 2.28 (1H, dd, J = 6 Hz, J = 3.5 Hz), 2.58 (1H, dd, J = 20 Hz, J = 3.5 Hz), 2.88 (1H, dd, J = 20 Hz, J = 6 Hz); ^{13}C-nmr (CDCl$_3$): δ = 27.2 (q), 28.6 (q), 33.4 (t), 33.7 (s), 37.1 (s), 54.5 (d), 113.1 (s), 115.0 (s), 197.5 (s), 203.1 (s).

11. ^{1}H-nmr (CDCl$_3$): δ = 1.00 (9H, s), 1.40 (9H, s), 2.24 (0.1H, br. s), 2.58 (0.5H, br. s), 2.80 (0.5H, br. s). Mass: m/e 221 (M^{+}).

12. ^{1}H-nmr (CDCl$_3$): δ = 0.98 (9H, s), 1.36 (9H, s), 2.18 (1H, dd, J = 3.5 Hz, J = 6 Hz), 2.48 (1H, dd, J = 3.5 Hz, J = 20 Hz), 2.74 (1H, dd, J = 6 Hz, J = 20 Hz), 5.86, 7.08 (each 1H, br. s, disappeared with D$_2$O).

13. IR (KBr): νmax = 2225, 1710, 1590 cm^{-1}. ^{1}H-nmr (CDCl$_3$): δ = 1.00 (9H, s), 1.52 (9H, s), 2.42 (1H, d, J = 1 Hz), 5.00 (1H, d, J = 1 Hz).

14. IR (KBr): νmax = 2225, 1710 cm^{-1}. ^{1}H-nmr (CDCl$_3$): δ = 1.21 (9H, s), 1.35 (9H, s), 6.76 (1H, s); ^{13}C-nmr (CDCl$_3$): δ = 27.6 (q), 28.9 (q), 32.5 (s), 35.6 (s), 97.0 (s), 113.2 (s), 136.1 (d), 146.3 (s), 181.3 (s), 194.5 (s).

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