Cyclodienones. Part 6. Preparation of 4-Azido-2,4,6-tri-t-butylcyclohexa-2,5-dienone and its Thermal, Photo-, and Acid-catalyzed Decomposition [1,2]

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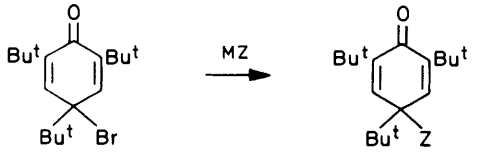
Preparation of 4-azido-2,4,6-tri-t-butylcyclohexa-2,5-dienone (3) from 4-bromo-2,4,6-tri-t-butylcyclohexa-2,5-dienone (1) and sodium azide is described. Treatment of (3) with concentrated sulphuric acid afforded 2,6-di-t-butyl-*p*-benzoquinone (7) in 75% yield, while the reaction at −10 °C in chloroform solution gave a tri-t-butylazepinone (5) and 3,5-di-t-butyl-*o*-benzoquinone (8). Photolysis of (3) in benzene afforded 2,4-di-t-butylcyclopenta-2,4-dienone (11), which was isolated as the dimer (12). Thermolysis of (3) in boiling toluene gave 6-amino-2,4-di-t-butylphenol (17), 2,4,6,8-tetra-t-butyl-1*H*-phenoxazin-1-one (21), and 2-cyano-9,9a-dihydro-3,5,7,9a-tetra-t-butylcyclopenta[*b*][1,4]benzoxazin-1(3a*H*)-one (22) in 15, 15, and 48% yields, respectively. When the thermolysis was carried out with very low reagent concentrations, 5-cyano-2,4-di-t-butylcyclopenta-2,4-dienone (23), in addition to the phenol (17), was obtained. The compound (23) was also obtained by thermolysis of (3) in boiling acetic anhydride and in boiling toluene containing acetic anhydride. The reaction pathway for the formation of compounds (17), (22), and (23) on thermolysis of the azide (3) is also discussed.

It is well known that the decomposition of certain cyclic azides often results in ring expansion.[3]

It has been previously reported that 4-bromo-2,4,6-tri-t-butylcyclohexa-2,5-dienone (1) reacts with nucleophiles such as alcohols,[4] glycols,[5] sodium phenolates,[6] and amines [7] to afford the corresponding 4-substituted 2,4,6-tri-t-butylcyclohexa-2,5-dienones (2) in good yields. These results suggest that the reaction of the cyclohexadienone (1) with sodium azide may give 4-azido-2,4,6-tri-t-butylcyclohexa-2,5-dienone (3).



(1) (2)

M = H, Z = OR
M = H, Z = O(CH$_2$CH$_2$)OH
M = H, Z = piperidino
M = H, Z = morpholino
M = Na, Z = OAr

It is also well known that decomposition of t-azides affords Stieglitz rearrangement products (Scheme 1). Therefore, formation of the iminoquinone (4) and/or the ring-expanded compound (5) from the decomposition of (3) might be expected. We undertook the present work in order to clarify whether the formation of either or both of these products occurs.

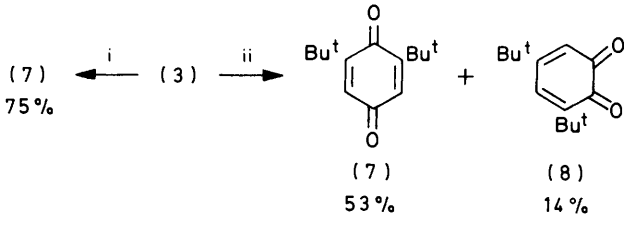
Results and Discussion

Reaction of the Cyclohexadienone (1) *with Sodium Azide.*— When compound (1) was treated with sodium azide in dimethylformamide (DMF) at room temperature for 24 h, the expected product (3) was obtained in 85% yield.†

However, this reaction did not proceed in tetrahydrofuran and diethyl ether. The structure of compound (3) was easily confirmed by its spectral data: the protons of the t-butyl groups appeared at δ 0.98 (9 H) and 1.27 (18 H), respectively, as singlets, and the olefinic protons were observed at δ 6.65 (2 H) as a singlet.

From the n.m.r. data, the possible structure (6) can be excluded.

Sulphuric Acid-catalyzed Decomposition of the Azide (3).— Treatment of the azide (3) with concentrated sulphuric acid in chloroform at −10 °C afforded 2,6-di-t-butyl-*p*-benzoquinone (7) [10] and 3,5-di-t-butyl-*o*-benzoquinone (8) [11] in 53 14% yields, respectively, while the decomposition with sulphuric acid without solvent at room temperature gave only the *p*-isomer (7) in 75% yield.

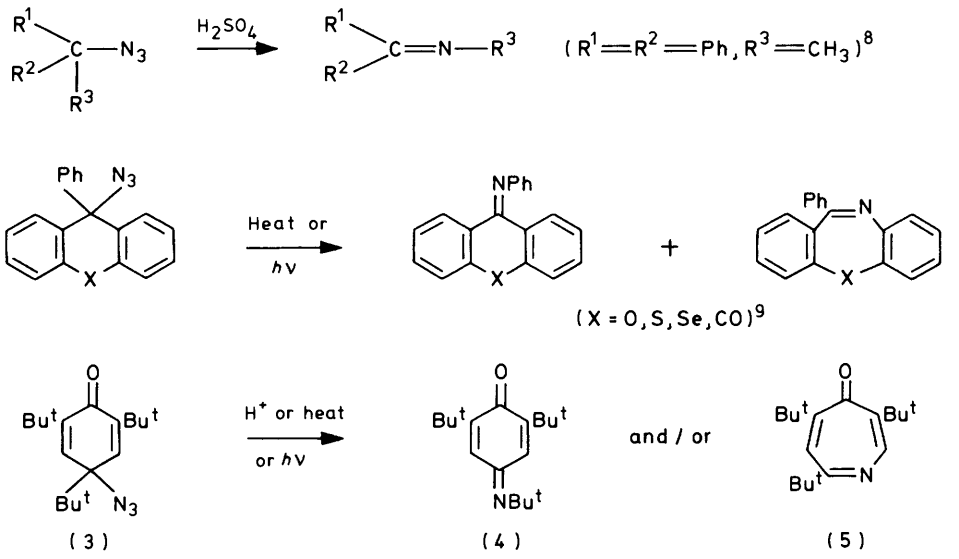


Reagents: i, conc. H_2SO_4 at room temp.; ii, conc. H_2SO_4 in $CHCl_3$ at −10 °C

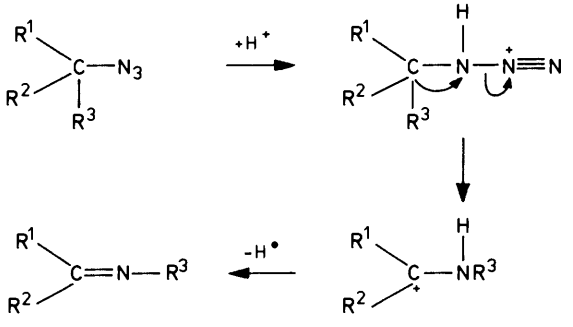
The formation of compound (7) suggests that the iminoquinone (4) must be formed initially, and then hydrolysed to give (7); the ring-expanded product (5), which is another expected product, was not formed in this reaction.

It should be noted that compound (8) was obtained only at low temperatures, as mentioned above.

† Under the same conditions, 4-azido-4-methyl-2,6-di-t-butylcyclohexa-2,5-dienone is also obtained by the reaction of 4-bromo-4-methyl-2,6-di-t-butylcyclohexa-2,5-dienone and sodium azide. However, the other dienones either do not react with sodium azide or give only tar.



Scheme 1.

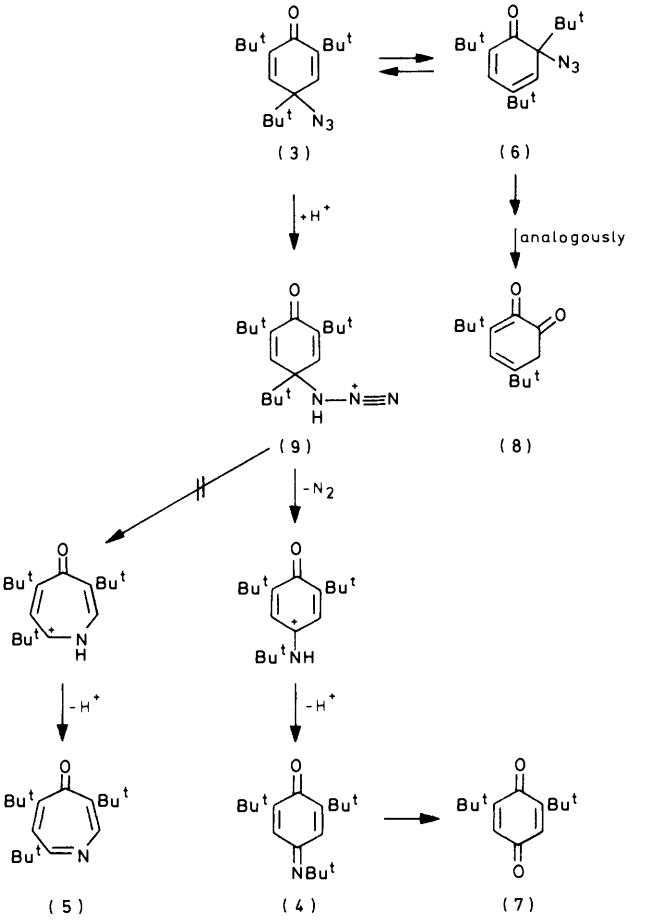


Scheme 2.

The proposed mechanism of the acid-catalyzed Stieglitz rearrangement is shown in Scheme 2.[3] Accordingly, the routes for the formation of the benzoquinones (7) and (8) could be as shown in Scheme 3. At room temperature, the t-butyl groups of the azide (3) could rearrange to the protonated nitrogen atom before migration of the azide group occurs. Hydrolysis of the iminoquinone (4) which is formed should take place easily to afford the *p*-benzoquinone (7). However, at lower temperatures, the rearrangement of the t-butyl group could be slower, so that the azide group of compound (3) may move to the carbon atom at position-2 to give the 2-azide (6).

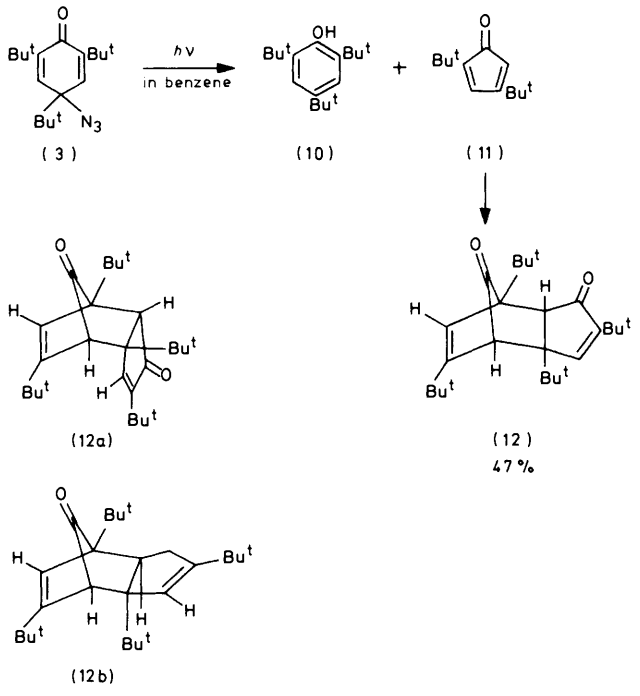
The cleavage of the C–C ring-bond in the formation of the azepine (5), which is expected as the other possible product from the Stieglitz rearrangement of (3), may need more energy than the cleavage of the C–C bond between the t-butyl group and the ring carbon atom.

Photo-decomposition of the Azide (3).—When a benzene solution of the azide (3) was irradiated for 48 h with a high-pressure Hg lamp, 2,4-di-t-butylcyclopenta-2,4-dienone (11) was formed together with 2,4,6-tri-t-butylphenol (10), but neither the expected imino-compound (4) nor the azepine (5) was found. Compound (11) is very labile and dimerizes easily into (12) on standing at room temperature for two days, on heating on a water-bath for a few minutes, or by treatment with silica gel (Scheme 4). Thus, isolation of the pure monomer

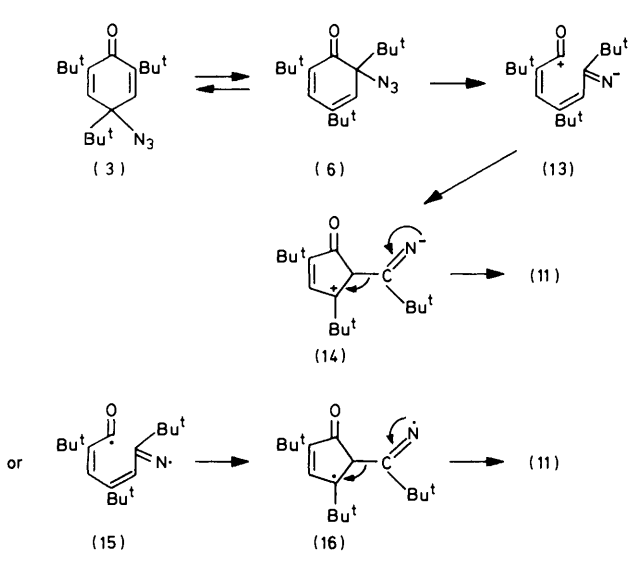


Scheme 3.

(11) was difficult by the usual methods. Therefore the dimer (12), in place of (11), was isolated from the reaction mixture after it had been heated on a water-bath for a few hours. The m.p. and spectral data for (12) are identical with those given



Scheme 4.



Scheme 5.

in the literature.[12] However, its stereochemistry [(12a) or (12b)] is still obscure.

Based on the results described above, the tentative routes for the formation of compound (11) from the azide (3) are as shown in Scheme 5. Unfortunately, it is not yet clear whether the ionic or the radical reaction predominates.

Thermal Decomposition of the Azide (3).—Thermal decomposition of compound (3) was carried out in boiling toluene or acetic anhydride; the results are summarized in the Table and Scheme 6.

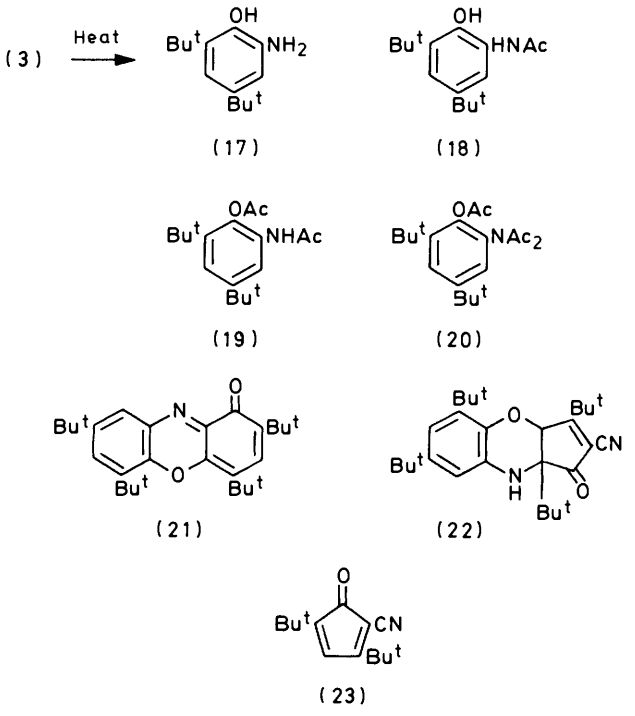
As is shown in Run 1 of the Table, the thermal decomposition of the azide (3) in boiling toluene afforded 2-amino-4,6-di-t-butylphenol (17), 2,4,6,8-tetra-t-butyl-1*H*-phenoxazin-1-one (21), and 2-cyano-9,9a-dihydro-3,5,7,9a-tetra-t-butylcyclopenta[*b*][1,4]benzoxazin-1(3a*H*)-one (22) in 15, 15 and 48% yields, respectively. Although Stegmann and Scheffler [13] reported that the oxidation of the phenol (17) with air, in pyridine, affords the phenoxazinone (21) with m.p. 208 °C, the m.p. of (21) obtained in the present work was 220—221 °C. We therefore reinvestigated the oxidation of (17) according to the reported method,[13] and found that the sample thus prepared had a m.p. of 220—211 °C, which is the same as for our sample. Therefore, the sample obtained by Stegmann and Scheffler must have been impure.

The structures of compounds (22) and (23) were confirmed by their elemental analyses and spectral data as well as by the chemical conversions shown in Scheme 7. When the cyclopentabenzoxazinone (22) was treated with acetic anhydride in the presence of sulphuric acid, the *N*-acetylated compound

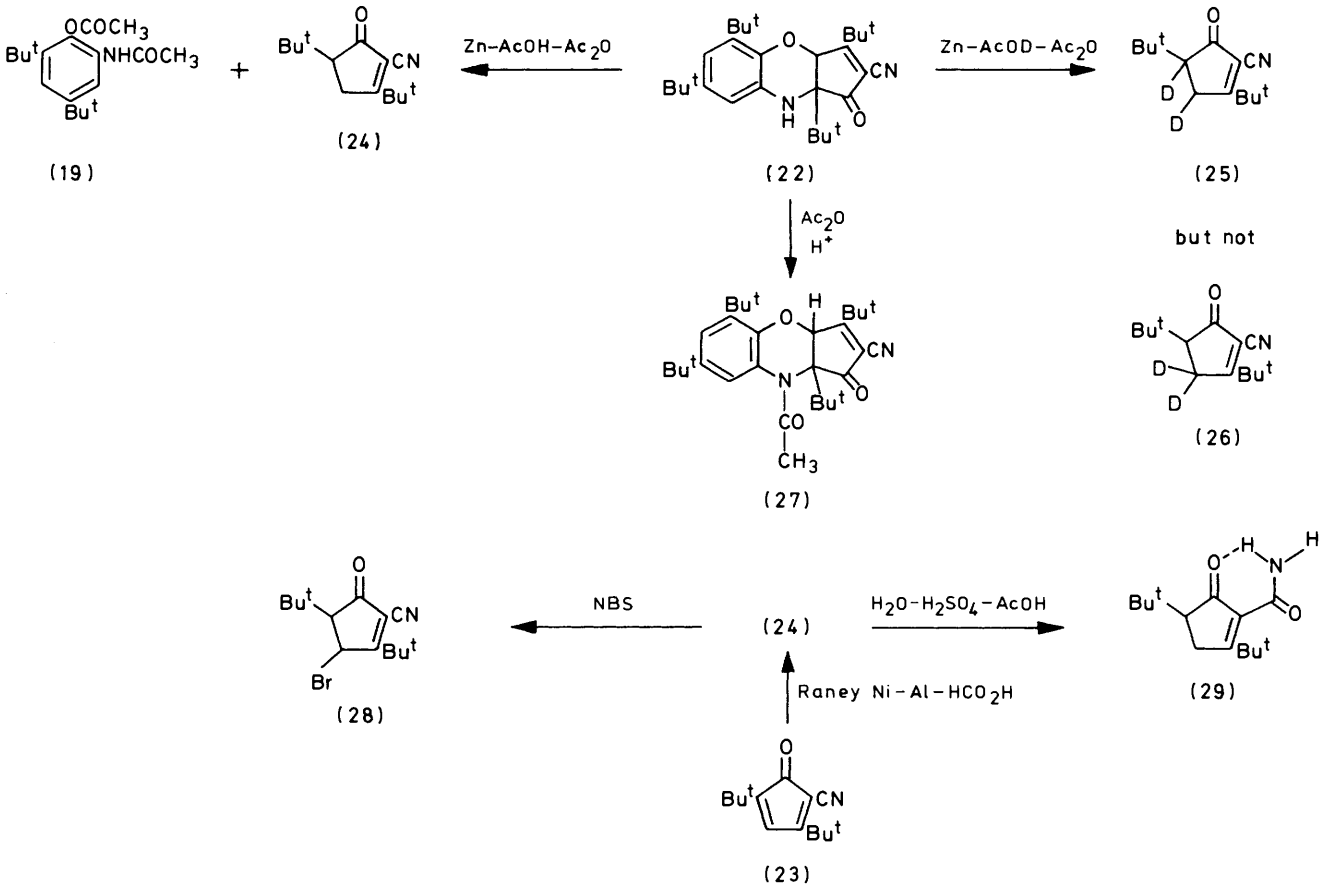
Table. Thermal Decomposition of the azide (3) in boiling toluene or acetic anhydride [a]

Run	Solvent	Additional substrate	Time (h)	Product [Yield (%)]
1	Toluene		1	(17) [15], (21) [15], (22) [48]
2 [b]	Toluene		2	(17) [48], (23) [50]
3 [c]	Toluene	Ac_2O	1	(18) [47], (23) [50]
4 [d]	Toluene	AcOH	1	(21) [46], (22) [32], (23) [13]
5	Ac_2O		1—4	(19) [39], (20) [6], (23) [50]

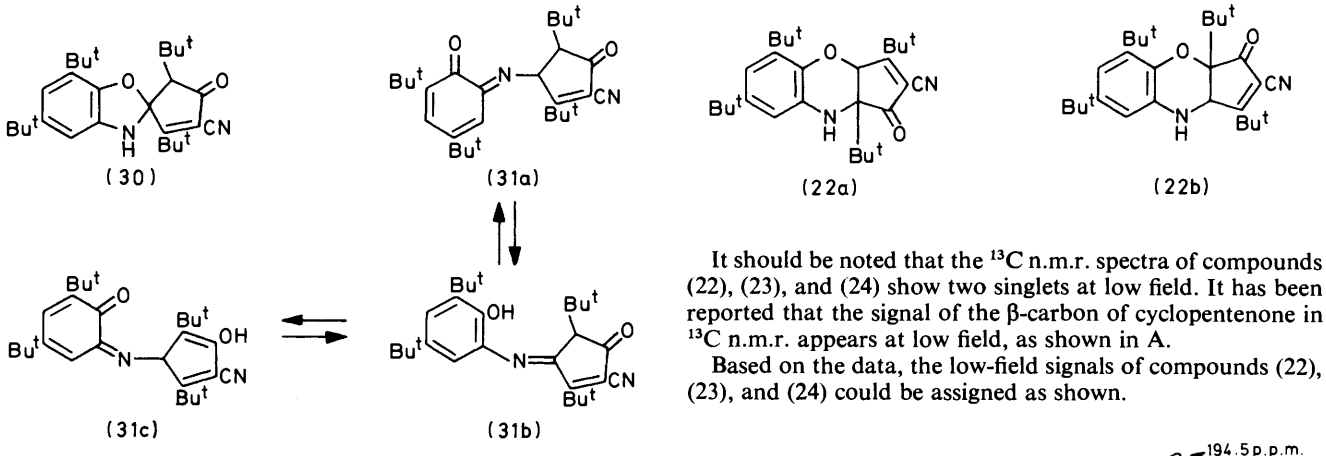
[a] Compound (3) (1 g) was dissolved in toluene or Ac_2O (50 ml) unless otherwise indicated. [b] Very dilute conditions. [c] Ac_2O (1 mol equiv.). [d] AcOH (1 mol equiv.).



Scheme 6.



Scheme 7.

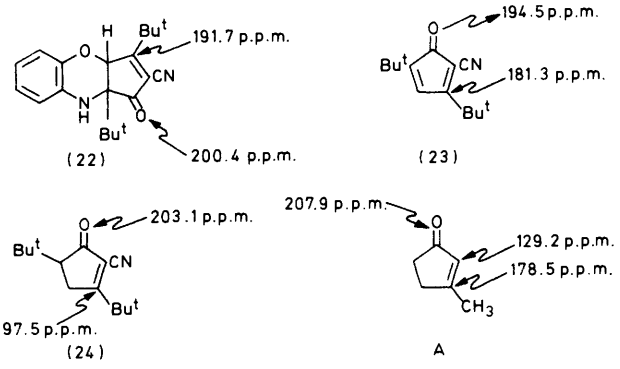


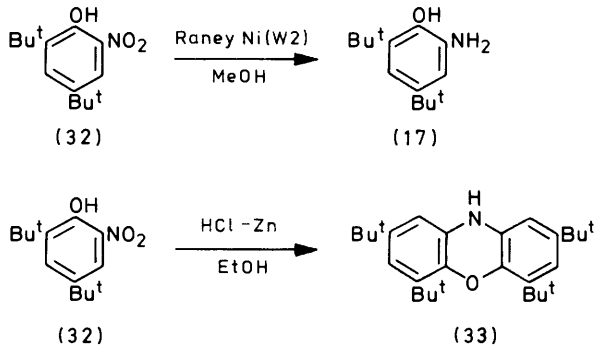
Scheme 8.

(27) was obtained. The reduction of (22) with Zn powder in a mixture of acetic acid and acetic anhydride afforded the products (19) and (24) in 60 and 65% yield, respectively. When this reduction was carried out in acetic [^{2}H]acid, the 4,5-dideuterio-derivative (25) was obtained, but not the 4,4-dideuterio-derivative (26). It was also found that hydrolysis of (22) under various conditions did not give any products. These findings exclude the spiro- (30) and imino-structures (31) (Scheme 8) from the possible structures for (22). However, the ring-junction stereochemistry is still obscure.

It should be noted that the ^{13}C n.m.r. spectra of compounds (22), (23), and (24) show two singlets at low field. It has been reported that the signal of the β-carbon of cyclopentenone in ^{13}C n.m.r. appears at low field, as shown in A.

Based on the data, the low-field signals of compounds (22), (23), and (24) could be assigned as shown.





Scheme 9.

Hydrolysis of the cyanide (24) afforded 2-carbamoyl-3,5-di-t-butylcyclopent-2-enone (29) in 29% yield. It should be noted that, in the ^{1}H n.m.r. spectra of (29), the two NH_2 protons appeared at δ 5.86 and 7.08, as broad singlets. The signal at δ 7.08 is probably due to a proton and is hydrogen-bonded to the carbonyl group. This means that in (29) the amido-group must be adjacent to the carbonyl group, and that the cyano-group in (23) is at C-2 and adjacent to the carbonyl group. Bromination of the cyclopentabenzoxazinone (22) with *N*-bromosuccinimide (NBS) in a solution of carbon tetrachloride gave 4-bromo-2-cyano-3,5-di-t-butylcyclopent-2-one (28), which afforded (23) again when treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Reduction of (23) with Raney Ni–Al alloy in formic acid afforded the cyanide (24) in 70% yield.

The structure of compound (17) was confirmed by comparison with a sample prepared by the reduction of the nitro-compound (32) (Scheme 9). During an investigation of the reduction of (32), we were interested to find that reduction with Zn powder and hydrochloric acid in ethanol gave 2,4,6,8-tetra-t-butylphenoxazine (33).[13]

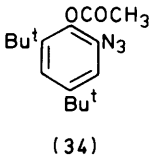
It is clear that two molecules of the azide (3) should participate in the formation of compounds (21) and (22). In order to obtain only monomeric compounds, the thermal decomposition of (3) was carried out with very low reagent concentrations. As was expected, products (17) and (23) were obtained in 48 and 50% yields, but neither (21) nor (22) was found. It was also found that, in the thermal decomposition of (3) in toluene in the presence of acetic anhydride, compounds (18) and (23) were obtained in 48 and 50% yields, respectively, even though the thermolysis was not carried out with low concentrations. The thermal decomposition of the azide (3) in neat acetic anhydride afforded compounds (19), (20), and (23) in 39, 6, and 50% yields, respectively.

In contrast to the acetic anhydride reaction, addition of acetic acid afforded products (23), (21), and (22) in 13, 46, and 32% yields, respectively (Run 4 in the Table). For the preparation of the polycyclic compounds (21) and (22), this decomposition might be useful.

It was found that the thermolysis of the azide (3) in DMF at 135 °C for 2 h in the presence of acetic anhydride afforded compounds (18), (19), (23), and 2-azido-4,6-di-t-butylphenyl acetate (34) in 9, 28, 37, and 6% yields, respectively. The formation of (34) may prove to be significant in considering the reaction pathways for the thermolysis of (3).

Compounds (17) and (23) seem to be intermediates in the formation of the cyclopentabenzoxazinone (22). However, reaction of (17) with (23) in boiling toluene did not give any products, and the starting compounds were recovered in almost quantitative yields.

Although the detailed reaction mechanism of the thermal



(34)

decomposition of (3) is still obscure, the proposed reaction pathways for the formation of compounds (17), (22), and (23) are shown in Scheme 10. After the azido-group of compound (3) migrated to form the isomer (6), de-t-butylation or loss of nitrogen could occur to give intermediate (39) or (35). The nitrene intermediate (40) would then be formed from (39) and/or (35). The formation of compounds (23) and (17) might be explained by the reaction of the intermediate (38) with intermediate (41) or (40). Either of the nitrene intermediates (40) or (35) might react with the cyclopentadienone (23) to give compound (22) *via* the aziridine intermediate (42) or (43).

With very low concentrations of reagents, the reaction of (23) with the intermediate (40) or (35) might be inhibited since the chance of a collision between these reaction components would be very small. Addition of acetic anhydride might accelerate the formation of intermediate (35) or (39) from the 2-azide (6). Therefore, the reaction of the cyclopentadienone (23) with (40) or (35) might not occur. Although isolation of the acetate (34) described above might support the formation of (39), it is not clear whether intermediate (35) or (39) predominates.

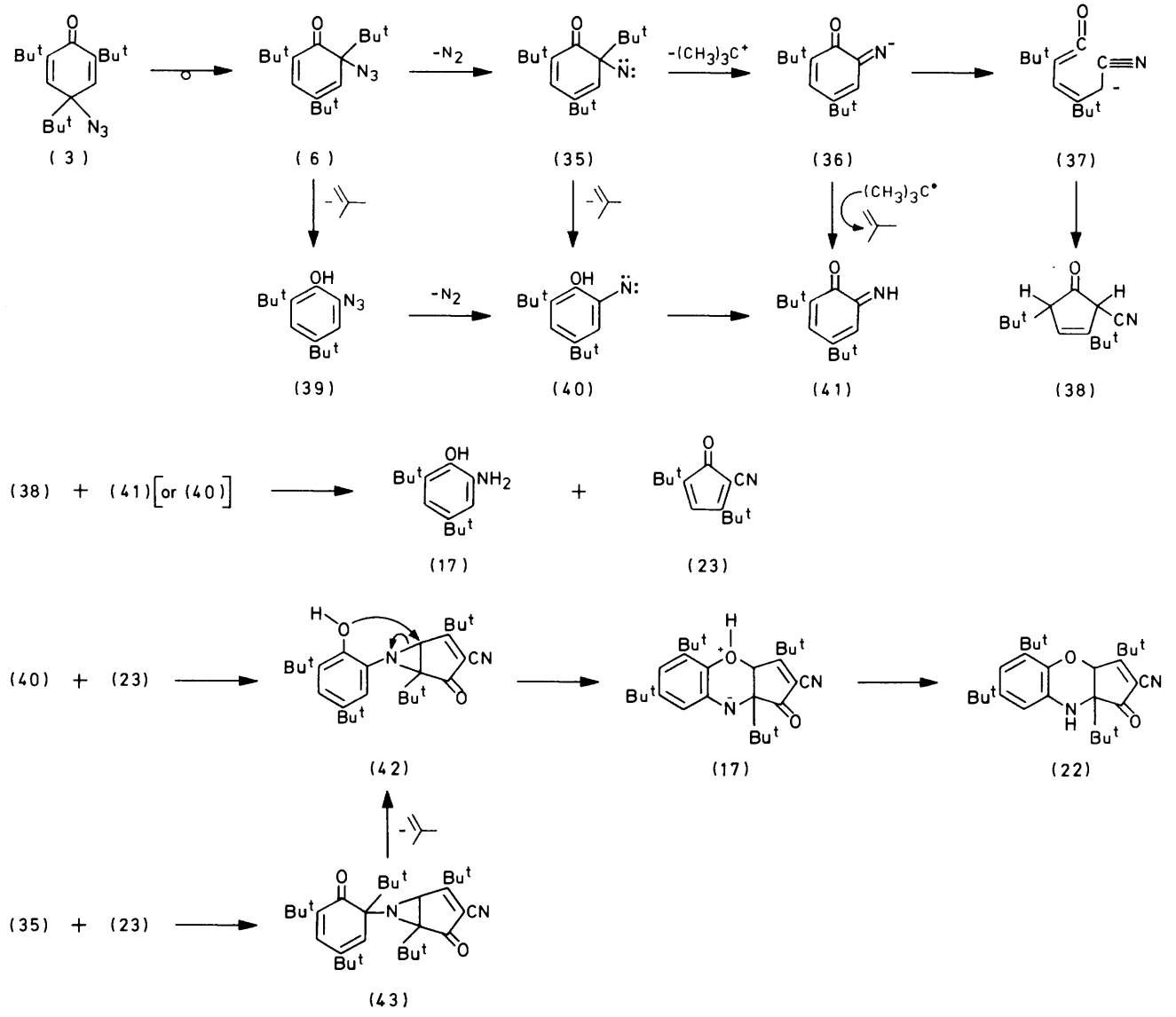
Experimental

Preparation of 4-*Azido*-2,4,6-*tri*-t-*butylcyclohexa*-2,5-*dienone* (3).—A solution of 4-bromo-2,4,6-tri-t-butylcyclohexa-2,5-dienone (1) [15] (54.5 g, 160 mmol) and sodium azide (12.1 g, 180 mmol) in DMF (390 ml) was stirred at room temperature for 6 h and then poured into a large amount of ice–water containing sodium chloride. The precipitates were washed with water and cooled methanol to give the *product* (3) (34.1 g, 80%) which was recrystallized (MeOH) as pale yellow prisms, m.p. 41—42 °C; $\nu_{max.}$ (KBr) 2 100 (N_3), and 1 660 and 1 640 cm^{-1} (CO); δ (^{13}C) ($CDCl_3$) 25.5 (q), 29.7 (q), 35.4 (s), 39.0 (s), 68.6 (s), 136.2 (d), 150.3 (s), and 185.35 p.p.m. (s) (Found: C, 71.15; H, 9.65; N, 13.75. $C_{18}H_{29}ClN_3O$ requires C, 71.25; H, 9.62; N, 13.85%).

Sulphuric Acid-catalyzed Decomposition of the Azide (3) *in Chloroform.*—To a solution of compound (3) (1 g, 3.3 mmol) in chloroform (50 ml) at −10 °C, sulphuric acid (2 ml) was added during 5 min with stirring.

After the reaction mixture had been stirred for an additional 15 min, it was poured into a large amount of ice–water. The chloroform layer was separated, washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue which was chromatographed on silica gel with benzene to afford 2,6-di-t-butyl-*p*-benzoquinone (7) (0.386 g, 53%) as yellow needles (H_2O–MeOH), m.p. 63.5—64.5 °C (lit.,[10] 65 °C), and 2,6-di-t-butyl-*o*-benzoquinone (8) (0.104 g, 14%) as maroon needles (H_2O–acetone), m.p. 114—115 °C (lit.,[11] 113—114 °C).

Sulphuric Acid-catalyzed Decomposition of the Azido-compound (3).—Compound (3) (1 g, 3.3 mmol) was added slowly to concentrated sulphuric acid (2 ml) and the reaction mixture was stirred for 2 days at room temperature. The resulting precipitates were filtered off to give the *p*-benzoquinone (7) (0.53 g, 73%).



Scheme 10.

Photodecomposition of the Azide (3).—A solution of compound (3) (2 g, 6.6 mmol) in dry benzene (50 ml) under a stream of nitrogen was irradiated with a high-pressure lamp for 4 h. It was then evaporated under reduced pressure to leave a residue which was chromatographed on silica gel, using benzene–hexane (1 : 1) as eluant, to give the dimer (12) (0.6 g, 47%) as colourless prisms, m.p. 150—151 °C (lit.,[12] m.p. 151—153 °C). The residue described above was also treated carefully without using chromatography to give crude 2,4-di-t-butylcyclopentadienone (11); however, this is spontaneously converted into the dimer (12), thus making the isolation of pure (11) very difficult. Therefore, the spectral data of pure (11) could not be obtained. Compound (12): δ ($CDCl_3$) 0.98, 1.04, 1.13, and 1.18 (each 9 H, s), 2.95 (1 H, s), 3.18 (1 H, d, *J* 1.5 Hz), 5.88 (1 H, d, *J* 1.5 Hz), and 6.76 (1 H, s); δ (^{13}C) ($CDCl_3$) 27.1 (q), 27.6 (q), 28.4 (q), 28.75 (q), 32.0 (s), 32.2 (s), 33.7 (s), 36.0 (s), 50.6 (d), 53.5 (d), 56.8 (s), 67.2 (s), 122.4 (d), 150.0 (s), 154.6 (d), 158.9 (s), 198.1 (s), and 205.7 p.p.m. (s) (Found: C, 81.05; H, 10.4. Calc. for $C_{26}H_{40}O_2$: C, 81.20; H, 10.48%).

Thermolysis of the Azide (3) *in Boiling Toluene*.—A solution of compound (3) (1 g, 3.3 mmol) in toluene (50 ml) was refluxed for 1 h and then evaporated under reduced pressure. To the residue was added a small amount of hexane to give the crystalline solid which was filtered off and recrystallized from hexane to afford 2-amino-4,6-di-t-butylphenol (17) (0.12 g, 15%) and 2-*cyano*-9,9a-*dihydro*-3,5,7,9a-*tetra*-t-*butylcyclopenta*[b][1,4]*benzoxazin*-1(3aH)-*one* (22) (0.294 g). The solution was chromatographed on silica gel with benzene to give (22) (0.05 g) and 2,4,6,8-*tetra*-t-*butyl*-1H-*phenoxazin*-1-*one* (21) (0.105 g, 15%). The total yield of (22) was 0.344 g (48%). Compound (17) was obtained as colourless prisms (hexane), m.p. 170.5—172 °C (lit.,[16] m.p. 169 °C); δ ($CDCl_3$) 1.26 and 1.40 (each 9 H, s), 2.8—4.7 (3 H, br signals, disappeared with D_2O), and 8.81 and 8.93 (each 1 H, d, *J* 1 Hz); *m/e* 221 (M^+).

Compound (21) was obtained as navy blue prisms (H_2O–MeOH), m.p. 220—221 °C; $\nu_{max.}$ (KBr) 1 460 cm^{-1} (CO); δ ($CDCl_3$) 1.32, 1.33, 1.48, and 1.52 (each 9 H, s), 7.40 (1 H, s), and 7.52 and 7.88 (each 1 H, d, *J* 2 Hz); δ (^{13}C) ($CDCl_3$) 29.05 (q), 30.3 (q), 31.2 (q), 34.6 (s), 34.9 (s), 121.0 (s), 127.7

(d), 128.8 (d), 133.6 (s), 135.9 (s), 137.2 (d), 140.3 (s), 146.8 (s), 146.9 (s), and 179.7 p.p.m. (s); *m/e* 421 (M^+) (Found: C, 79.65; H, 9.3; N, 3.3. $C_{28}H_{39}NO_2$ requires C, 79.26; H, 9.32; N, 3.32%). Compound (22) was obtained as orange yellow plates (hexane), m.p. 184—185 °C; $\nu_{max.}$ (KBr) 3 440 (NH), 2 240 (CN), and 1 735 cm^{-1} (CO); δ ($CDCl_3$) 0.95, 1.26, 1.40, and 1.62 (each 9 H, s), 4.28 (1 H, s), 5.23 (1 H, s), and 6.62 and 6.78 (each 1 H, d, *J* 3 Hz); δ (^{13}C) ($CDCl_3$) 26.1 (q), 29.35 (q), 30.3 (q), 31.55 (q), 34.4 (s), 34.7 (s), 36.9 (s), 38.2 (s), 67.4 (s), 79.2 (d), 110.8 (d), 112.25 (s), 114.5 (d), 117.55 (s), 133.9 (s), 140.0 (s), 145.7 (s), 191.7 (s), and 200.4 p.p.m. (s); *m/e* 439 (M^+); $\lambda_{max.}$ (log ε) (EtOH) 213.0 (4.69), 320.05 (shoulder 4.23), and 292.5 (3.56) nm (Found: C, 76.75; H, 9.15; N, 6.35. $C_{28}H_{40}N_2O_2$ requires C, 77.02; H, 9.23; N, N, 6.42%).

Because of the instability of compound (17), the evaporated residue described above was treated with acetic anhydride and then chromatographed on silica gel to give the *N*-acetyl derivative (18), together with (21), and (22).

Thermolysis of the Azide (3) *under Highly Dilute Conditions.*—To 250 ml of boiling toluene, a solution of compound (3) (1 g) was added during 1 h. After the reaction mixture had been refluxed for an additional 1 h, it was treated with acetic anhydride and evaporated under reduced pressure to leave a residue which was chromatographed on silica gel with chloroform to give the amino-phenol (17) (0.423 g, 48%) and 3,5-*di*-t-*butyl*-2-*cyanopentadienone* (23) (0.356 g, 50%) as orange red prisms (hexane), m.p. 128.5—129.5 °C; $\nu_{max.}$ (KBr) 2 225 (CN) and 1 710 cm^{-1} (CO); δ ($CDCl_3$) 1.31 and 1.35 (each 9 H, s) and 6.76 (1 H, s); δ (^{13}C) ($CDCl_3$) 27.6 (q), 28.9 (q), 32.5 (s), 35.6 (s), 97.0 (s), 113.3 (s), 136.1 (d), 146.3 (s), 181.3 (s), and 194.5 p.p.m. (s); *m/e* 217 (M^+) (Found: C, 77.45; H, 9.0; N, 6.35. $C_{14}H_{19}NO$ requires C, 77.38; H, 8.81; N, 6.45%).

Thermolysis of the Azide (3) *in Boiling Toluene with Acetic Anhydride.*—A solution of compound (3) (5.734 g, 190 mmol) and acetic anhydride (10 ml) in toluene (280 ml) was refluxed for 1 h and then worked up as described above to give the cyanide (23) (2.703 g, 50%) and the *N*-acetyl derivative (18) (2.336 g, 47%).

Thermolysis of the Azide (3) *in Boiling Toluene with Acetic Acid.*—A solution of compound (3) (1 g) and acetic acid (1 ml) in toluene (50 ml) was refluxed for 1 h and then worked up as described above to give the cyclopentabenzoxazine (22) (0.176 g, 32%), the phenoxazine (21) (0.323 g, 46%), and the cyanide (23) (0.044 g, 13%).

Thermolysis of the Azide (3) *in Acetic Anhydride.*—A solution of compound (3) (1 g) in acetic anhydride (30 ml) was refluxed for 15 min and then poured into a large quantity of ice–water and neutralized with sodium hydrogen carbonate. The resulting precipitates were dissolved in chloroform and the solution was dried and chromatographed on silica gel with chloroform to give compound (23) (0.357 g, 50%), 2-acetylamino-4,6-di-t-butylphenyl acetate (19) (0.391 g, 39%), and 2-*diacetylamino*-4,6-*di*-t-*butylphenyl acetate* (20) (0.066 g, 6%). The latter compound (20) can also be prepared by acetylation of (19) on heating with acetic anhydride; it was obtained as colourless prisms (hexane), m.p. 130—131 °C; $\nu_{max.}$ (KBr) 1 760, 1 730, and 1 710 cm^{-1} (CO); δ ($CDCl_3$) 1.33 and 1.35 (each 9 H, s), 2.25 (3 H, s), 2.30 (6 H, s), 7.12 and 7.53 (each 1 H, d, *J* 2.5 Hz) (Found: C, 69.05; H, 8.55; N, 3.95. $C_{20}H_{29}NO_4$ requires C, 69.13; H, 8.41; N, 4.03%).

Nitration of 2,4-*Di-t-Butylphenol.*—To a solution of 2,4-di-t-butylphenol in acetic acid (100 ml) was added concentrated nitric acid (4.2 ml) at 5—10 °C. After the reaction mixture had been stirred for 1.5 h, it was poured into a large amount of ice–water, neutralized with sodium hydrogen carbonate, and extracted with benzene. The benzene solution was washed with water, dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue to which a small amount of cooled methanol was added to give 2,4-di-t-butyl-6-nitrophenol (32) (15.8 g 62%) as pale yellow prisms (MeOH–H_2O), m.p. 60—61 °C (lit.,[17] m.p. 59—60 °C).

Reduction of Compound (32) *with Raney Nickel* (*W*-2).—A mixture of the nitrophenol (32) and Raney Nickel (W-2) in methanol (30 ml) was stirred at room temperature until the yellow colour disappeared (*ca.* 2—3 h). After the excess of Raney Nickel had been filtered off, the filtrate was evaporated to afford crude compound (17) (1.59 g, 46%).

Reduction of the Nitrophenol (32) *with* Zn–HCl.—A mixture of compound (32) (5.53 g, 22 mmol), Zn powder (5.4 g), concentrated hydrochloric acid (14 ml), and ethanol (150 ml) was refluxed for 1 h and the reaction mixture was then evaporated under reduced pressure to leave a residue. A small amount of cooled methanol was added to give crude 2,4,6,8-*tetra*-t-*butylphenoxazine* (33) (2.12 g, 48%) which was recrystallized (MeOH–H_2O), 1 : 1) to give the pure compound (33) together with a dark violet compound (33′) which was the stable radical form proposed by Stegmann and Scheffler.[13] Compound (33) was obtained as red violet prisms (MeOH–H_2O), m.p. 188—191 °C; $\nu_{max.}$ (KBr) 3 440 cm^{-1} (NH); *m/e* 407 (M^+) and 406 ($M^+ - 1$) (Found: C, 82.5; H, 10.15; N, 3.4. $C_{28}H_{41}NO$ requires C, 82.50; H, 10.14; N, 3.44%).

Reaction of the Cyclopentabenzoxazine (22) *with Acetic Anhydride.*—To a solution of compound (22) (0.102 g, 0.23 mmol) in acetic anhydride (16 ml) was added a drop of concentrated sulphuric acid. The reaction mixture immediately changed from yellow to colourless. It was then heated at 90 °C for 60 min and poured into a large amount of ice–water. The resulting precipitate was filtered off to give 9-*acetyl*-2-*cyano*-9,9a-*dihydro*-3,5,7,9a-*tetra*-t-*butylcyclopenta*[b][1,4]*benzoxazin*-1(3a*H*)*one* (27) (0.11 g, 99%) as colourless prisms (hexane), m.p. 189—190 °C; $\nu_{max.}$ (KBr) 2 240 (CN), and 1 740 and 1 680 cm^{-1} (CO); δ ($CDCl_3$) 0.79, 1.33, 1.44, and 1.56 (each 9 H, s), 1.97 (3 H, s), 5.43 (1 H, s), and 7.32 and 7.26 (each 1 H, d, *J* 1 Hz); δ (^{13}C) ($CDCl_3$) 22.8 (q), 26.55 (q), 29.2 (q), 30.0 (q), 31.4 (q), 34.6 (s), 37.0 (s), 37.3 (s), 70.9 (s), 84.8 (d), 112.8 (s), 119.1 (s), 122.1 (d), 122.8 (d), 131.5 (s), 139.2 (s), 145.7 (s), 147.3 (s), 171.6 (s), 180.8 (s), and 189.9 p.p.m. (s); $\lambda_{max.}$ (log ε) (EtOH) 210.0 (4.59), 223.0 (shoulder 4.38), and 275.0 (3.53) nm (Found: C, 75.35; H, 8.7; N, 8.85. $C_{30}H_{42}N_2O_3$ requires C, 75.27; H, 8.84; N, 5.85%).

Reduction of the Cyclopentabenzoxazine (22) *with* Zn *Powder in Acetic Acid.*—A mixture of compound (22) (1.00 g, 2.3 mmol) acetic anhydride (10 ml) and acetic acid (30 ml) was heated with a water-bath (80—90 °C) and Zn powder (7.5 g) was added during 30 min. The reaction mixture was poured into a large amount of ice–water, neutralized with sodium hydrogen carbonate, extracted with chloroform. The chloroform extract was dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue which was chromatographed on silica gel, using chloroform as an eluant, to afford the acetate (19) (0.42 g, 60%) and 2-*cyano*-3,5-*bi*-t-*butylcyclopent*-2-*enone* (24) (0.327 g, 65%) as colourless prisms (hexane), m.p. 78—79 °C; $\nu_{max.}$ (KBr) 2 225 (CN), 1 707 (CO), and 1 602 cm^{-1} (C=C); δ ($CDCl_3$) 1.00 and 1.40 (each 9 H, s), and 2.28 (1 H, dd, *J* 6, 20 Hz); δ (^{13}C) ($CDCl_3$) 27.2 (q), 28.6 (q), 33.4 (t), 33.7 (s), 27.1 (s), 54.5 (d), 113.1 (s), 115.9 (s), 197.5

(s), and 203.1 p.p.m. (s); *m/e* 219 (M^+) (Found: C, 76.45; H, 9.65; N, 6.3. $C_{14}H_{21}NO$ requires C, 76.77; H, 9.65; N, 6.39%).

Reduction of the Cyclopentabenzoxazine in Acetic [^{2}H]*Acid.*—A reduction similar to that described above was carried out in acetic [^{2}H]acid and 2-*cyano*-3,5-*di*-t-*butyl*[4,5-$^2H_2$]*cyclopent*-2-*enone* (25) (46%) was obtained as colourless prisms (hexane), m.p. 72—73 °C; $\nu_{max.}$ (KBr) 2 225 (CN), 1 709 (CO), and 1 600 cm^{-1} (C=C); δ ($CDCl_3$) 1.00 and 1.40 (each 9 H, s), 2.24 (0.1—0.2 H, br s), 2.58 (0.5 H, br s), and 2.80 (0.5 H, br s); *m/e* 221 (M^+), 220 ($M^+ - 1$), and 219 ($M^+ - 2$) (Found: C, 75.9; H, 9.7; N, 6.3. $C_{14}H_{19}D_2NO$ requires C, 75.97; H, 9.65; N, 6.33).

Bromination of the Cyclopent-2-*enone* (24).—A mixture of compound (24) (0.2 g, 0.9 mmol) NBS (0.2 g, 1.1 mmol), benzoyl peroxide (0.014 g, 0.1 mmol), and carbon tetrachloride (15 ml) was gently heated for 1 h and then refluxed for an additional 1 h. The precipitated solid was filtered off and the filtrate was evaporated under reduced pressure to leave a residue which was chromatographed to give 4-*bromo*-2-*cyano*-3,5-*di*-t-*butylcyclopent*-2-*enone* (28) (0.08 g, 30%) of (28), starting compound (24) (0.056 g, 30%), and a mixture of (28) and (24) (0.024 g). Compound (28) was obtained as pale yellow prisms (hexane), m.p. 82—84 °C; $\nu_{max.}$ (KBr) 2 225 (CN), 1 710 (CO), and 1 590 cm^{-1} (C=C); δ ($CDCl_3$) 1.00 and 1.52 (each 9 H, s), and 2.42 and 5.00 (each 1 H, d, *J* 1 Hz) (Found: C, 56.4; H, 6.75; N, 4.7. $C_{14}H_{20}BrNO$ requires C, 56.13; H, 6.70; N, 4.75%).

Treatment of the Bromo-compound (28) *with Base.*—A mixture of compound (28) (50 mg) and a drop of DBU in triethylamine (1 ml) was stirred for 30 min at room temperature. The reaction mixture was poured into a large amount of ice–water, extracted with chloroform and the extracts dried (Na_2SO_4) and evaporated under reduced pressure to give the crude dienene (23) in almost quantitative yield.

Reduction of the Dienone (23) *to the Cyclopentenone* (24).—The mixture of compound (23) (0.1 g, 0.46 mmol), Raney Ni–Al alloy (0.1 g), and 75% formic acid (10 ml) was refluxed for 1 h and then poured into a large amount of water. The precipitated crystals were recrystallized from hexane to give compound (24) (0.07 g, 70%) as colourless prisms, m.p. 78—79 °C.

The Hydrolysis of the Cyclopentenone (24).—A mixture of compound (24) (0.5 g, 2.3 mmol) water (3 ml), concentrated sulphuric acid (1.6 ml), and acetic acid (10 ml) was refluxed for 2 days and then poured into a large amount of ice–water, neutralized with sodium carbonate and extracted with chloroform. The extracts dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue which was chromatographed on silica gel ($CHCl_3$ and ethanol as eluants). From the ethanolic solution 2-*carbonyl*-3,5-*di*-t-*butylcyclopent*-2-*enone* (29) (0.14 g, 29%) was obtained as a colourless, amorphous solid (hexane), m.p. 134—134.5 °C; $\nu_{max.}$ (KBr) 3 400 and 3 150 (NH_2), and 1 680 cm^{-1} (CO); δ ($CDCl_3$) 0.98 and 1.36 (each 9 H, s), 2.18 (1 H, dd, *J* 2.5, 5 Hz), 2.48 (1 H, dd, *J* 3.5, 20 Hz), 2.74 (1 H, dd, *J* 6, 20 Hz), and 5.86 and 7.08 (each 1 H, br s, dd, disappeared with D_2O); δ (^{13}C) ($CDCl_3$) 27.3 (q), 28.4 (q), 32.9 (t), 33.6 (s), 36.8 (s), 54.5 (d), 134.1 (d), 166.2 (s), 190.7 (s), and 208.4 p.p.m. (s) (Found: C, 71.1; H, 10.0; N, 5.75. $C_{14}H_{23}NO_2$ requires C, 70.85; H, 9.77; N, 5.90%).

The Decomposition of the Azide (3) *in DMF–Acetic Anhydride.*—A solution of compound (3) (1 g) and acetic anhydride (0.5 ml) in DMF (50 ml) was heated at 135 °C (oil-bath temperature) for 2 h and then poured into a large amount of ice–water. The resulting precipitate was dissolved in chloroform and the solution was chromatographed on silica gel using chloroform–ethyl acetate (4 : 1) as eluant to give the products (18) (9%), (19) (28%), (23) (37%) and a small amount of 2-azido-4,6-di-t-butylphenyl acetate (34) (*ca.* 4%). The elemental analysis of (34) could not be carried out since it was too unstable to be purified by the usual method; therefore, its structure was confirmed only by the i.r. and ^{1}H n.m.r. spectral data. It was obtained as an orange red liquid; $\nu_{max.}$ (NaCl) 2 100 (N_3) and 1 762 cm^{-1} (CO); δ ($CDCl_3$) 1.32 and 1.33 (each 9 H, s), 2.32 (3 H, s), and 7.02 and 7.15 (each 1 H, d, *J* 3 Hz).

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