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SYNTHESIS AND PHOTOCHEMICAL REACTIVITY OF O-ALKYLMALEIMIDE

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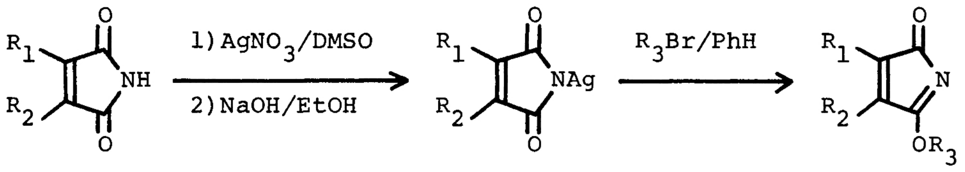
Irradiation of O-alkylmaleimide, prepared by the reaction of silver maleimide with alkyl bromide, resulted in Norrish type II elimination presumably initiated by γ-hydrogen abstraction of excited carbon-nitrogen double bond.

Recently there has been a growing interest in the photochemical reactivity1) of carbon-nitrogen double bond with the anticipation of extending well-documented photochemical reactions often observed2) with structually related carbon-carbon and carbon-oxygen double bonds. Norrish type II photoeliminations, for example, have been reported2) for various ketones with γ-hydrogen in accessible locations, but similar reactivity for imine is rare and only a carbon-nitrogen double bond incorporated into six-membered ring has been reported1,3,4) to undergo the photoelimination. We wish to report here the first example of the photoelimination which involves γ-hydrogen abstraction by nitrogen of the carbon-nitrogen double bond in five-membered ring, i.e., O-alkylmaleimide. A useful extension of a previously unestablished synthesis of O-alkylmaleimide will be also described.

Although several literature examples5) describe O-alkylation of succimide to form O-alkylsuccimide, little efforts have been made to synthesize O-alkylmaleimide (**2**). Lerner et al6) reported the first synthesis of this type of compound, i.e., O-(1-adamantyl)maleimide, which was found to be formed in their preparation of N-substituted maleimide by direct coupling of alkyl halide with silver maleimide. We have examined the method as a general route to O-alkylmaleimide and found that tertiary as well as secondary alkyl substituted **2** can be obtained in pure form only under very carefully controlled conditions. A typical procedure consists of the addition of the alkyl bromide to a well-stirred suspension of freshly prepared



(1) (2)

a: $R_1=R_2=H$, R_3=t-Bu b: $R_1=R_2=H$, R_3=i-Pr
c: $R_1=R_2=Ph$, R_3=t-Bu d: $R_1=R_2=Ph$, R_3=i-Pr

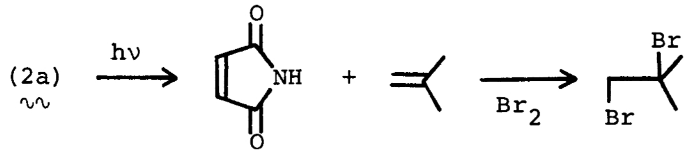
silver maleimide in benzene in the dark at room temperature. In all cases, better yield of purer products were generally obtained by avoiding the unneccessary longer contact of the product with silver salts by careful monitoring of the progress of the reaction since O → N isomerization was known[5)] to be catalyzed by silver salts at a higher temperature. The reaction with t-butyl bromide was typical; the reaction was completed almost instantaneously (10 sec) and longer reaction time led to complex mixture. The results are summarized in Table 1. O-i-Propylmaleimide (2b, d) is the first isolated compound of this type which carries alkyl group other than bulky tertiary alkyl group. The reaction with primary halide (e.g., EtBr and $PhCH_2I$) resulted in a ca 1:1 (NMR) mixture of N- and O-alkylmaleimides and attempts to separate them were unsuccessful. The structure 2 was clearly differentiated from N-derivative by ^1H NMR and IR; characteristic absorption of olefinic protons for 2a~b appeared at δ 6.4 and 6.8 and the conjugated C=C and C=N bonds were also evident at 1600 and 1530 cm^{-1}.[7)]

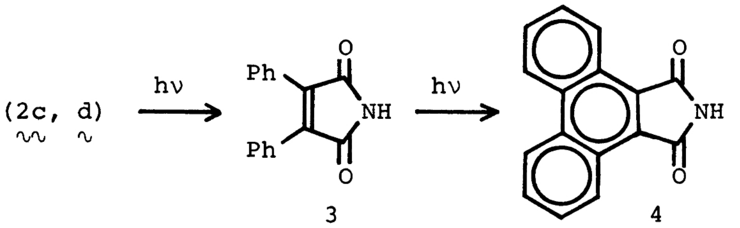
Table 1. O-Alkylmaleimide (2) prepared[7)]

Reaction		Product		
Temp. (°C)	Time	Structure	m.p. (°C)	Yield (%)
20	10sec	2a	<30	80
35	20hr	2b	<30	75
20	10sec	2c	220-221 (dec)	81
35	20hr	2d	220-222 (dec)	70

Irradiation of O-t-butylmaleimide (2a) in $CDCl_3$ in a quartz NMR tube with unfiltered light from a 300-W high-pressure mercury lamp was monitored by NMR, which revealed rapid disappearance of the characteristic olefinic protons of the starting material and concurrent appearance of new olefinic protons at δ 5.60 and

4.75, attributable to maleimide (**1a**) and isobutylene, respectively. Irradiation carried out in an infrared solution cell also indicated rapid shift of the characteristic absorption of **2a** to the spectrum which is completely superimposable upon those of **1a**. After most of **2a** was consumed, the reaction mixture was divided into two portions. To one-half of the reaction mixture was added dilute bromide solution and the resulting solution was analyzed by GC which showed the presence of 49% of the dibromide of isobutylene. Silica gel chromatography of the second half of the reaction mixture afforded **1a** (83%). Similar irradiation of **2b** also resulted in the formation of the corresponding maleimide (**1b**, 80%). Irradiation of diphenyl derivative (**2c**, **d**) gave diphenylmaleimide (**3**) along with small amount of phenanthrene-9,10-dicarboximide (**4**), which increased with irradiation time. Control experiments showed that **4** was formed not directly from **2** but from **3** presumably via photocyclization.[8] There was no sign of type I cleavage in the present photolysis





3 **4**

although O-alkylsuccinimide, a dihydro derivative of **2**, almost exclusively undergoes type I cleavage upon irradiation to give cyclopropyl isocyanate.[5] Irradiation of **2** in the presence of olefin (e.g., ethyl vinyl ether) in an attempt to obtain cycloadduct also resulted in the formation of maleimide. This is in sharp contrast with that observed for 3-alkoxyisoindolone, a benzo analog of **2**, which gave (2 + 2) cycloadduct to the carbon-nitrogen double bond upon irradiation with olefin.[9]

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7) All compounds gave reasonable spectroscopic data and elemental analyses to the assigned structures. Pmr data (δ in $CDCl_3$) are as follows: **2a**; 1.68 (s, 9H), 6.40 and 6.77 (q, 5.2 Hz, 2H). **2b**; 1.45 (d, 6 Hz, 6H), 5.43 (sept, 6 Hz, 1H), 6.45 and 6.87 (q, 5.2 Hz, 2H). **2c**; 1.72 (s, 9H), 7.2∼7.5 (m, 10H). **2d**; 1.50 (d, 6 Hz, 6H), 5.52 (sept, 6 Hz, 1H), 7.2-7.5 (m, 10H).

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