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INTRAMOLECULAR PHOTO[2+2]CYCLOADDITION OF 2-ALLYLOXY- AND
2-ALLYLAMINOCYCLOHEX-2-ENONES: FORMATION OF 2-OXA- AND
2-AZA-BICYCLO[2.1.1]HEXANE SYSTEMS

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Photoirradiation of 2-allyloxy- and 2-(allylacetamido)-cyclohex-2-enones gave 2-oxa- and 2-aza-bicyclo[2.1.1]hexane systems as the major products.

KEYWORDS — photocycloaddition; 2-allyloxycyclohex-2-enone; 2-allylaminocyclohex-2-enone; 2-oxabicyclo[2.1.1]hexane; 2-azabicyclo[2.1.1]hexane; long-range coupling; N-acylenamine

We have previously reported that irradiation of 3-allyloxy- and 3-allylamino-cyclohex-2-enones (1) gives 2-oxa- and 2-aza-bicyclo[2.1.1]hexane systems (2).¹⁾ Since then several papers have appeared reporting similar reactions on the related systems.²⁾ We have now investigated the photochemical behavior of 2-allyloxy- (4) and 2-allylamino-cyclohex-2-enones (6) and (11).

X=O, NMe, NAc etc.

Compound 4 was prepared in 74% yield by refluxing 1,2-cyclohexanedione (3) with allylalcohol in benzene in the presence of *p*-toluenesulfonic acid. Irradiation³⁾ of 4 in degassed benzene in the presence of acetophenone gave a 2-oxabicyclo[2.1.1]hexane 5, mp 64-66°C, as the major product (40-47%). The elemental analysis and molecular weight [m/z 152 (M^+)] of 5 indicate that it is an isomer of 4. The infrared (IR) (1705 cm^{-1} in CHCl_3), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectra show no unsaturation. The distinguishing features of the NMR spectrum (90 MHz) of 5 are Ha and Hb, which occurred at δ 3.82 and 3.93 as an AB quartet ($J=6$ Hz). The structure of 5 was deduced from analysis of the NMR spectrum using a shift reagent [$\text{Eu}(\text{FOD})_3$] and spin decoupling experi-

ments. The stereochemistry of **5** was defined by a large long-range coupling ($J=8$ Hz) between Hc and He: such coupling would occur only if these protons were in W-configuration in the bicyclo[2.1.1]hexane.⁴⁾ Final confirmation of structure **5** was given by an X-ray structure analysis.⁵⁾

Compound **6** was prepared in 46% yield by refluxing **3** with allylamine in benzene followed by treatment with acetyl chloride in the presence of triethylamine. Irradiation of **6** in benzene in the presence of acetophenone gave two products which could be separated by column chromatography on silica gel using AcOEt:n-hexane (1:1). The minor product [ca. 9%, an oil] was assigned **7** from the spectral evidence. The elemental analysis and mass spectrum of **7** indicate the molecular formula $C_{11}H_{15}NO_2$. Its IR spectrum ($CHCl_3$) shows two strong carbonyl absorptions at 1720 and 1635 cm^{-1} and the UV (EtOH) spectrum is that of a typical six-membered N-acylenamine with λ_{max} 231 nm ($\log \epsilon$ 3.67).⁶⁾ The NMR spectrum ($CDCl_3$) reveals a singlet (3H, $NCOCH_3$) at δ 2.21, a doublet of triplets (1H, H-3, $J=8$ and 4 Hz) at δ 4.82, a doublet (1H, H-8a, $J=6$ Hz) at δ 5.21, and a broad doublet (1H, H-2, $J=8$ Hz) at δ 6.56. The remaining signal is a multiplet between δ 1.4 and 2.8 (9H). The stereochemistry is not clear at this time. The formation of **7** may proceed via initial hydrogen abstraction by the carbonyl oxygen⁷⁾ to give a biradical **10** which may cyclize. The major product was isolated as its hydrate **9** in ca. 43% yield. When **9** was dried at 70°C *in vacuo* for 20 h, the ketone **8**, mp 111–114°C, was obtained as a pure form but easily absorbed water to revert to the hydrate form **9**. The IR spectrum ($CHCl_3$) of **8** shows two carbonyl absorption at 1705 and 1640 cm^{-1} , and its UV and NMR spectra show no unsaturation. The NMR spectrum of **8** indicates an AB quartet at δ 3.42 and 3.61 ($J=8$ Hz) due to Ha and Hb, and a singlet (3H, $NCOCH_3$) at δ 1.99. Final confirmation of structure **8** was made by an X-ray structure analysis of its hydrate **9**.⁵⁾ The hydrate **9** is stabilized by the formation of hydrogen bond between one of two hydroxyl groups and the acetyl carbonyl oxygen.

Irradiation of compound 11, prepared from 3 and *N*-methylallylamine, afforded a very complex mixture, and no further investigation was carried out.

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