sodium cyanide, and lithium perchlorate, are not catalysts, but sodium fluoroborate, boron trifluoride etherate, and triphenylphosphine do catalyze the reaction. The mechanism by which these compounds initiate addition deserves further study.

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Supplementary Material Available: Complete experimental details and spectroscopic data (6 pages) are available. Ordering information is given on any current masthead page.

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(1) See, for example, L. S. Hegedus and E. L. Waterman, *J. Am. Chem. Soc.*, **96**, 6789 (1974); K. Sato, S. Inoue, and K. Saito, *J. Chem. Soc., Perkin Trans. 1*, 2289 (1973); C. D. Snyder and H. Rappaport, *J. Am. Chem. Soc.*, **96**, 8046 (1974); A. S. Kende, T. Tsay, and J. E. Mills, *ibid.*, **98**, 1967 (1976).
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(3) All new compounds possessed NMR, IR, and high resolution mass spectra in accord with the assigned structures. See paragraph at the end of the paper about supplementary material.
(4) This is an adaptation of the method of A. McKillop and D. Young, who recently reported the oxidation of *p*-hydroquinone via mercuric oxide in methanol. A. McKillop and D. Young, *Synth. Commun.*, **7**, 467 (1977).
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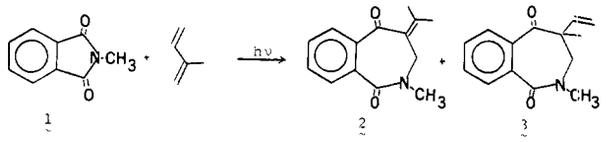
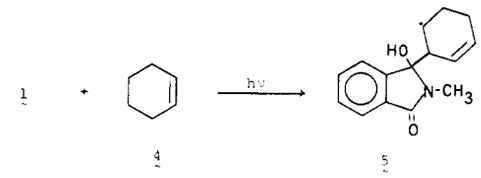
Photochemical Addition of Alkenes to *N*-Methylphthalimides. Formation of 3,4-Benzo-6,7-dihydroazepine-2,5-diones

Summary: The photochemical reactions of *N*-methylphthalimide with a number of alkenes in acetonitrile solution to give substituted 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones is described.

Sir: Recently there has been a great deal of interest in the photochemistry of cyclic imides. It has been shown that appropriately N-substituted phthalimides[1–13] and succinimides[14] undergo type II processes involving *N*-alkyl or -aryl chains and that *N*-alkenylsuccinimides afford intramolecular Paterno–Buchi products.[15] We recently reported[16] that dienes efficiently add to *N*-methylphthalimide (**1**) to give 6-methylene (**2**) or 6-vinyl (**3**) substituted 3,4-benzo-6,7-dihydro-



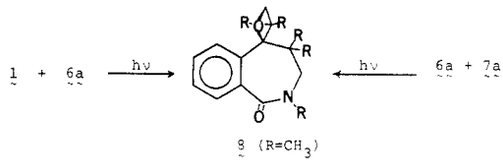
1-methylazepine-2,5-diones in an essentially unprecedented reaction that is formally a $[\pi^2 + \sigma^2]$ photochemical cycloaddition. During our investigation of the scope of this reaction with respect to acceptable variations in the π^2 component we confirmed the report of Kanaoka and Hatanaka[17] that cyclohexene undergoes photochemical reaction with **1** to afford only the photoreduction product **5** in poor yield.



However, when **1** (2 g) was irradiated in the presence of a 50-fold molar excess of 2-methylpropene (**6a**) in acetonitrile

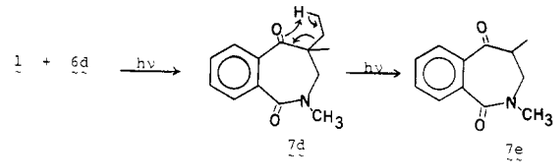
6a, $R_1=R_2=CH_3$, $R_3=R_4=H$ — **7a**, $R_1=R_2=CH_3$
b, $R_1=CH_2CH_3$, $R_2=R_3=R_4=H$ — **b**, $R_1=CH_2CH_3$, $R_2=H$
c, $R_1=(CH_2)_3CH_3$, $R_2=R_3=R_4=H$ — **c**, $R_1=(CH_2)_3CH_3$, $R_2=H$
d, $R_1=CH_2CH_3$, $R_2=CH_3$, $R_3=R_4=H$ — **d**, $R_1=CH_2CH_3$, $R_2=CH_3$
e, $R_1=R_2=R_3=CH_3$, $R_4=H$ — **e**, $R_1=CH_3$, $R_2=H$
f, $R_1=CH_2CH_3$, $R_2=R_3=CH_3$ $R_4=H$ — **f**, $R_1=R_2=H$
g, $R_1=R_2=R_3=R_4=CH_3$

solution with an unfiltered (quartz) 450-W Hanovia lamp for a period of 6 h, workup[18] of the reaction mixture gave two products identified as **7a** and **8** in 32 and 12% yields, respec-



tively. The structure of the major product 3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione (**7a**, mp 88–89 °C) was based on the following spectroscopic evidence: NMR ($CDCl_3$) δ 1.28 (s, 6 H), 3.22 (s, 3 H), 3.55 (s, 2 H), 7.32–7.94 (m, 4 H); IR (CCl_4) 1695 and 1660 cm^{-1}; *m/e* 217 (15). The minor product was identified as the oxetane **8**: NMR ($CDCl_3$) δ 0.74 (s, 6 H), 1.41 (s, 3 H), 1.70 (s, 3 H), 3.17 and 2.74 (AB pattern, J = 14 Hz, 2 H), 3.20 (s, 3 H), 4.39 and 3.98 (AB pattern, J = 5 Hz, 2 H), 7.13–7.70 (m, 4 H); IR ($CHCl_3$) 1630 cm^{-1}; *m/e* 273 (37). The structure and mode of formation of **8** was confirmed by irradiating **7a** in the presence of 2-methylpropene (**6a**). The product **8** was obtained in 17% yield.

In a similar manner irradiation of 2-methyl-1-butene and **1** afforded a 43% yield of **7e** (mp 75–76 °C): NMR ($CDCl_3$) δ



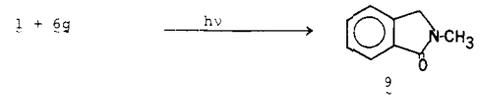
1.21 (d, J = 7 Hz, 3 H), 3.02–2.80 (m, 1 H), 3.20 (s, 3 H), 3.66 (m, 2 H), 7.38–8.00 (m, 4 H); IR ($CHCl_3$) 1690 and 1635 cm^{-1}; *m/e* 203 (30). Compound **7e** is presumably a secondary photoproduct of **7d**.[19]

The parent 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione (**7f**) was obtained in 60% yield from 1-butene and in 46% yield from 1-hexene via **1** → **7b** → **7f** and **1** → **7c** → **7f** sequences.

Table I. Ionization Potentials of Olefins and Benzazepindione Yields

alkene	**6b**	**6c**	**6a**	**6d**	2-butene	cyclopentene	cyclohexene	**6e**	**6f**
yield (%)	60	46	44	43	~32[24]	0[17]	0[17]	0	0
IP (EV)	9.58[21]	9.46[21]	9.23[21]	9.12[22]	9.13[21]	9.01[22]	8.95[22]	8.68[21]	8.53[23]

Suprisingly, irradiation of 1 with 2-methyl-2-butene or 2-methyl-2-pentene gave none of the expected substituted 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones and 2,3-dimethyl-2-butene gave a 5% yield of *N*-methylphthalimidine (**9**) as the only isolable product.[20]



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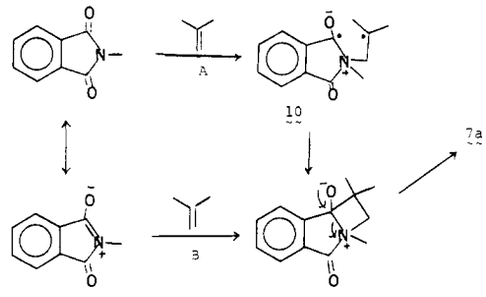
There are several noteworthy points concerning these results. The observed reaction is totally regiospecific as was the corresponding reaction with dienes[16] and we suggest mechanistic routes A or B as the most reasonable ones. The reactivity



of the alkenes generally correlates with their ionization potentials (Table I), those alkenes with ionization potentials above 9 eV being reactive and those with ionization potentials below 9 eV unreactive. Clearly, electron-transfer processes cannot be important to these reactions unless the apparent correlation is due to counteracting steric effects. An alternative interpretation is that electron-transfer quenching of the reaction is taking place with those alkenes having low ionization potentials.[25] These points are being investigated.

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(24) Preliminary experiments indicate that a mixture of *cis*- and *trans*-2-butene affords a mixture of *cis*- and *trans*-3,4-benzo-6,7-dihydro-1,6,7-trimethylazepine-2,5-diones. The stereochemistry of the products obtained from the pure alkenes is being investigated at present.
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Sensitized Photoreduction of Dioxetanes to *cis*-1,2-Glycols: Solvent and Sensitizer Dependencies on the Singlet Oxygen Oxidation

Summary: Dioxetanes are convertible into *cis*-1,2-glycols by visible-light irradiations with relatively large amounts of xanthene dyes, such as Rose Bengal, in protic solutions under even aerated conditions to provide a new experimental probe for dioxetanes.

Sir: Previously we have reported[1] that the singlet oxygen oxidation of spirocyclic vinylcyclopropane **1** has given a new type of oxidation product **2** together with dialdehyde **3.** For the mechanism of formation of **2** there might be several possibilities, but at least a direct responsibility of singlet oxygen should be clear, since we have shown recently that quenchings of singlet oxygen by sodium azide have resulted in the complete suppression of formation of both **2** and **3.**[2] In this paper, we will further present evidences to support the concomitant formation of **2** and **3** by the reaction in various solvents and by an observation of unprecedented photosensitized reduction of dioxetanes to *cis*-1,2-glycols.

First of all, the relative yields of **2** and **3** in the reaction exhibited a marked solvent dependency as compiled in Table I.

It is clear that the polarity of solvents used plays no significant role, because in carbon disulfide and in pyridine the formation of **2** is predominant in each case. Interestingly, the formation of **2** in such inert solvents should be a conclusive evidence for its genesis with singlet oxygen. Except in a case with a benzene solution, where we had to use a polymer-supported sensitizer, the formation of **3** was favored in the reaction with protic solvents, and it is controlled by adjusting the solvent compositions as shown in the cases of a methanol–pyridine mixture.

In general, changes in sensitizers are known to be unimportant for singlet-oxygen oxidations. Comparative yields with Methylene Blue (MB) and Rose Bengal (RB) show this to be true for the process which leads to **2.** However, a dramatic change was observed for the yields of the dioxetane-related **3** when the reaction was carried out in methanol; with MB, **3** was the major product accompanied by trace amounts of **2,** but with RB, approximately equal amounts of **3** and the newly identified *cis*-glycol **4,** colorless needles, mp 56–57 °C, was formed. In the methanol–pyridine solvent mixtures and in methanol, the combined yields of **3** and **4,** with RB sensitization, were identical within experimental error to the yield of **3** with MB sensitization. Therefore, **4** has been derived from the precursor of **3**, i.e., the dioxetane (A) or its precursor (C) (Scheme I).

The structure of **4** was established by IR (ν_{OH} at 3450 cm^{-1}) and NMR ($CLCl_3$) [δ 0.30–0.75 (7 H, m), 0.88 (1 H, m), 2.01 (1 H, m, $W_{h/2}$ = 8 Hz), 2.31 (1 H, m, $W_{h/2}$ = 8 Hz), 2.55 (2 H,

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