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SENSITIZED PHOTO-OXYGENATION OF ACYCLIC CONJUGATED DIENES

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Abstract—Sensitized photo-oxygenation of a wide variety of acyclic 1,3-dienes was investigated. The 1,4-cycloaddition of singlet oxygen to acyclic conjugated dienes was closely related to the thermal Diels–Alder reaction in stereospecificity, and steric and electronic effects of substituents. Reactivity order of singlet oxygen toward conjugated dienes and isolated C—C double bonds was exhibited as follows: trisubstituted mono-olefins > 2-substituted 1,3-dienes > disubstituted mono-olefins.

Sensitized photo-oxygenation of olefins is now widely used in organic synthesis. The 1,4-cycloaddition of singlet oxygen ($^1O_2$) provides a potential tool for simultaneous functionalization of both termini of conjugated dienes.[1] The 1,4-cycloaddition of $^1O_2$ with cyclic conjugated systems and aromatic systems was found early in singlet oxygen chemistry and is now accepted as a general concept in this field.[2] On the other hand, there were formerly small examples of the 1,4-cycloaddition of $^1O_2$ toward acyclic conjugated dienes. In the last 15 years, several examples including its synthetic application have been reported.[1,2] However, information concerning the oxygenation of acyclic dienes is still lacking. We now wish to describe the scope of the 1,4-cycloaddition of $^1O_2$ to the acyclic conjugated dienes.

RESULTS AND DISCUSSION

The oxygenation of methyl-substituted 1,3-*butadienes*†

Isoprene (**1**) is one of the simplest acyclic 1,3-dienes which can formally undergo three types of singlet oxygenation, 1,4-cycloaddition, 1,2-cycloaddition and 'ene' reaction. The 1,4-cycloaddition leads to 4-methyl-3,6-dihydro-1,2-dioxin (**2**), whereas 'ene' reaction and 1,2-cycloaddition produce, respectively, 2-hydroperoxymethyl-1,3-butadiene and carbonyl compounds, such as methacrolein and methyl vinyl ketone through to dioxetanes.

When a solution of **1** and a catalytic amount of Rose Bengal as a sensitizer in $CFCl_3$ containing 2% methanol were irradiated with a halogen lamp (500 W) in an O_2 atmosphere at 0–5° for 7 hr, the endoperoxide **2** was obtained as a main product (50% yield) after distillation. To survey the other products, the oxygenation of **1** was carried out in a tetraphenylporphine–CCl_4 system for convenience of analysis. After 0.6 equivalent of O_2 was consumed, an insoluble polymeric tar formed in *ca* 10% yield. The NMR spectrum of the photolysate in CCl_4 soln displayed the peaks due to **1** and **2** and also small peaks from aldehydes, hydroperoxides and conjugated carbonyls. The results showed that the 1,4-cycloaddition of $^1O_2$ surpasses the other two reaction modes for isoprene (**1**). Similar photo-oxygenation of (*E*)-1,3-pentadiene (**3**), (*E,E*)-2,4-hexadiene (**5**) and (*E*)-2-methyl-1,3-pentadiene (**7**) afforded, respectively, the endoperoxides **4**, **6** and **8** as the main products. The yields and physical properties of these peroxides are shown in Tables 1 and 2 and Fig. 1.

The oxygenation of phenyl-substituted 1,3-*butadiene*

Most styrene- or stilbene-type olefins have been known to undergo 1,2-cycloaddition of $^1O_2$ to the side chain or 1,4-cycloaddition of $^1O_2$ to the conjugated diene system comprising an aromatic unsaturation and side chain.[4] Contrary to these olefins, phenyl-substituted 1,3-dienes mainly underwent the 1,4-cycloaddition of $^1O_2$ to the acyclic conjugated system. Thus, 1-phenyl- (**9**) and 2-phenyl-1,3-butadiene (**11**) gave the corresponding 1,2-dioxins, **10** and **12**, as shown in Tables 1 and 2 and Fig. 2.

Disubstituted dienes, (*E,E*)-1-phenyl-1,3-pentadiene (**13**) and (*E,E*)-1,4-diphenyl-1,3-butadiene (**15**)‡ were also reacted with $^1O_2$ to afford the 1,4-endoperoxides, **14** and **16**, in 82% and 92% yields, respectively. These peroxides as well as **6** were not contaminated with their stereoisomers. Consequently, the 1,4-cycloaddition of $^1O_2$ to acyclic conjugated dienes proceeded in a stereospecific manner. In accord with the cardinal stereochemical principle of the Diels–Alder reaction and the stereochemical course of the 1,4-addition of $^1O_2$ to cyclic diene systems,[2] two substituents of the peroxides **6**, **14** and **16** must possess a *cis* configuration to each other. The peroxide, **16**, has in fact been confirmed to possess *cis*-diphenyl substituents.[5]

Steric and electronic effects on the 1,4-*cycloaddition of* $^1O_2$ *to acyclic conjugated dienes*

Acyclic dienes are free to take the *cis* and *trans* conformations. If the reaction of diene with dienophile is concerted, or nearly so, it can take place only in the *cis* orientation. Steric factors in the diene play a crucial role in *cis* and *trans* conformational isomerism. A *cis*-1-substituent on the diene increases the strain energy of the *cis* conformation relative to the *trans*. On the contrary, a bulky substituent at the 2-position of the diene makes the *trans* conformation less stable.

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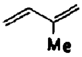
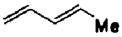
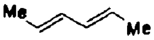
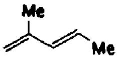
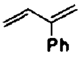
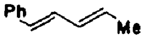
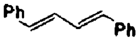
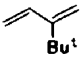
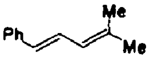
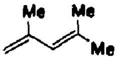
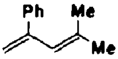
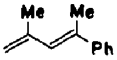
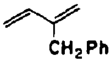
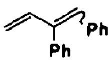
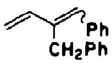
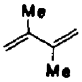
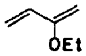
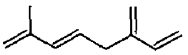
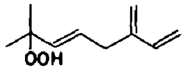
† A part of this work has been reported as a preliminary communication.[3]

‡ Preparation of the 1,4-endoperoxide, **16**, has been reported.[5]

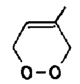
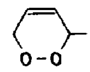
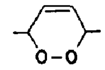
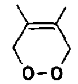
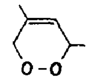
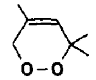
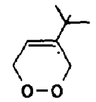
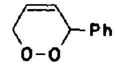
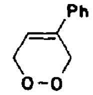
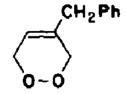
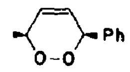
Table 1. The 1,4-cycloaddition of $^1O_2$ to acyclic conjugated dienes

Acyclic conjugated diene			3,6-Dihydro-1,2-dioxyn (yield, %)	
1			**2**	(50)
3			**4**	(31)
5			**6**	(56)
7			**8**	(58)
9			**10**	(27) (76)
11			**12**	(57)
13			**14**	(82)
15			**16**	(92) (68)[5]
17			**18**	(62)
19			**20**	(28)
26			**27**	(41)
28		(28–30 = 55:45)	**29**	(78) (29–31 = 52:48)
30			**31**	
32			**33**	(84)
35			**36**	(77)
37			**38**	(31)
39			**40**	(10)
41			**42**	(20)
43			**44**	(43)
49			**50**	(79)
47			**51**	(45)

Accordingly, *cis*-1-substituted 1,3-butadiene is far less reactive with dienophiles than the *trans* isomer and a 2-substituted diene, such as 2-t-butyl-1,3-butadiene (**17**) reacts easily with dienophiles. These are uniformally true in the Diels–Alder reaction[6] and are expected in the 1,4-cycloaddition of $^1O_2$ to acyclic 1,3-dienes (Fig. 3).

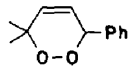
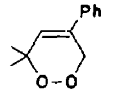
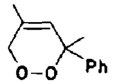
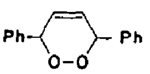
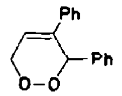
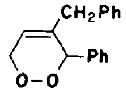
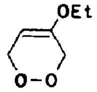
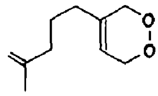
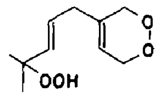
For study of the *cis*-substituent effect, the sensitized photo-oxygenation of 1,1-disubstituted 1,3-butadienes were investigated, since pure *cis*-1-substituted 1,3-butadienes were less available than 1,1-disubstituted ones. Photo-oxygenation of 4-methyl-1-phenyl-1,3-pentadiene (**19**) afforded the 1,4-endoperoxide (**20**) only in a 28% yield. The sensitized photo-oxygenation of 2,5-dimethyl-2,4-hexadiene (**21**) gave no 1,4-endoperoxide but a mixture of hydroperoxides (**22** and **23**) and 3-

Table 2. Physical properties of 3,6-dihydro-1,2-dioxins

	1,4-Endoperoxide		b.p. [m.p.] [°C (Torr)]	NMR (δ)	IR (cm^{-1})	MS (*m*/*z*) (%)
C_4		**42**	105–108	4.46 (4H, m), 5.90 (2H, m)	1050, 1035	86 [M]$^+$, 68 (68), 54 (100), 39 (74)
C_5		**2**	132	1.66 (3H, s with fc), 4.30 and 4.40 (4H, two m), 5.60 (1H, m)	1060, 1015	100 [M]$^+$ (29), 82 (100), 68 (49), 53 (69)
		**4**	125	1.19 (3H, d, J = 7.0 Hz), 4.36–4.90 (3H, m), 5.89 (2H, m)	1055, 1015	100 [M]$^+$ (5), 82 (17), 68 (100), 67 (32), 53 (25), 43 (80)
C_6		**6**	82 (17)	1.22 (6H, d, J = 6.0 Hz), 4.46 (2H, q with fc, J = 6 Hz), 5.77 (2H, br s)	1040, 1017	114 [M]$^+$ (2), 96 (10), 82 (100), 67 (47), 43 (69)
		**40**	84 (20)	1.62 (6H, br s), 4.21 (4H, br s)	1040, 1010	114 (trace), 96
		**8**	—	1.13 (3H, d, J = 6.0 Hz), 1.66 (3H, s with fc), 4.18 (2H, q_{AB} with fc, J_{AB} = 15.0 Hz), 4.50 (1H, m), 5.43 (1H, m)	1063, 1036	96 (100), 95 (41), 81 (16), 67 (61), 65 (15), 53 (28), 43 (39)
C_7		**27**	73–74	1.18 (6H, s), 1.65 (3H, s with fc), 4.16 (2H, br s), 5.41 (1H, s with fc)	1063, 1015	127 [M – 1]$^+$ (2), 113 (12), 111 (100), 83 (11), 67 (16), 55 (12), 43 (54), 41 (20)
C_8		**18**	107 (19)	1.10 (9H, s), 4.46 (4H, m), 5.50 (1H, m)	1043, 1007	142 [M]$^+$ (14), 124 (24), 110 (23), 109 (93), 95 (45), 85 (38), 81 (47), 67 (100)
C_{10}		**10**	94 (1.0)	4.50 (2H, m), 5.48 (1H, m), 6.01 (2H, br s), 7.25 (5H, m)	1066, 1033, 1002	162 [M]$^+$ (trace), 144 (100), 116 (17), 115 (87), 105 (21), 89 (10), 77 (11)
		**12**	[50–50.5]	4.57 and 4.74 (4H, two m), 6.15 (1H, m), 7.20 (5H, m)	1065, 1030	162 [M]$^+$ (trace), 144 (100), 115 (66), 89 (10), 63 (10)
C_{11}		**33**	—	3.20 (2H, br s), 4.23 and 4.36 (4H, two m), 5.47 (1H, m), 6.92–7.27 (5H, m)	1072, 1052, 1035, 1015	176 [M]$^+$ (10), 158 (100), 129 (95), 115 (38), 98 (37), 91 (87), 77 (20)
		**14**	—	1.24 (3H, d, J = 7.0 Hz), 4.53 (2H, q with fc, J = 7.0 Hz), 5.28 (1H, m), 5.89 (2H, m), 7.20 (5H, m)	1055, 1036, 1030, 1016	176 [M]$^+$ (8), 158 (100), 144 (86), 129 (86), 115 (54), 105 (97), 91 (24), 77 (73)

continued

Table 2—*continued*

1,4-Endoperoxide		b.p. [m.p.] [°C (Torr)]	NMR (δ)	IR (cm^{-1})	MS (*m/z*) (%)
C_{12}	 **20**	—	1.23 (3H, s), 1.34 (3H, s), 5.33 (1H, s with fc), 5.80 (2H, m), 7.20 (5H, m)	1050, 1030	190 [M]$^+$ (trace), 172 (100), 157 (31), 129 (37), 128 (28), 105 (56), 91 (71), 77 (48), 43 (50)
	 **29**	127 (0.4)	1.32 (6H, s), 4.70 (2H, d, J = 0.2 Hz), 6.10 (1H, t, J = 0.2 Hz), 7.40 (5H, m)	1075, 1040, 1010	190 [M]$^+$ (18), 175 (54), 173 (16), 158 (10), 147 (53), 143 (33), 129 (43), 105 (26), 103 (28), 97 (23), 91 (31), 77 (34), 43 (100)
	 **31**	[51.5–52.5]	1.45 (3H, s), 1.66 (3H, br s), 4.22 (2H, q_{AB} with fc, J_{AB} = 15 Hz), 5.90 (1H, s with fc), 7.40 (5H, m)	1076, 1030, 1012	190 [M]$^+$ (3), 175 (85), 173 (14), 158 (43), 143 (95), 129 (52), 105 (83), 103 (23), 91 (31), 77 (77), 43 (100)
C_{16}	 **16**	[83.5–84.0]	5.60 (2H, s), 6.28 (2H, s), 7.45 (10H, m)	1060, 1010	238 [M]$^+$ (11), 220 (76), 206 (29), 133 (22), 115 (38), 105 (100), 77 (62)
	 **36**	[84]	4.66 (2H, q_{AB} with fc, J_{AB} = 17 Hz), 5.72 (1H, m), 6.35 (1H, m), 7.00–7.40 (10H, m)	1065, 1030	238 [M]$^+$ (17), 220 (100), 191 (54), 189 (21), 105 (63), 77 (26)
C_{17}	 **38**	—	3.04 (2H, q_{AB} with fc, J = 15Hz), 4.48 (2H, s with fc), 5.10 (1H, s with fc), 5.64 (1H, m), 6.88–7.30 (10H, m)	1055, 1030	252 [M]$^+$ (trace), 238 (100), 205 (17), 157 (22), 128 (18), 105 (18), 91 (52), 77 (25)
	 **44**	—	1.30 (3H, t, J = 7.0 Hz), 3.74 (2H, q, J = 7.0 Hz), 4.25 and 4.47 (4H, two m), 4.67 (1H, m)	1670, 1210, 1048	130 [M]$^+$ (40), 115 (20), 112 (44), 98 (62), 84 (36), 70 (45), 55 (100), 43 (69), 29 (91)
	 **49**	—	1.70 (3H, s with fc), 1.40–1.70 (2H, m), 1.85–2.10 (4H, m), 4.30 (2H, m), 4.40 (2H, m), 4.60 (2H, m), 5.55 (1H, m)	1035, 1010	168 [M]$^+$ (1), 150 (19), 137 (12), 135 (11), 107 (16), 99 (15), 94 (58), 82 (57), 41 (100)
	 **51**	—	1.29 (6H, s), 2.71 (2H, m), 4.31 and 4.42 (4H, two m), 5.57 (3H, m), 8.13 (1H, br s)	1055, 1037, 1015	200 [M]$^+$ (trace), 164 (2), 135 (4), 93 (13), 83 (16), 81 (21), 79 (19), 69 (50), 55 (47), 41 (100)

methyl-2-butenal.† These results were in striking contrast to those with **13** and **5**. In the case of 3-ethoxy-4-methyl-1-phenyl-1,3-pentadiene (**24**), no 1,4-cycloadduct was obtained but 1,2-addition of $^1O_2$ occurred to give ethyl cinnamate (**25**) in a 85% yield. These facts showed that the *cis*-1-substituent on the dienes makes 1,4-addition of $^1O_2$ difficult and, consequently, other oxygenation (1,2-addition) and/or 'ene' reactions take place (Fig. 4).

On the other hand, 1,1,3-trisubstituted dienes, such as 2,4-dimethyl- (**26**), 4-methyl-2-phenyl- (**28**) and 2-methyl-4-phenyl-1,3-pentadiene (**30**) easily underwent oxygenation with $^1O_2$ to give the corresponding dioxins **27**, **29** and **31** in moderate yields as shown in Tables 1 and 2. As was expected, introduction of a substituent at the 2-position of the dienes favoured 1,4-cycloaddition. Further examples were as follows: 2-t-butyl- (**17**) and 2-benzyl-1,3-butadiene (**32**) were combined with $^1O_2$ to afford, respectively, the dioxins **18** (62%) and **33** (84%).

A sterically conjested diene, 2,3-diphenyl-1,3-butadiene (**34**) gave, in contrast with above cases, few

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† The singlet oxygenation of the diene **21** has been studied in detail.[7]

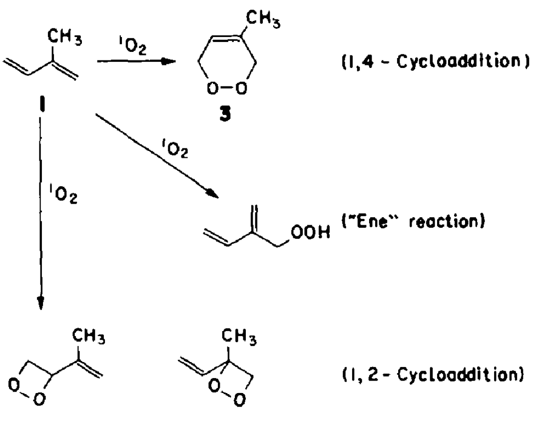

Fig. 1.

photo-oxygenation products. Singlet oxygen, however, added in moderate yields to the 1,3-dienes bearing two bulky substituents at the 1- and 2-positions as exemplified by 1,2-diphenyl- (**35**) and 2-benzyl-1-phenyl-1,3-butadiene (**37**). 2,3-Dimethyl-1,3-butadiene (**39**) afforded a 1,4-endoperoxide, **40**, in poor yield, though it is known as a reactive diene giving 1,4-adducts in high yields in the Diels–Alder reaction. The butadiene with no substituent, 1,3-butadiene (**41**) itself, had less reactivity than alkyl- and phenyl-substituted dienes, though a 1,2-dioxin (**42**) was predominantly formed together with acrolein (**42**–acrolein, 3 : 1). This is rather surprising, because the diene **41** is known to exist almost exclusively in the *trans* form,[8] which should lead to a 1,2-dioxetane. The result shows that the 1,4-cycloaddition of $^1O_2$ is a thermodynamically more favourable process than the 1,2-cycloaddition.†

In the thermal Diels–Alder reaction with maleic anhydride, the order of reactivity of acyclic dienes is: **11** > **39** > **1** > **9** > **15**.[10] On the other hand, the order of reactivity of the dienes with $^1O_2$ was qualitatively: **15** > **17** ⩾ **11** > **39** > **1** > **9**. The results exhibited that the 1,4-cycloaddition of $^1O_2$ to acyclic conjugated dienes is related to the thermal Diels–Alder reaction, except in the case of **15**.‡

Introduction of an electron releasing substituent to a diene increases the reactivity of the diene toward dienophiles and, conversely, an electron withdrawing group decreases the reactivity in the thermal Diels–Alder reaction. These trends were also observed in the reaction of acyclic dienes with $^1O_2$, though the results were qualitative; 2-ethoxy-1,3-butadiene (**43**) was smoothly oxygenated to a dioxin **44** (43% yield). On the other hand, chloroprene (2-chloro-1,3-butadiene, **45**) consumed little O_2 and afforded only polymeric tar even after a long period of irradiation (Fig. 5).

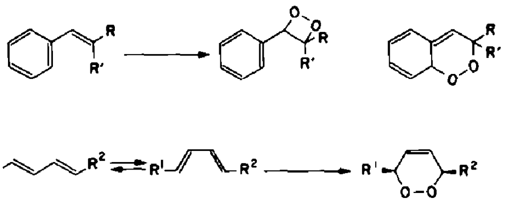

Fig. 2.

Reactivity order of 2-*alkyl substituted* 1,3-*butadiene and mono-olefins*[11]

As mentioned before, the 1,4-cycloaddition of $^1O_2$ occurs predominantly with 2-alkyl- and 2-phenyl-substituted 1,3-butadienes. We now examined the singlet oxygenation of some monoterpenes bearing both an isolated double bond and a 2-substituted 1,3-diene unit.

β-Myrcene (**46**) has a trialkyl substituted isolated double bond, while α-myrcene (**49**) bears a dialkyl substituted one. Both terpenes have a 2-substituted conjugated diene system. The terpene **46** is known to react with $^1O_2$ exclusively giving a mixture of hydroperoxides **47** and **48**.[12] Thus, the trialkyl substituted double bond is more reactive toward $^1O_2$ than the 2-substituted 1,3-diene. Prolonged reaction of **46** with $^1O_2$ gave, however, the 1,4-endoperoxides formed from **47** and **48**.

On the other hand, the terpene **49** was oxygenated by $^1O_2$ to give a 1,4-endoperoxide **50** in 79% yield. The results showed the dienophilic reactivity of $^1O_2$ surpasses the other two modes of reaction (mainly the 'ene' reaction) which occurs on a 1,1-dialkyl substituted double bond. The triene **47** also gave an endoperoxide, **51**, in 45% yield (selectivity: 63%). In conclusion, the reactivity of C—C double bonds toward $^1O_2$ roughly follows the order: trisubstituted mono-olefin > 1,3-diene with an alkyl substituent on the 2-position > disubstituted mono-olefin (Fig. 6).

CONCLUSION

Acyclic conjugated dienes were shown to undergo 1,4-cycloaddition of $^1O_2$ more generally with cyclic conjugated dienes. Although further detailed mechanistic and stereochemical studies are required, the reaction of $^1O_2$ with open-chained dienes is recognized to be closely related to the thermal Diels–Alder reaction concerning stereospecificity, steric and electronic effects, except for particular cases.

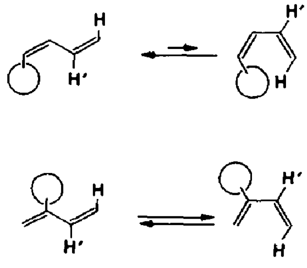

Fig. 3.

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† Theoretical calculations have been reported to support the 1,4-cycloaddition of $^1O_2$ as a more favourable process than the 1,2-cycloaddition.[9]

‡ In the thermal Diels–Alder reaction, the reaction rates of acyclic dienes treated here were known to vary by a factor of more than 200. On the other hand, the rates of singlet oxygenation of these dienes (as the consuming rates of O_2) varied only by a factor of *ca* 10.

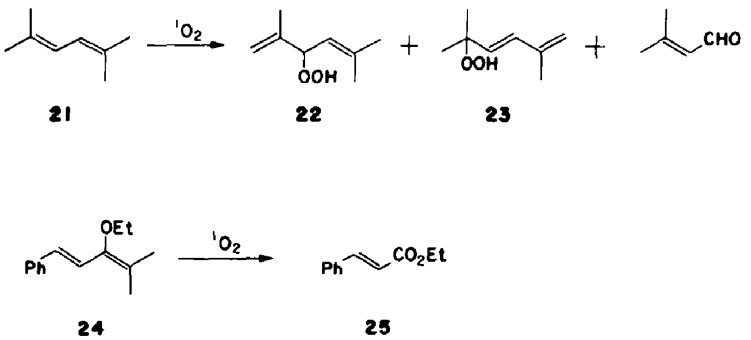

Fig. 4.

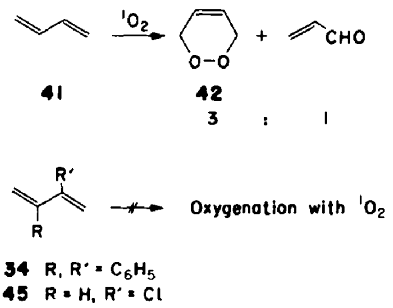

Fig. 5.

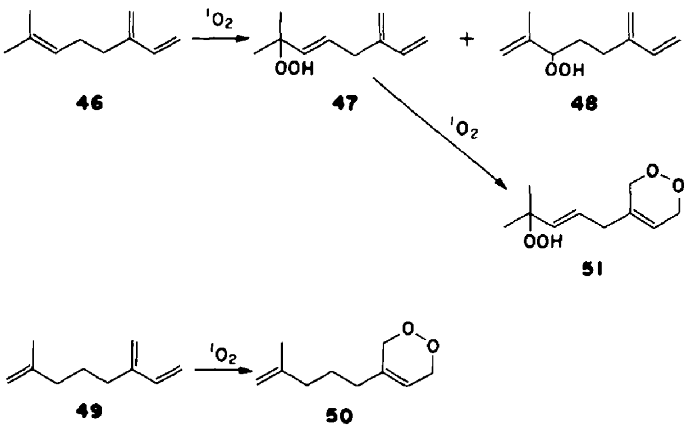

Fig. 6.

Reactivity order of $^1O_2$ toward conjugated dienes and isolated C—C double bonds bonds was exhibited to be: trisubstituted mono-olefins > 2-substituted 1,3-dienes > disubstituted mono-olefins. Based on these results, one should be able to predict roughly whether the 1,4-cycloaddition of $^1O_2$ to acyclic conjugated dienes can be used for the desired synthesis (see Tables 1 and 2).

EXPERIMENTAL

All b.ps and m.ps are uncorrected. ^{1}H-NMR spectra were recorded with a Varian HA-100 spectrometer, with TMS as internal standard. Mass spectra were obtained with a Hitachi RMU-6E spectrometer. IR spectra were recorded with a Hitachi EPI-G3 spectrometer.

Materials. Commercially available **1**, (*E*)-**3**, (*E*,*E*)-**5**, **39**, **45** and **46** were distilled before use. Gas of 1,3-butadiene (**41**) was used without purification.

The other olefins were prepared according to the procedures in the lit. or their modification and purified by distillation or recrystallization. B.ps or m.ps of the olefins were as follows: **7**, b.p. 70–70.5° (lit.[13] 69–71°); (*E*)-**9**, b.p. 76°/5.5 Torr (lit.[14] 78–81°/8 Torr); **11**, b.p. 69°/18 Torr (lit.[15] 57–61°/12 Torr); (*E*,*E*)-**13**, b.p. 107–108°/11 Torr (lit.[16] 115–118°/18 Torr); (*E*,*E*)-**15**, m.p. 149–150° (lit.[17] 150°); **17**, b.p. 100–101° (lit.[18] 100°); **19**, b.p. 126–130°/5 Torr (lit.[19] 247–

248°); **26**, b.p. 94–96° (lit.[20] 94–96°); **32**, b.p. 50°/0.1 Torr (modification of lit.[21]); **34**, m.p. 47° (lit.[22] 46–47°); **43**, b.p. 94° (lit.[23] 96.5°); and **49**,[24] b.p. 60–63°/17 Torr.

Dehydration of 4-methyl-2-phenyl-3-penten-2-ol has been reported to give **28**.[25] The olefin **28** was, however, contaminated with isomeric **30** (55 : 45). The mixture was used for the oxygenation without separation.

Sensitized photo-oxygenation of acyclic conjugated dienes. Carried out as follows, unless otherwise stated. Photolytic apparatus consisted of a water-jacketed Pyrex immersion well containing a halogen lamp (Toshiba JD, 100 V 500 W). The immersion well fitted into a Pyrex reaction vessel which had a gas inlet and an outlet, through which O_2 was circulated by means of a pump. O_2 uptake was measured volumetrically in the buret. The reaction vessel was immersed in water or an ice-water bath.

A soln (250 ml) of a diene (50 mmol) and a catalytic amount of a sensitizer (0.2 g) was irradiated with the photolytic apparatus described above at 0–30°. After more than 0.9 equivalent of O_2 was consumed, the soln was washed with 250 ml of $Na_2S_2O_3$ aq, successively with 250 ml of caustic water, and then dried over $MgSO_4$, concentrated at room temp or below under reduced pressure. The residue was purified by distillation, crystallization, or chromatography on silica gel (Wako C-200).

The photolytic reactions of the diene **1**, **7**, **9**, **15**, **21**, **24**, **41**, or a mixture of **28** and **30** are described in detail as representatives.

Irradiation of 2-*methyl*-1,3-*butadiene* (*isoprene*, **1**). A soln of **1** (4.0 g, 0.059 mol) and Rose Bengal (0.2 g) in trichlorofluoromethane (250 ml) containing 2% MeOH was irradiated at 0–5° for 7 hr. The soln was treated as mentioned above and concentrated at 0–5° under reduced pressure to afford 3.2 g of greenish yellow oil. This material was distilled at 30° (bath temp.) at 0.2 Torr and trapped at −78°. Thus, **2** was obtained as a colourless liquid, b.p. 132°, in a 50% yield (2.95 g).

Irradiation of 2-*methyl*-1,3-*pentadiene* (**7**). A soln containing 2.7 g (0.033 mol) of **7** and 0.2 g of Rose Bengal in 250 ml of a mixed solvent of CH_2Cl_2 and 5% MeOH was irradiated at 15–17°, until 710 ml (0.9 equivalent) of O_2 was consumed (6 hr). After the above-mentioned work-up, the crude product was distilled at 30° (bath temp.) at 0.1 Torr and trapped at −78°. Thus, **8** was yielded as a colourless oil in a 58% yield.

Similarly, **4** and **40** were prepared from (*E*)-**3** and **39**, respectively (Tables 1 and 2).

Irradiation of trans-1-*phenyl*-1,3-*butadiene* (**9**). The diene **9** (4.0 g, 0.031 mol) was oxygenated under the following conditions: Rose Bengal, 5% MeOH–CH_2Cl_2, 15–17°, 21 hr. After the usual work-up, the crude photolysate, which was observed to contain more than 70% **10** and a slight amount of cinnamaldehyde by its NMR spectrum analysis, was chromatographed. Elution with hexane afforded 381 mg (9%) of 2-phenylfuran, b.p. 107–108°/18 Torr, 1343 mg (27%) of **10** as a colourless oil, b.p. 94°/1.0 Torr, and 394 mg (10%) of cinnamaldehyde, successively. Further elution with CH_2Cl_2 gave 1807 mg of an alcoholic mixture. Treatment of this alcoholic mixture with several drops of conc H_2SO_4 in MeOH (20 ml) for 5 min at ambient temp. gave 1410 mg of 2-phenylfuran (40% yield based on **9**).

In a similar manner, the following dienes were oxygenated (quantity of the starting material and reaction time are shown in parentheses): **37** (0.013 mol, 10 hr), **19** (0.003 mol, 15 hr), **26** (0.021 mol, 8 hr), **17** (0.045 mol, 11 hr), **32** (0.008 mol, 10 hr), and **43** (0.051 mol, 4 hr). All the endoperoxides obtained from these dienes were stable under the chromatographic conditions (SiO_2–hexane).

Irradiation of (E,E)-1,4-*diphenyl*-1,3-*butadiene* (**15**). The diene, **15** (3.2 g, 0.016 mol) was oxygenated (CH_2Cl_2–5% MeOH, 15–17°, 19 hr) and worked-up as usual. The crude **16** was crystallized from EtOH at dry-ice–EtOH temp. to give **16** as colourless needles, m.p. 83.5–84° (lit.[5] 81–82°), in a 92% yield (3.40 g).

Similarly, **11** and **35** were converted into the corresponding dioxin **12** and **36**.

Irradiation of 1,3-*butadiene* (**41**). A soln of 20 g (0.37 mol) of **41** and 0.2 g of Rose Bengal in 250 ml of triethylene glycol dimethyl ether was irradiated at 30° with the aforesaid apparatus fitted with a condenser cooled at dry ice–EtOH temp. The reaction was monitored by GLPC analysis, accomplished by a Hitachi Perkin–Elmer F6-D instrument utilizing a 1 m × 0.25 cm, 20% SE-30 on a Chromosorb P 60–80 column. After 15 hr *ca* 90% of **41** was consumed and the formation of acrolein and **42** was observed (1 : 3). The mixture was distilled at 5–10 Torr at 60–70° (bath temp.), and all the volatile materials were trapped at −78°. The distillate was washed with water, dried over $MgSO_4$, and distilled again to yield **42** as a colourless liquid, b.p. 108°, in a 20% yield (6.0 g).

Irradiation of 2,5-*dimethyl*-2,4-*hexadiene* (**21**). The diene, **21** (1.1 g, 0.01 mol) was irradiated together with Rose Bengal in CH_2Cl_2–5% MeOH at 15–17° for 2 hr. NMR spectral analysis showed that the crude product included 3-methyl-2-butenal and hydroperoxides. Chromatographic purification (SiO_2/hexane–CH_2Cl_2, 4 : 1) gave no corresponding 1,2-dioxin but a mixture of the hydroperoxides (0.9 g) **22** and **23**. After reduction with triphenylphosphine, the hydroperoxidic mixture afforded 2,5-dimethyl-1,4-hexadien-3-ol [NMR(CCl_4) δ 1.62, 1.65, 1.80 (9H, m), 2.47 (1H, s), 4.55 (1H, d, J = 9 Hz), 4.63, 4.84 (1H, q, J = 1 Hz), 5.05 (1H, d of q, J = 9 and 1 Hz)] and 2,5-dimethyl-1,3-hexadien-5-ol [b.p. 75°/15 Torr, NMR(CCl_4) δ 1.26 (6H, s), 1.77 (3H, m), 2.67 (1H, s), 4.83 (2H, s), 5.62, 6.16 (2H, d, J = 16 Hz)].

Irradiation of 3-*ethoxy*-4-*methyl*-1-*phenyl*-1,3-*pentadiene* (**24**). A soln of **24** (1.01 g, 0.005 mol) and Rose Bengal in CH_2Cl_2–MeOH (250 ml) was irradiated at 15–17° for 7 hr. After the usual work-up, the product was chromatographed on silica gel. Elution with benzene afforded 0.74 g (83%) of **25** which was identical with the specimen.

Irradiation of a mixture of 4-*methyl*-2-*phenyl*-1,3-*pentadiene* (**28**) *and* 2-*methyl*-4-*phenyl*-1,3-*pentadiene* (**30**). A mixture of **28** and **30** (2.0 g, 0.013 mol, **28**/**30** = 55/45) was irradiated together with methylene blue in CH_2Cl_2 (250 ml) at 15–17° for 5 hr. The crude photolysate was chromatographed and eluted with hexane, affording a mixture of **29** and **31** as a colourless viscous oil in 78% yield (**29**–**31** = 52 : 48). When the mixture was dissolved in hexane (10 ml) and cooled at −78°, **31** was precipitated as colourless plates, m.p. 51.5–52.5°.

Irradiation of 7-*methyl*-5-*methylene*-1,7-*octadiene* (*α-myrcene*, **49**). The triene, **49** (3.96 g), and Rose Bengal were dissolved in MeOH (50 ml) and CH_2Cl_2 (200 ml) and irradiated at 15–17° for 3 hr. After the usual work-up, crude photolysate was chromatographed on silica gel. Elution with hexane gave **50** as a colourless oil in a 79% yield (3.85 g).

Irradiation of 6-*hydroperoxy*-7-*methyl*-5-*methylene*-1,7-*octadiene* (**47**). The triene, **47** (1.80 g), and tetraphenylporphine (50 mg) were irradiated in CCl_4 (250 ml) in O_2 for 4 hr. The photolysate was rotavolated and the residue was chromatographed on silica gel. Elution with hexane–CH_2Cl_2 (1 : 1) gave the starting material and then **51** as a colourless viscous oil in a 45% yield (conversion yield 63%).

Relative rate of 1,4-*cycloaddition of* $^1O_2$ *toward acyclic conjugated dienes.* A soln of 0.055–0.060 M acyclic dienes in CH_2Cl_2–5% MeOH (250 ml) was photo-oxygenated in the presence of Rose Bengal (0.2 g) with the above-mentioned apparatus at 15–17°. Until 0.2 equivalent of O_2 was consumed, the time course of O_2 uptake was measured. The relative rate of the oxygenation was observed as follows: **15**–**17**–**11**–**39**–**1**–**9** = 9.6 : 9.1 : 9.1 : 8.3 : 1.1 : 1.

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