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Thermolysis of 6-Hydroxyimino-1,3,5-tri-*t*-butyl-5-methyl-1,3-cyclohexadiene

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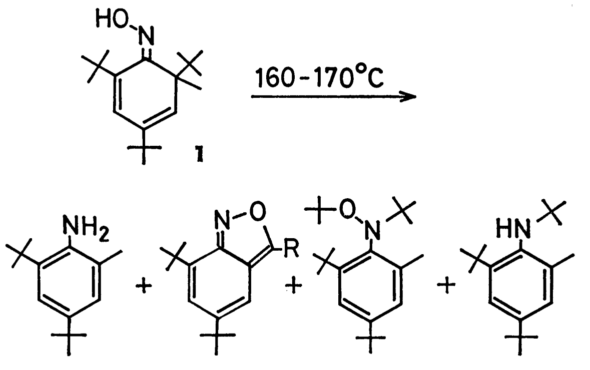
Synopsis. Mechanism of the thermolysis of the titile compound has been proposed, which begins with a homolytic cleavage leading to *t*-butyl radical and 2,4-di-*t*-butyl-6-methyl-1-nitrosobenzene. The reaction of the nitrosobenzene with *t*-butyl radical generated from photolysis of 2,2′-dimethyl-2,2′-azopropane is also described.

We have previously reported the photoreaction of cyclohexadienone oxime **1** proceeds *via* α-heterolytic cleavage, a new mode of photoreaction of an oxime.[1] In the present paper, we studied the thermal behavior of **1** and found that **1** underwent a decomposition through a homolytic pathway.

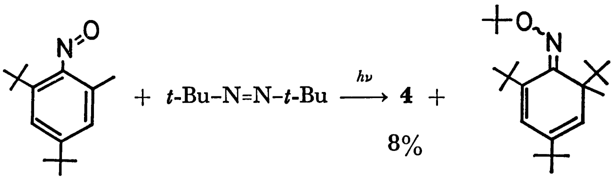
Results and Discussion

Reaction Products. Thermolysis of (*E*)-6-hydroxyimino-1,3,5-tri-*t*-butyl-5-methyl-1,3-cyclohexadiene (**1**) for 30 min at 160—170 °C afforded 2,4-di-*t*-butyl-6-methylaniline (**2**) (39%), 3,5,7-tri-*t*-butyl-2,1-benzisoxazole (**3**) (22%), *N*,*O*-di-*t*-butyl-*N*-(2,4-di-*t*-butyl-6-methylphenyl)hydroxylamine (**4**) (5%), and *N*-(*t*-butyl)-2,4-di-*t*-butyl-6-methylaniline (**5**) (9%). Identity of the products was established by their spectral and analytical data.



2 **3**: R=*t*-Bu **4** **5**
6: R=H

The structure of **4** was also confirmed by the fact that it was one of the products from the following reaction of 1,5-di-*t*-butyl-3-methyl-2-nitrosobenzene (**7**) with *t*-butyl radical generated from photolysis of 2,2′-dimethyl-2,2′-azopropane. Since the reaction of a nitrosobenzene with radicals is known to give a tri-substituted hydroxylamine[2] or a cyclohexadienone oxime derivative[3,4] depending on the relative bulkiness of the reagents, the formation of the hydroxylamine **4** and the cyclohexadienone oximes **8** is reasonable.



7 **8** 29%

Reaction Mechanism. Formation of **2** and **3** suggests that the nitrosobenzene **7** is formed as an intermediate, because thermal disproportionation of **7** has been reported to afford **2** and 5,7-di-*t*-butyl-2,1-benzisoxazole (**6**).[3]

Since the most reasonable mechanism for the formation of **7** is homolytic cleavage of **1** to give **9**, followed by loss of hydrogen atom, a plausible mechanism for the thermolysis of **1** is considered to be as shown in Scheme 1.[5]

$$1 \xrightarrow[-t\text{-Bu}\cdot]{\Delta} \underset{9}{\text{Ar-}\dot{\text{N}}\text{-OH}} \longrightarrow \underset{7}{\text{Ar-N=O}}$$

$$7 \xrightarrow{\Delta} 2 + 6; \quad 6 \xrightarrow{t\text{-Bu}\cdot} 3$$

$$7 \xrightarrow{t\text{-Bu}\cdot} \text{Ar-N}\genfrac{}{}{0pt}{}{\diagup\text{O}\cdot}{\diagdown t\text{-Bu}} \xrightarrow{t\text{-Bu}\cdot} 4 \xrightarrow{-t\text{-BuO}\cdot} \text{Ar}\dot{\text{N}}\text{-}t\text{-Bu} \longrightarrow 5$$

Ar = 2,4-di-*t*-butyl-6-methylphenyl

Scheme 1.

Attack of the *t*-butyl radical on **6** affords 3-substituted benzisoxazole **3**, because benzisoxazole is known to undergo a substitution reaction with a radical at the position 3.[3]

Radical attack at the nitroso nitrogen atom of **7** and subsequent reaction of the intermediate nitroxide radical with *t*-butyl radical gave **4**.[2–4] Aniline **5** is probably formed from further thermal reactions of **4** (see Scheme).

It is of interest that the thermolysis proceeds *via* homolysis, contrary to the photolysis which proceeds *via* α-heterolytic cleavage.[1]

Experimental

Thermolysis of Oxime 1. Oxime **1** (400 mg, 1.37 mmol)[6] was kept at 160—170 °C for 30 min in a sealed tube. The reaction mixture was subjected to preparative TLC (silica gel, hexane-dichloromethane (5:1)) to give four fractions. The first fraction afforded 21 mg (5%) of **4** as colorless oil, which was identical with the specimen obtained from the reaction of **7** with *t*-butyl radical (*vide infra*). IR (neat) 1200 cm^{-1} (C–O); NMR (CCl$_4$) δ 1.06 (9H, s), 1.19 (9H, s), 1.27 (9H, s), 1.52 (9H, s), 2.62 (3H, s), and 6.97 (2H, ABq, J=2.6 Hz, $\Delta\delta$=0.45); MS, *m*/*e* (rel intensity), 305 (M$^+$–C$_3$H$_6$, 2), 291 (3), 235 (7), 219 (16), 204 (66), 188 (8), 57 (78), and 41 (100). The second fraction afforded 80 mg (22%) of **3** as colorless crystals, mp 73—74 °C (CH$_3$OH). Found: C, 79.56; H, 10.10; N, 4.75%. Calcd for C$_{19}$H$_{29}$NO: C, 79.39; H, 10.10; N, 4.87%. IR (KBr) 1637, 1560, and 1537 cm^{-1};3) NMR (CCl_4) δ 1.31 (9H, s), 1.50 (9H, s), 1.59 (9H, s), and 7.13 (2H, ABq, J=1.5 Hz, $\Delta\delta$=0.18); UV$_{max}$ (hexane) 260 (ε 2390), 271.5 (3040), 282.5 (3860), and 317 nm (9520);3) MS, *m/e* (rel intensity), 287 (M$^+$, 33), 273 (57), 231 (97), 187 (11), 132 (18), and 57 (100). The third fraction afforded 30 mg (9%) of **5** as pale yellow oily material. IR (neat) 3500 cm^{-1}; NMR (CCl_4) δ 1.21 (9H, s), 1.28 (9H, s), 1.44 (9H, s), 2.32 (3H, s), 3.12 (1H, b), and 6.98 (2H, ABq, J=2.6 Hz, $\Delta\delta$=0.23); UV$_{max}$ (hexane) 248 (ε 5620) and 287 nm (sh, 1590); MS, *m/e* (rel intensity), 275 (M$^+$, 11), 260 (13), 219 (15), 204 (100), 188 (8), and 57 (28). The fourth fraction afforded 122 mg of yellow oil, which was purified with preparative TLC (silica gel, hexane–dichloromethane (2:3)) to give 107 mg (39%) of **2**, which was identified by comparison with an authentic sample (NMR, MS, and TLC).7)

Reaction of **7** *with* t-*Butyl Radical.* The nitrosobenzene **7** (235 mg, 1.01 mmol) and 2,2′-dimethyl-2,2′-azopropane (1.49 g, 10.5 mmol) were dissolved in benzene (180 ml), and the solution was irradiated for 1 h at 0—5 °C using a 100 W medium pressure mercury arc filtered through aq. $CuSO_4$ solution to cut off the light below about 340 nm and above 550 nm. Under these conditions, only the azopropane absorbed the light. After the solvent was removed under reduced pressure, the residue was subjected to preparative TLC (silica gel, hexane–dichloromethane (5:1)). The first fraction afforded 206 mg of colorless oily material, which was again subjected to preparative TLC (silica gel, hexane) to give three fractions A, B, and C. Fraction A gave 40 mg of **8** ((*Z*)-form) as white crystals. Fraction B gave 78 mg of colorless oily material, which was subjected to preparative TLC (silica gel, hexane) to afford 39 mg of **8** ((*Z*)-form) and 27 mg (8%) of **4** (by NMR and GLC). Thus the total amount of **8** ((*Z*)-form) was 79 mg (23%). Fraction C afforded 57 mg of colorless oil, which was purified by preparative TLC (silica gel) to give 21 mg (6%) of **8** ((*E*)-form). The configuration of **8** was tentatively assigned by analogy with **1**.6) **8** ((*Z*)-form): mp 89.0—89.7 °C (CH_3OH). Found: C, 79.75; H, 11.72; N, 3.85%. Calcd for $C_{23}H_{41}NO$: C, 79.48; H, 11.89; N, 4.03%. IR (KBr) 978 and 955 cm^{-1} (NO); NMR (CCl_4) δ 0.78 (9H, s), 1.10 (9H, s), 1.31 (18H, s), 1.55 (3H, s), 5.15 (1H, b, J=2.0 Hz), and 6.08 (1H, d, J=2.0 Hz); UV$_{max}$ (hexane) 264 (sh, ε 2650) and 315 (5630) nm. **8** ((*E*)-form): oil; IR (Nujol) 980 and 960 cm^{-1} (NO); NMR (CCl_4) δ 0.92 (9H, s), 1.09 (9H, s), 1.25 (9H, s), 1.33 (12H, s), 5.37 (1H, d, J=1.5 Hz), and 6.03 (1H, d, J=1.5 Hz); UV$_{max}$ (hexane) 254 (ε 2700) and 308 nm (5420). The second fraction afforded 50 mg (21%) of recovered **7**.

References

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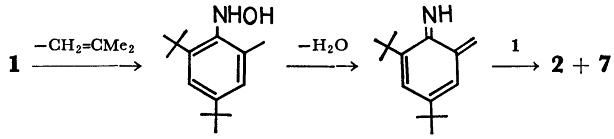
2) *E.g.*, B. A. Gingrass and W. A. Waters, *J. Chem. Soc.*, **1954**, 1920; A. B. Boyd, P. F. Soutern, and W. A. Waters, *ibid.*, **1958**, 2056.

3) T. Hosogai, N. Inamoto, and R. Okazaki, *J. Chem. Soc., C*, **1971**, 3399.

4) *Cf.* S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 369.

5) The following ionic pathway leading to the nitrosobenzene **7** and the aniline **2** is also possible, but the formation of **3** and **4** (hence **5**) cannot be explained without involvement of *t*-butyl radicals.



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