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The Photocycloaddition of 2-Cyclohexenone and Maleic Anhydride to $\Delta^{9,10}$-Octalin

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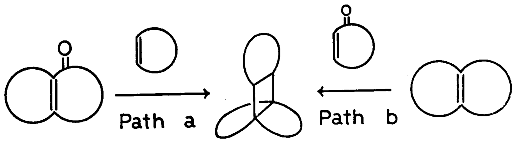
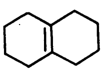
Synopsis. The photocycloaddition to $\Delta^{9,10}$-octalin (**1**) was investigated. Both 2-cyclohexenone and maleic anhydride reacted with **1** to afford the corresponding photocycloadducts, **2** and **3** respectively.

From the viewpoint of the synthesis of interesting cyclic compounds, increasing attention has been shown in the study of the photocycloaddition of cyclic enones to olefins.[1] Especially, for the synthesis of propellanones, the photocycloaddition of bicyclic enones to olefins has been generally employed as a convenient method.[2] More recently, we reported the photochemical synthesis of a new type of tetracyclic propellanone according to the above method (Path a).[3] Although the photocycloaddition of appropriate substances to bicyclic olefins, which have a central double bond, can be assumed to be an alternative method, no such study has yet been reported (Path b). In an extension of our study of the photochemical preparation of a variety of propellane derivatives, we wish to report here our preliminary finding concerning the photocycloaddition of some cyclic substrates to $\Delta^{9,10}$-octalin (**1**).

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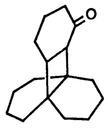
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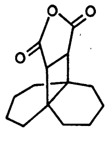
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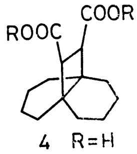

4 R=H
5 R=Me

First, we examined the photocycloaddition of 2-cyclohexenone to **1**. When a neat mixture of 2-cyclohexenone and a 6-molar excess of **1** was irradiated through a Pyrex filter, a cross cycloadduct **2** was given, along with 2-cyclohexenone dimers. The yield of **2** was estimated by glpc analysis to be 13% based on the quantity of **1** reacted. The structure was determined to be **2** on the basis of the spectral data and by elemental analysis, and also, most especially, by the fact that no hydrogenation occurred when the palladium-charcoal catalyst was used.[4]

Next, we examined the photocycloaddition of maleic anhydride to **1**. When an ethereal solution of maleic anhydride and a 2-molar excess of **1** was irradiated through a Pyrex filter, a cross cycloadduct **3** was given, along with a considerable amount of the maleic anhydride dimer. When **3** was chromatographed on silica gel, spontaneous hydrolysis occurred and an acid (**4**) was isolated in a 24% yield, based on the quantity of **1** reacted. By treatment with ethereal diazomethane, **4** was changed into an ester (**5**).

As has been described above, 2-cyclohexenone and maleic anhydride easily reacted with **1** to afford the corresponding tetracyclic [4.4.2]propellanone derivatives. In connection with the above study, we have also obtained some information about the attempted photocyclodimerization of **1**. Attempts at photosensitized cyclodimerization with acetone, benzophenone, and phenanthrene were unsuccessful, but photosensitization with triphenylene gave a cyclodimer, albeit in a low yield. A detailed study of the photocyclodimerization of **1** is now in progress.

Experimental

Generals. All the melting points and boiling points are uncorrected. The IR spectra were recorded with a JASCO IR-G spectrometer. The NMR spectra were recorded for a 5% solution in carbon tetrachloride or deuterochloroform, with tetramethylsilane as the internal standard, on a JEOL JNM-3H-60 spectrometer. All the irradiations were carried out using a 500-W high-pressure mercury arc under a nitrogen atmosphere at room temperature. Analytical glpc was carried out on a Hitachi 063 gas chromatograph employing the following columns: a) 20% PEG-20M, b) 3% SE-30, c) 20% DC-550, and d) 10% FFAP.

Reagents. The $\Delta^{9,10}$-octalin (**1**) was prepared by the method of Dauben and was purified by nitrosyl-chloride treatment.[5] The maleic anhydride and the 2-cyclohexenone were purified by distillation before use. The triphenylene was recrystallized from methanol.

Photocycloaddition of 2-Cyclohexenone to 1. A neat mixture of 2-cyclohexenone (1.60 g, 16.7 mmol) and **1** (14.0 g, 103 mmol) was irradiated through a Pyrex filter for 3 hr. The photolysate was vacuum-distilled to give 13.3 g of recovered **1** (bp 60—65 °C/10 mmHg) and 2.32 g of viscous oil (bp 140—180 °C/10^{-3} mmHg). The latter was chromatographed on silica gel (200 mesh, 50 g) and was eluted initially with petroleum ether (400 ml) and then with ether (400 ml). The concentration of the latter eluate afforded 1.2 g of an oil which consisted of the cross adduct **2** and two cyclohexenone dimers.[6] The yield of **2** was estimated by glpc analysis to be 13% on the basis of **1** reacted. Preparative glpc using Column a) and d) gave an analytical sample; IR (neat) 1705 cm^{-1} (C=O); NMR (CCl$_4$) δ 1.00—2.80 (m); Mass *m/e* 232 (M$^+$); Found: C, 82.41; H, 10.39%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%; 2,4-dinitrophenylhydrazone, mp 161—163 °C. By treatment with a 5% palladium–charcoal catalyst under hydrogen, **2** was not hydrogenated (in methanol, room temp., 1 atom).[4]

Photocycloaddition of Maleic Anhydride to 1. A solution of maleic anhydride (5.4 g, 55 mmol) and **1** (15.0 g, 110 mmol) in dry ether (130 ml) was irradiated through a Pyrex filter for 60 hr. The maleic anhydride dimer which was thus precipitated from the reaction mixture was removed by filtration, and then the ether was evaporated. The residual oil was vacuum-distilled to give 8.8 g of recovered **1** (bp 53 °C/3 mmHg) and 7.0 g of a viscous oil (bp 145—150 °C/10^{-3} mmHg) showing two characteristic IR absorptions ascribable to **3** at 1860 and 1790 cm^{-1}. The anhydride fraction was chromatographed on silica gel (200 mesh, 185 g). Elution with benzene–ether (95: 5, 10 l) brought about spontaneous hydrolysis to give 2.80 g of the acid **4** in a 24% yield, based on the quantity of **1** reacted. Recrystallization from aq. methanol provided an analytical sample; mp 181—182 °C; IR (KBr) 1700 cm^{-1} (COOH); NMR ($CDCl_3$) δ, 11.35 (s, 2H, COOH), 1.0—3.0 (m, 18H, others); Mass *m/e*, 234 (M^+-H_2O), 135; Found: C, 66.37; H, 7.99%. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99%. By treatment with ethereal diazomethane, **4** was changed into the dimethyl ester **5**, which showed an IR absorption at 1715 cm^{-1} and an NMR absorption at δ 3.70 (methyl ester).

References

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2) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); P. E. Eaton and N. Kyi, *ibid.*, **93**, 2786 (1971); P. E. Eaton and G. H. Temme, *ibid.*, **95**, 7508 (1973); see also R. L. Cargill, T. E. Jackson, N. P. Peet, and D. M. Pond, *Accounts Chem. Res.*, **7**, 106 (1974) and references cited therein.

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4) In order to exclude the possibility of an allylic type of adduct, we attempted the catalytic hydrogenation.

5) W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).

6) Identification was made by comparison with authentic materials.