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Photochemical and Thermal Reactions of Cyclohexadienone Oximes

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Photolysis of (*E*)-1-hydroxyimino-2,4,5-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**1**) and the corresponding (*Z*)-isomer in methanol, benzene, or pentane afford 1,3,5-tri-*t*-butyl-5-cyano-1,3-cyclohexadiene (**3**), 5-*t*-butyl-7-cyano-2,2,3,8,8-pentamethyl-3,4,6-nonatriene (**4**), 5-*t*-butyl-3-cyano-2,2,7,8,8-pentamethyl-3,4,6-nonatriene (**5**), 5-*t*-butyl-7-cyano-2,3,3,8,8-pentamethyl-1,4,6-nonatriene (**6**), 5-*t*-butyl-3-cyano-7-methoxy-2,2,7,8,8-pentamethyl-3,5-nonadiene (**7**), 5-*t*-butyl-7-cyano-7-methoxy-2,2,3,8,8-pentamethyl-3,5-nonadiene, and 2,4-di-*t*-butyl-6-cyano-7,7-dimethyl-1,3,5-octatriene (**9**). The presence of an oxaziridine in the reaction mixture has been confirmed by iodometry. The photoreaction in the presence of 1,3-pentadiene or oxygen gives essentially the same results, suggesting the involvement of the singlet excited state in these photoreactions. Thermal Beckmann rearrangement of **1** has been conducted for comparison to give only **6**, **7**, and **9**. The photochemical formation of **3**—**9** has been rationalized in terms of the "free" cyclopentadienyl cation formed by ionic α-cleavage of the oxime. Photoreaction of 1-hydroxyimino-2,4,6-tri-*t*-butyl-2,4-cyclohexadiene with one alkyl group at 6-position gives 5-*t*-butyl-7-cyano-2,3,8,8-tetramethyl-1,4,6-nonatriene, 5-*t*-butyl-3-cyano-8-methoxy-2,2,7,8-tetramethyl-4,6-nonadiene, 5-*t*-butyl-7-cyano-2-methoxy-2,3,8,8-tetramethyl-3,5-nonadiene, and 1,3-di-*t*-butyl-5-cyano-3-methoxy-6,6-dimethyl-1,4-heptadiene.

Since the first report on photo-Beckmann rearrangement by de Mayo in 1963,[1] there have been numerous reports on the photoreaction of oximes.[2] There are also many investigations concerning cyclohexadienones.[3,4] On the contrary, however, there has been no report on the photoreaction of cyclohexadienone oximes, probably because of the limited availability of the material.

Since we recently discovered the facile one-step synthesis of oximes of cyclohexadienones from the reactions of 2,4,6-tri-*t*-butylnitroso(or nitro)benzene with Grignard reagents,[5,6] we undertook the study on the photoreaction of these sterically hindered cyclohexadienone oximes[7] and a full account is described in this paper.

Reaction Products. Irradiation of (*E*)-1-hydroxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**1**) in solution (methanol, pentane, or benzene) (medium pressure mercury lamp, Pyrex-filter) afforded 1,3,5-tri-*t*-butyl-5-cyano-1,3-cyclohexadiene (**3**), 5-*t*-butyl-7-cyano-2,2,3,8,8-pentamethyl-3,4,6-nonatriene (**4**), 5-*t*-butyl-3-cyano-2,2,7,8,8-pentamethyl-3,4,6-nonatriene (**5**), 5-*t*-butyl-7-cyano-2,3,3,8,8-pentamethyl-1,4,6-nonatriene (**6**), 5-*t*-butyl-3-cyano-7-methoxy-2,2,7,8,8-pentamethyl-3,5-nonadiene (**7**), 5-*t*-butyl-7-cyano-7-methoxy-2,2,3,8,8-pentamethyl-3,5-nonadiene (**8**), and 2,4-di-*t*-butyl-6-cyano-7,7-dimethyl-1,3,5-octatriene (**9**) along with some recovered **1** and the isomer **2**. The yields of the products and the reaction conditions are shown in Table 1.

When (*Z*)-oxime (**2**) was irradiated under the identical conditions, isomerization into **1** was observed at first and the final products and their yields were essentially the same as those from **1**.

Formation of oxaziridine (**10**), which is considered to be an intermediate leading to an amide in photo-Beckmann rearrangement[2] and in some cases characterized in solution,[8] was also observed in the reaction of **1** in methanol; treatment of the reaction solution, after irradiation for 3.8 h, with sulfuric acid and potassium iodide, followed by titration of the liberated iodine and the subsequent titration of the consumption of the acid,[9] indicated the yield of the oxaziridine was about 6%.

The structural assignment of **3**, **7**, and **9** is straightforward from their analytical and spectral data, and it was confirmed by the chemical behavior as shown in Scheme 1.

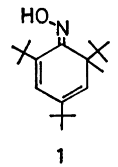
Treatment of **7** with trifluoroacetic acid in benzene led to formation of **9** (95%), which was also obtained in irradiation of **1** in benzene for 4 h (14%). Triene (**9**) underwent cyclization to give **3** (96%) upon irradiation with Pyrex-filtered light for 6 h in methanol, suggesting that **3** is a secondary product formed *via* **9**.

Ether (**7**) is not a precursor of other products, be-

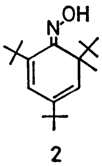
Table 1. Yields (%) of products in photoreactions of **1** and **2**

Starting material	Solvent	Reaction time (h)	Yields (%)								
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	Methanol	7.5	11	6	19	11	7	5	16	2	1
2	Methanol	7.5	0	6	33	5	—	3	22	3	—
1	Pentane	9.3	—	—	5	11	7	—	—	—	—
1	Benzene	4.0	9	4	11	tr	6				14
1	Methanol[a]	7.5	8	10	12	6	8	2	17	2	—
1	Methanol[b]	7.5		7	19	13	8	3	16	2	1

a) In the presence of 1,3-pentadiene. b) In the presence of oxygen.



1



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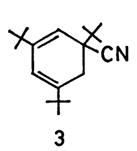

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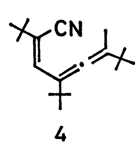

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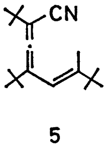

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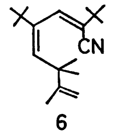

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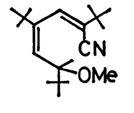

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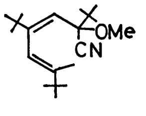

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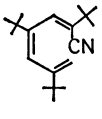

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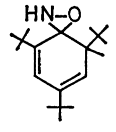

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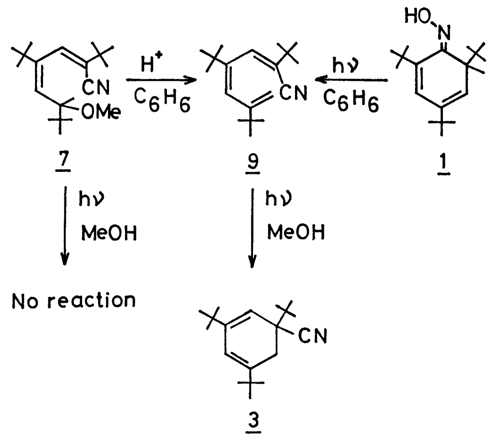
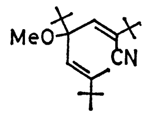


Scheme 1.

cause no change was observed in the irradiation of **7** for 7.5 h in methanol.

The NMR spectrum of **6** showed two *t*-butyl groups (δ 1.08 and 1.19), two methyl protons attached to the saturated carbon (1.19), methyl protons bound to the olefinic carbon (1.68) splitting with a small coupling constant, two equivalent olefinic protons (4.70) appeared as multiplet, and two olefinic protons (5.42 and 6.38) appeared as a doublet. The IR spectrum showed the presence of cyano (2235 cm^{-1}) and terminal methylene (889 cm^{-1}) groups. The UV spectrum of **6** had an absorption maximum at 257 nm which is consistent with the structure of a conjugated diene.

The NMR spectrum of **8** showed three *t*-butyl groups (δ 1.02 and 1.15 (1:2)), methyl protons bound to the olefinic carbon (1.83), methoxyl protons (3.35), and olefinic protons (5.04 and 5.42). The signal of the methyl protons shows a small coupling constant, suggesting that the methyl group may be attached to a fully substituted olefinic carbon. The IR spectrum showed the existence of a cyano group (2225 cm^{-1}), although absorption intensity was very week. This phenomenon suggests that the cyano group is located on the carbon to which an ether group attaches[10]. The UV spectrum of **8** had absorption maxima at 234(sh) and 262(sh) nm which indicated a conjugated diene and ruled out the structure (**11**).



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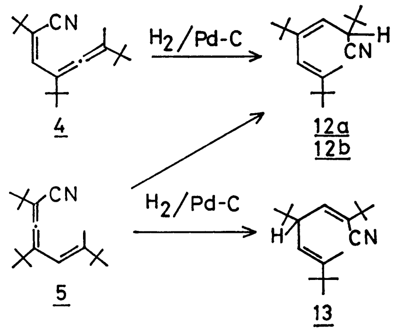
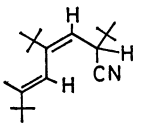
The long range coupling of two olefinic protons indicates the presence of a double bond between these protons and is consistent with this assignment.

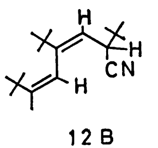
The IR spectra of **4** and **5** indicated the existence of an allenic group (1950 cm^{-1}). Their ^{1}H-NMR spectra showed three *t*-butyl groups (δ 1.08 (18 H) and 1.21 (9 H) for **4**, δ 1.05, 1.10, and 1.28 for **5**), a methyl group on sp^2 carbon (δ 1.81 for **4**, 1.72 for **5**), and an olefinic proton (δ 6.36 for **4**, 6.56 for **5**). Since both of the methyl protons appeared as singlet and the coupling constant between the olefinic proton and the methyl protons was estimated to be very small, it is impossible from ^{1}H-NMR spectra to determine whether the methyl groups are bound to an olefinic carbon or an allenic carbon. The mass spectra of those products were similar to each other. The ^{13}C-NMR spectrum of **4** showed an allenic carbon at 198.5 ppm, a cyano group at 117.5 ppm, and a methyl group on sp^2 carbon at 14.4 ppm. Single resonance spectrum showed the signal of the cyano carbon splitted to doublet ($^3J_{CH}$=15.8 Hz). This coupling suggested the existence of β-proton, therefore, the cyano and methyl groups must be bound to olefinic and allenic carbons, respectively. These facts support the structure **4**. Therefore, **5** is considered to be an isomeric allene as shown, although satisfactory elemental analysis and ^{13}C-NMR spectrum could not be obtained because of paucity of the sample. That **4** and **5** have an allenic structure isomeric each other, was also established by catalytic hydrogenation.



Thus, hydrogenation of **4** afforded conjugated diene **12a** as a result of the reduction of the allenic group followed by 1,5-hydrogen shift, while hydrogenation of **5** afforded **12b** and **13**. The signal pattern of NMR spectra of **12a** and **12b** resembled each other but their chemical shifts were slightly different, suggesting they are geometric isomers having the same gross structure. They are probably (**12A**) and (**12B**), although the spectral data are insufficient to establish which is which.

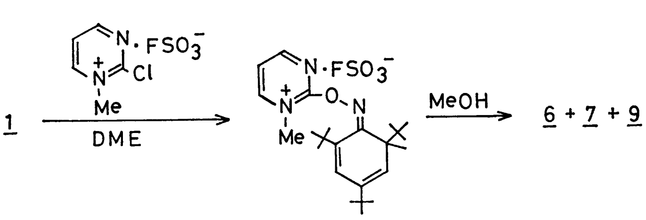


12 A



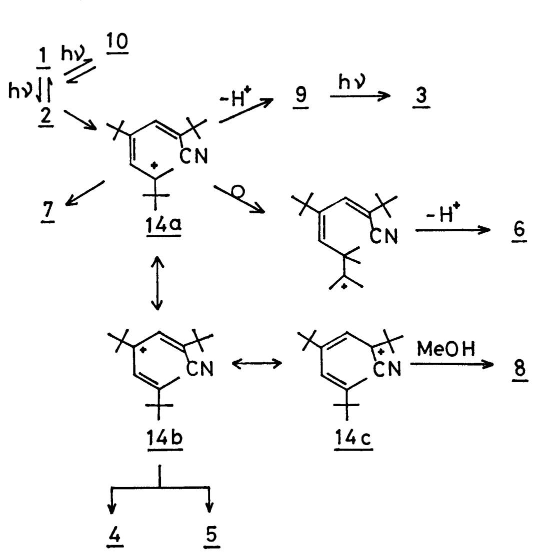
12 B

Thermal Beckmann Rearrangement. Reaction of **1** with 2-chloro-1-methylpyrimidinium fluorosulfate[11] followed by quenching with methanol, gave **6** (9%), **7** (6%), and **9** (46%).

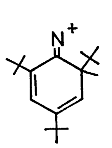


Reaction Mechanism. The products (**3**—**9**) are considered to be formed *via* heterolytically produced pentadienyl cation as depicted in Scheme 2. Since the photoreaction of **1** was not quenched by 1,3-pentadiene and oxygen, it probably proceeds *via* the singlet state.

Isomerization between oximes **1** and **2** occurs at first, as generally observed in the reaction of oximes. From this photochemical equilibrium mixture is formed oxaziridine (**10**), which probably reverts to the oxime mixture photochemically, thermally, and/or during the treatment with silica gel. Heterolytic α-cleavage and fission of the N–O bond of the oxime afford pentadienyl cation (**14**), with formal canonical structures (**14a**), (**14b**), and (**14c**). Whether these bond cleavages are simultaneous or stepwise could not be established experimentally, but involvement of nitrenium ion (**15**) seemes unlikely in view of the known propensity of this kind of nitrenium ion to undergo intramolecular C–H insertion.[12] However, the possibility that oxaziridine (**10**) is a direct precursor of **14** can not be eliminated completely, although it appears quite unlikely.



Scheme 2.



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The most obvious feature of this photoreaction is that all the products are formed *via* ionic processes. Contrary to frequent observations of nitrile formation in the ground state Beckmann rearrangement, photo-Beckmann fission is observed only rarely,[2] and more importantly the formation of nitriles in the excited state reaction has been explained by a homolytic process.[13,14]

The present reaction represents the first and unequivocal example of a heterolytic α-cleavage of an oxime. There seem two reasons for the facile heterolytic α-cleavage; one is that the carbonium ion formed is a stabilized pentadienyl cation with two alkyl groups on its terminal and the other is that oxaziridine, even if it is formed, would suffer strain by bulky *t*-butyl groups, thus reverting to the starting oxime.

The heterolytic pathway seems to be operative even in nonpolar solvent such as pentane, although the reaction is apparently more complex; the products identified were **3**, **4**, and **5** (Table 1).

The discrepancy in the products between the excited and ground state reactions is most likely due to the difference in nature of an intermediate in both reactions. The products of the thermal Beckmann fission are only those that are formally derived from canonical structure **14a**, suggesting the participation of the solvent (for **7**) and neighboring bonds (for **6** and **9**) in the product forming process. On the contrary, in the photoreaction, the pentadienyl cation **14** appears to be formed as a "free" carbonium ion without such assistance. The formation of the products (**4**, **5**, and **8**), characteristic of the excited state reaction, is reasonably explained in terms of canonical structures (**14b**) and (**14c**), that is, deprotonation from **14b** affords **4** and **5** and addition of methanol to **14c** gives **8**. This reactivity is most likely accounted for in the light of characteristics of a "free" (or "hot") carbonium ion[15] that reactions occur at a position(s) other than that where a carbonium ion is initially generated.

This sort of "free" carbonium ions have recently been invoked in the photoreactions of alkyl and vinyl halides in order to rationalize the difference in reactivity between the photochemical and solvolytic reactions.[16,17]

Photoreaction of 2,4-Cyclohexadienone Oxime with One Alkyl Group at 6-Position. In order to examine the relationship between structure and reactivity in the photoreaction of 2,4-cyclohexadienone oximes, the photoreaction of the oxime with only one alkyl group at the 6-position was carried out.

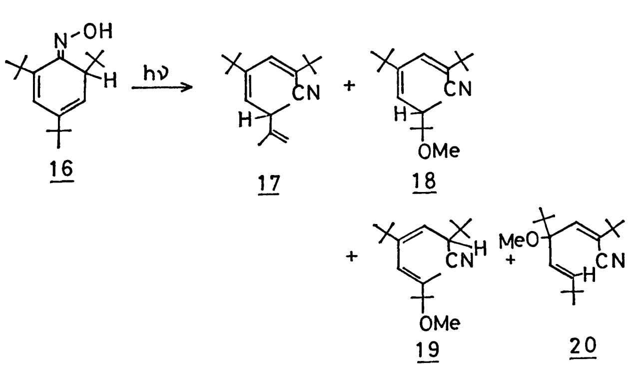
Irradiation of 1-hydroxyimino-2,4,6-tri-*t*-butyl-2,4-

cyclohexadiene (**16**) in methanol (medium pressure mercury arc, Pyrex-filter) for 17.5 h afforded 5-*t*-butyl-7-cyano-2,3,8,8-tetramethyl-1,4,6-nonatriene (**17**), 5-*t*-butyl-3-cyano-8-methoxy-2,2,7,8-tetramethyl-4,6-nonadiene (**18**), and recovered oxime **16**. When the reaction time was prolonged to 36.5 h products obtained were **17**, **18**, 5-*t*-butyl-7-cyano-2-methoxy-2,3,8,8-tetramethyl-3,5-nonadiene (**19**), and 1,3-di-*t*-butyl-5-cyano-3-methoxy-6,6-dimethyl-1,4-heptadiene (**20**).

The yield of the products and the reaction conditions are shown in Table 2.

TABLE 2. YIELDS (%) OF PRODUCTS IN PHOTOREACTION OF **16**

Solvent	Reaction time (h)	Yields (%)				
		16	**17**	**18**	**19**	**20**
Methanol	17.5	6	20	18	—	—
Methanol	36.5	0	19	8	14	5



Irradiation (Pyrex-filtered light in methanol, 11.5 h) of **18** led to formation of **19** (94%). This suggests that **19** is a secondary product from **18** *via* photochemically allowed antarafacial 1,5-hydrogen shift.[18]

Elimination of methanol from **18** by trifluoroacetic acid in benzene, which converted **7** to **9**, was unsuccessful, probably because stabilization of carbonium ion formed is not sufficient in this case.

Although satisfactory elemental analysis could not be obtained, the structure of the products were confirmed by their spectral data.

The ^{1}H-NMR spectrum of **18** showed two *t*-butyl groups (δ 1.09 and 1.25), two methyl groups (1.00), methine proton with intricate splitting (1.85—2.46), methoxyl protons (3.08), and two olefinic protons (5.34 and 6.41), one methyl signal appearing as a doublet at δ 0.98.

The ^{13}C-NMR spectrum showed the presence of a cyano carbon at 117.4, three methyl carbons (δ 23.3, 21.6, and 14.2), a methoxyl carbon (48.8), and a tertiary carbon α to oxygen (77.1).

Molecular ion peak on the mass spectrum of **18** was not observed, but the fact that the base peak was *m/e* 73, assignable to $[(CH_3)_2(OCH_3)C]^+$, is consistent with the structure proposed in view of high stability of $[(CH_3)_2(OCH_3)C]^+$ and pentadienyl radical.

The easy 1,5-prototropy of **18** leading to **19** remains to be accounted for. Considering interactions between bulky *t*-butyl groups, configuration of **18** may be favorable for such a 1,5-hydrogen migration. It is interesting that similar phenomenon was observed in the hydrogenation of allene (**4**) as described before. The signal patterns of the NMR spectra of **12** and **19** resemble each other.

Formation of **20** can be explained formally by the reaction of methanol with pentadienyl cation with a canonical structure similar to **14b** shown in Scheme 2.

Therefore, the reaction of oxime (**16**) is essentially the same as that of **1** in the sense that it proceeds mainly *via* heterolytic α-cleavage, although the reaction is more complex.

Experimental

All melting points were not corrected. The IR and UV spectra were recorded with Hitachi EPI-G2 and EPS-3 spectrophotometers respectively. The ^{1}H-NMR and ^{13}C-NMR spectra were measured with Hitachi R-20B (60 MHz) and JEOL JNM-FX60 spectrometers using tetramethylsilane as an internal standard. The mass spectra were recorded with a Hitachi RMU-6L mass spectrometer. The photolyses were carried out using a 100 W medium pressure mercury lamp with a Pyrex filter, and nitrogen gas was passed through the solution before (about 15 min) and during irradiation unless otherwise noted. Gas chromatographic separation was performed using a JEOL-750 (versamide 900) unless otherwise noted.

*Photolysis of (*E*)-1-Hydoxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (1) in Methanol.* Oxime **1**[6] (450 mg, 1.55 mmol) in methanol (90 ml) was irradiated at 0—5 °C for 7.5 h. The solvent was removed under reduced pressure and the residue was subjected to preparative thin layer chromatography (TLC) (SiO_2, hexane-dichloromethane (4 : 1)) to be divided into five fractions.

The first fraction gave 28 mg (6%) of (*Z*)-isomer of (**1**).[6]

The second (white crystals) was a mixture of **4** (42 mg), **6** (16 mg), **8** (10 mg, 2%), and **9** (5 mg, 1%) according to the peak area on the gas chromatogram. Each product was isolated by means of gas chromatography (GLC) (in glass column at 135 °C). **4**: mp 54.0—55.0 °C (from methanol); IR (KBr) : 2220 (CN) and 1950 cm^{-1} (C=C=C); ^{1}H-NMR (CCl_4) : δ 1.08 (s, 18H), 1.21 (s, 9H), 1.81 (s, 3H), and 6.36 (s, 1H); ^{13}CNMR ($CDCl_3$) : 198.5 ppm, 136.4, 122.7, 117.5, 112.9, 109.9, 35.6, 34.3, 34.0, 29.5, 29.1, 28.8, and 14.4; λ_{max} (hexane) : 270.5 nm (ε 9060); MS : *m/e* 273 (M$^+$, 22%), 258 (17), 217 (40), 202 (100), 160 (29), and 57 (59). Found: C, 83.72; H, 11.71; N, 5.00%. Calcd for $C_{19}H_{31}N$: C, 83.45; H, 11.43; N, 5.12%. **6**: mp 48.5—49.5 °C (from methanol); IR (KBr) : 2235 (CN) and 889 cm^{-1} (C=CH$_2$); NMR (CCl_4) : δ 1.08 (s, 9H), 1.19 (s, 15H), 1.68 (d, *J*=0.8 Hz, 3H), 4.07 (m, 2H), 5.42 (d, *J*=1.5 Hz, 1H), and 6.38(d, *J*=1.5 Hz, 1H); λ_{max} (hexane) : 257 nm (ε 1530); MS : *m/e* 273 (M$^+$, 6.7%), 258 (14), 216 (38), 202 (37), 160 (30), and 57 (100). **8** : oil; IR ($CHCl_3$) : 2225 cm^{-1} (CN); NMR (CCl_4) : δ 1.02 (s, 9H), 1.15 (s, 18H), 1.83 (d, *J*=1.3 Hz, 3H), 3.35 (s, 3H), 5.04 (d, *J*=2.3 Hz, 1H), and 5.42 (m, 1H); λ_{max} (hexane) : 234(sh) (ε 4060) and 262(sh) nm (1500); MS : *m/e* 305 (M$^+$, 0.4%), 202 (13), 160 (12), and 57 (100). **9** : oil; IR (neat) : 2225 (CN), 1609, and 899 cm^{-1} (C=CH$_2$); NMR (CCl_4) : δ 1.09 (s, 9H), 1.13 (s, 9H), 1.18 (s, 9H), 4.68 (dd, *J*=1.5 Hz, 1H), 4.95 (d, *J*=1.5 Hz, 1H), 6.09 (dd, *J*=1.5 Hz, 1H), and 6.50 (d, *J*=1.5 Hz, 1H); λ_{max} (hexane): 262 nm (ε 6700); MS: *m/e* 273 (M$^+$, 1.5%), 217 (23), 160 (64), 57 (100), and 41 (46),

The third farction was a mixture of **3** (80 mg, 19%), **5**

(31 mg, 7%), **4** (3 mg, total yield 11%), and **6** (6 mg, total yield 5%) according to the peak area on the gas chromatogram, and they were purified by preparative GLC to give each product in a pure state. **3**: mp 137.1—137.8 °C (from methanol); IR (KBr) : 2235 cm^{-1} (CN); NMR (CCl_4) : δ 1.10 (s, 18H), 1.14 (s, 9H), 2.22 (d, J=2.4 Hz, 1H), 2.31 (s, 1H), 5.29 (d, J=1.7 Hz, 1H), and 5.95 (m, 1H); λ_{max} (hexane): 261 nm (ε 5950); MS : m/e 273 (M$^+$, <1%), 160 (13), and 57 (100). Found: C, 83.15; H, 11.67; N, 5.28%. Calcd for $C_{19}H_{31}N$: C, 83.45 : H, 11.43; N, 5.12%. **5** : oil; IR (neat) : 2225 (CN) and 1950 cm^{-1} (C=C=C); NMR (CCl_4) : δ 1.05 (s, 9H), 1.10 (s, 9H), 1.28 (s, 9H), 1.72 (s, 3H), and 6.56 (s, 1H); λ_{max} (hexane) : 258 nm (ε 14900); MS : m/e 273 (M$^+$, 6%), 217 (43), 202 (100), 160 (22), and 57 (80).

The fourth fraction (144 mg) was a mixture of **7** (78 mg, 16%) and recovered oxime **1** (48 mg, 11%) according to the signal intensity on the NMR spectrum. **7**: oil; IR (neat) : 2220 cm^{-1} (CN); NMR (CCl_4) : δ 0.88 (s, 9H), 1.12 (s, 9H), 1.18 (s, 3H), 1.22 (s, 9H), 3.16 (s, 3H), 5.55 (d, J=1.8 Hz, 1H), and 6.50 (d, J=1.8 Hz, 1H); λ_{max} (hexane): 259(sh) (ε 3380), 306(sh) (1530), and 325(sh) nm (920); MS : m/e 273 (M$^+$−CH_3OH, <1%), 160 (16), and 57 (100).

*Photolysis of (*Z*)-1-Hydroxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (2) in Methanol.* Methanol solution (80 ml) of oxime (**2**) (394 mg, 1.35 mmol) was irradiated for 7.5 h under the same conditions as those of the photolysis of oxime **1**. After the removal of the solvent, the reaction products were analyzed by a combination of preparative TLC and GLC as described above for **1** (see Table 1).

Photolysis of Oxime (1) in Pentane or Benzene. Oxime **1** (450 mg, 1.55 mmol) in pentane or benzene (90 ml) was irradiated (9.3 h for the pentane solution and 4 h for the benzene solution) under the same conditions as those of the photolysis in methanol. The products were purified by TLC (see Table 1).

Photolysis of Oxime (1) in the Presence of 1,3-Pentadiene. Oxime (**1**) (450 mg, 1.55 mmol) and 1,3-pentadiene (608 mg, 8.9 mmol) in methanol (90 ml) was irradiated for 7.5 h. The reaction products were analyzed by TLC and GLC as above (see Table 1).

Photolysis of Oxime (1) in the Presence of Oxygen in Methanol. Oxime (**1**) (450 mg, 1.55 mmol) was dissolved in methanol (90 ml). After being flashed with oxygen, the solution was irradiated for 7.5 h at 0—5 °C, during which oxygen was passed through. The identification and determination of the yields of the reaction products were carried out by TLC and GLC (see Table 1).

Determination of the Oxaziridine Concentration and "B.O. value" in the Photolysis of Oxime (1) in Methanol. Oxime (**1**) (450 mg, 1.55 mmol) in methanol (90 ml) was irradiated under the same conditions as those of the photolysis in methanol. After irradiation for 3.8 h, a part of the solution (10 ml) was treated with sulfuric acid (0.01767 N, 50 ml) and potassium iodide (1 g), and then the liberated iodine was titrated with a standard solution of sodium thiosulfate (0.010029 N, 1.95 ml). Then the amount of the acid consumed to liberate iodine was determined by back titration with 0.009280 N potassium hydroxide. The amount of the species which liberated iodine was 0.00978 mmol (6%) and that of consumed acid was 0.036 mmol, thus the "B. O. value" being 3.68. This value suggested that the species was oxaziridine[9].

Reaction of 7 with Trifluoroacetic Acid. To a benzene solution (40 ml) of **7** (39 mg, 0.13 mmol), a drop of trifluoroacetic acid was added with stirring. After additional stirring for 26 h at room temperature, the solvent was removed under reduced pressure to give 33 mg (95%) of **9** as yellow tar (by NMR).

Photoreaction of 9 in Methanol. A mixture of trienes (**9**) and (**6**) (64.8 mg), which contained 57.6 mg (0.21 mmol) of **9** according to the GLC (DOS column, 180 °C) was dissolved in methanol (13 ml) in a Pyrex glass tube, flashed with nitrogen, and was externally irradiated for 6.3 h at 0—5 °C. TLC purification afforded 12 mg of **6** as white crystals and 55 mg (96%) of **3** (by NMR).

Test for Photostability of 7 in Methanol. Product **7** (99 mg, 0.32 mmol) in methanol (90 ml) was irradiated for 7.8 h under the same conditions as those of the photolysis of oxime **1** in methanol. Removal of the solvent resulted in almost complete recovery of **7** (97 mg) according to GLC. Some very small peaks other than that of **7** were observed by GLC, but they were not **3**, **4**, **5**, **6**, **8**, and **9**.

Hydrogenation of 4. A solution of **4** (78 mg, 0.29 mmol) in ethanol (8 ml) and acetic acid (0.05 ml) was hydrogenated over 10% palladium on charcoal (30 mg) under atmospheric pressure for at room temperature. After the mixture was filtered and the catalyst was washed with ethanol, the solvent was evaporated from the combined filtrates under reduced pressure. The residue was chromatographed on alumina with carbon tetrachloride as eluent to give 51 mg of colorless tarry material, which was purified by preparative GLC to give 11 mg (14%) of **12a** as a colorless oil: NMR (CCl_4): δ 1.01 (s, 9H), 1.13 (s, 18H), 1.84 (d, J=1.6 Hz, 3H), 3.17 (d, J=10.8 Hz, 1H), 5.18 (dd, J=2.2 and 10.8 Hz, 1H), and 5.41 (m, 1H).

Hydrogenation of 5. A solution of **5** (40 mg, 0.15 mmol) in ethanol (6 ml) containing a few drops of acetic acid was hydrogenated over a spatula of 10% palladium on charcoal under atmospheric pressure for 22 h at room temperature. After treatment similar to that mentioned above was obtained 26 mg of colorless tarry material, which was further purified by the preparative GLC to give 11 mg (27%) of **13** as colorless crystals and 8 mg (19%) of **12b** as colorless tar. **13**: NMR (CCl_4): δ 0.90 (s, 9H), 1.07 (s, 9H), 1.19 (s, 9H), 1.71 (d, J=1.5 Hz, 1H), 3.24 (dd, J=9.8 and 10.6 Hz, 1H), 5.09 (dd, J=1.5 and 9.8 Hz, 1H), and 5.86 (d, J=10.6 Hz, 1H); λ_{max} (hexane): 240(sh) nm (ε 8200); MS: m/e 275 (M$^+$, 1%). **12**: NMR (CCl_4): δ 0.99 (s, 9H), 1.08 (s, 9H), 1.15 (s, 9H), 1.62 (d, J=1.5 Hz, 3H), 2.94 (d, J=11.2 Hz, 1H), 5.25 (dd, J=1.5 and 11.2 Hz, 1H), and 5.61 (m, 1H); MS: m/e 275 (M$^+$, <1%).

Reaction of Oxime (1) with 2-Chloro-1-methylpyrimidinium Fluorosulfate. A mixture of 179 mg (0.62 mmol) of oxime (**1**) and 173 mg (0.68 mmol) of pyrimidinium salt in anhydrous 1,2-dimethoxyethane (6 ml) was stirred at room temperature under argon atmosphere. After 8.3 h, absolute methanol (20 ml) was added. After stirring for 17.4 h at room temperature, the reaction mixture was poured into water, and the mixture was extracted with dichloromethane. The extract was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 156 mg of yellow, partly crystalline material, which was subjected to preparative TLC (SiO_2, hexane–dichloromethane (5:1)) to give **9** (79 mg, 46%), **6** (15 mg, 9%), and **7** (12 mg, 6%).

*Photolysis of 1-Hydroxyimino-2,4,6-tri-*t*-butyl-2,4-cyclohexadiene (16) in Methanol.* a) Oxime (**16**)[19] (450 mg, 1.62 mmol) in methanol (90 ml) was irradiated at 0—5 °C for 17.5 h. The solvent was removed *in vacuo*, and the residue was subjected to preparative TLC (SiO_2, hexane–dichloromethane (4:1)) to give two fractions.

One fraction was 129 mg of yellow, partly crystalline material. According to the peak area on the GLC, it seemed to be a mixture of **17** (85 mg, 20%), recovered oxime (**16**) (28 mg, 6%), and 16 mg of unidentified materials. **17** was isolated by GLC as colorless tarry material. **17**: IR (neat): 2220 (CN) and 889 cm^{-1} ($C{=}CH_2$); NMR (CCl$_4$): δ 1.10 (s, 9H), 1.19 (d, J=7 Hz, 3H), 1.26 (s, 9H), 1.63 (dd, J=1.2 Hz, 3H), 2.8 (m, 1H), 4.60 (m, 2H), 5.27 (dd, J=9 and 1.2 Hz, 1H), and 6.46 (d, J=1.2 Hz, 1H); MS: *m/e* 259 (M$^+$, 2.5%), 203 (21), 202 (21), 188 (36), 146 (23), and 57 (100).

Another fraction was 197 mg of brown tar, which was again purified with preparative TLC (SiO$_2$, hexane–dichloromethane (1:1)) to afford **18** (84 mg, 18%) as pale yellow tar; IR (neat): 2220 cm^{-1} (CN); ^{1}H-NMR (CCl$_4$): δ 0.98 (d, J=7 Hz, 3H), 1.00 (s, 6H), 1.09 (s, 9H), 1.25 (s, 9H), 1.85—2.46 (m, 1H), 3.08 (s, 3H), 5.34 (dd, J=10.5 and 2.2 Hz, 1H), and 6.41 (d, J=2.2 Hz, 1H); ^{13}C-NMR (CDCl$_3$): 143.9 ppm, 140.0, 128.5, 127.8, 117.4, 77.1, 48.8, 40.3, 36.6, 35.3, 29.3, 28.9, 23.2, 21.6, and 14.2; $\lambda_{\max}$ (hexane): 250 nm (ε 2580); MS: *m/e* 276 (M$^+$$-CH_3$, $<1\%$), 73 (100), and 57 (31).

b) Oxime (**16**) (343 mg, 1.24 mmol) in methanol (80 ml) was irradiated as described in a) except that the reaction time was 36.5 h. Similar treatment gave 38 mg (19%) of **17**, 19 mg (5%) of **20**, 50 mg (14%) of **19**, and 29 mg (8%) of **18**. **19** was purified by GLC. **19**: IR (neat): 2225 cm^{-1} (CN); NMR (CCl$_4$): δ 0.99 (s, 9H), 1.12 (s, 9H), 1.29 (s, 6H), 1.81 (d, J=2.4 Hz, 3H), 3.08 (s, 3H), 3.17 (d, J=10.2 Hz, 1H), 5.13 (dd, J=10.2 and 2.4 Hz, 1H), and 5.55 (m, 1H); $\lambda_{\max}$ (hexane): 293(sh) nm (ε 970); MS: *m/e* 259 (M$^+$$-CH_3$OH, 6%), 244 (15), 202 (25), 188 (21), 146 (39), and 57 (100). **20**: IR (neat): 2220 cm^{-1} (CN); NMR (CCl$_4$): δ 0.99 (s, 9H), 1.14 (s, 9H), 1.25 (s, 9H), 3.27 (s, 3H), 5.24 (d, J=14.4 Hz, 1H), 5.75 (d, J=14.4 Hz, 1H), and 6.28 (s, 1H); MS: *m/e* 276 (M$^+$$-CH_3$, 1%), 234 (54), 202 (21), 193 (32), 188 (13), 178 (32), 146 (14), and 57 (100).

*Photoreaction of **18** in Methanol.* Diene (**18**) (56 mg, 0.19 mmol) in methanol (80 ml) was irradiated for 11.5 h under the same conditions as those of the photolysis of oxime (**16**). Removal of the solvent afforded 53 mg (94%) of **19** and a trace of recovered **18** (by GLC).

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