Table II. Behavior of Triphenyl(methyl)stibonium Bromide in Acetonitrile at 25 °C[a]

| Run | Concn ($C$) × $10^3$ mol/l. | $\Lambda$ | $\Lambda_x$ | $\alpha$ | $k$ = rate/$\alpha^2C^2$ × $10^5$ l mol$^{-1}$ s$^{-1}$ | $\sqrt{\alpha C}$ × $10^2$ |
|---|---|---|---|---|---|---|
| 3 | 5.987 | 80.0 | 126.4 | 0.633 | 18.60 | 6.16 |
| 1 | 5.234 | 85.4 | 127.0 | 0.672 | 18.40 | 5.93 |
| 1 | 3.604 | 93.4 | 129.3 | 0.723 | 17.58 | 5.10 |
| 3 | 3.085 | 96.0 | 130.1 | 0.737 | 21.82 | 4.77 |
| 2 | 2.849 | 98.3 | 130.5 | 0.752 | 22.98 | 4.63 |
| 1 | 1.802 | 107.0 | 132.7 | 0.806 | 22.52 | 3.81 |
| 3 | 1.462 | 109.8 | 133.7 | 0.821 | 23.90 | 3.46 |
| 2 | 1.425 | 110.7 | 133.7 | 0.828 | 20.98 | 3.43 |
| 3 | 0.7803 | 118.6 | 136.0 | 0.872 | 26.48 | 2.61 |
| 1 | 0.7208 | 121.1 | 136.2 | 0.889 | 32.03 | 2.53 |

[a] $\Lambda$ = observed molar conductance; $\Lambda_x$ = molar conductance expected in the absence of ion pairing; $\Lambda_x$ was determined by an iterative process using the Kohlrausch–Onsager equation $\Lambda_x = \Lambda_0 - S[\Lambda/\Lambda_x C]^{1/2}$, $S = 0.7374\Lambda_0 + 233.6$, $\Lambda_0$ for $(C_6H_5)_3SbCH_3Br$ = 143; $\alpha$ = degree of dissociation = $\Lambda/\Lambda_x$ = $[Br^-]/C$ = $[(C_6H_5)_3SbCH_3^+]/C$; $C$ = total salt concentration; $\alpha C = \mu$ = ionic strength.

In agreement with the Debye–Hückel theory,[4] we found that a plot of log (rate/$\alpha^2C^2$) vs. the square root of ionic strength gives a straight line plot for the data from which $k^0 = 3.4 \times 10^{-4}$ M$^{-1}$ s$^{-1}$ was determined by extrapolation of the data for run 3. The theoretical slope based on the dielectric constant of acetonitrile (35.95)[5] is −3.28; the experimental slope was −4.32.

$$\log \frac{\text{rate}}{\alpha^2C^2} = \log k^0 + \log (\gamma_A\gamma_B/\gamma_{\neq})$$

$$\log \gamma_A\gamma_B = 2Z_AZ_BA\sqrt{\mu}$$

where $\gamma_{\neq} = 1$, $A = 1.64$ for dielectric constant 35.95, $Z_A$ and $Z_B$ are the ionic charges (+1, −1), and $\mu$ is the ionic strength which in this case is equal to $\alpha C$ at any concentration.

In theory $k^0$ is the sum of two contributions in the form $k^0 = k_1{}^0k_A + k_2{}^0$, where $k_1{}^0$ is the rate constant for collapse of ion pairs, $k_A$ is the ion association constant, and $k_2{}^0$ is the rate constant for direct reaction of free ions. However, it is impossible to separate $k^0$ into its parts for the reasons discussed by Pocker and Parker.[3]

As calculated from electrical conductance measurements, the degree of dissociation of the salt varied from 0.633 at $5.99 \times 10^{-3}$ M to 0.889 at $0.721 \times 10^{-3}$ M. During the course of the study, the limiting ionic conductances of triphenyl(methyl)stibonium cation (47 ± 5), tetraphenylstibonium cation (41 ± 4), and $BF_4^-$ anion (104 ± 7) were estimated. The values are reasonable compared to the ionic conductances of tetraphenylarsonium cation (55.8) and perchlorate anion (103.8) reported in the literature.[6,7]

## Experimental Section

Triphenyl(methyl)stibonium tetrafluoroborate was prepared by treating triphenylstibine with trimethyloxonium tetrafluoroborate in boiling methylene chloride for 2.5 h. Anal. Calcd for $C_{19}H_{18}SbBF_4$: C, 50.17; H, 4.00; Sb, 26.76. Found: C, 50.45; H, 4.06; Sb, 26.51. The bromide salt was prepared by adding the corresponding potassium salt to a solution of the stibonium tetrafluoroborate in 95% ethanol and removal of the precipitated $KBF_4$ by filtration. Anal. Calcd for $C_{19}H_{18}SbBr$: C, 50.94; H, 4.05; Sb, 27.18. Found: C, 50.67; H, 4.11; Sb, 27.32. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and antimony analyses were performed by Mrs. D. E. Knight at N.C.S.U.

Acetonitrile was purified for conductance measurements by standing over NaOH pellets and molecular sieve for several days followed by distillation through a column packed with molecular sieve. The specific conductance of the solvent used in the measurements was usually $30 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$ at 25 °C, but no significant difference was noted using solvent with specific conductance as high as $200 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$ provided this correction was applied to the measured conductances of salt solutions.

Conductance and kinetic measurements were made in an enclosed fill-type Beckman cell with cell constant 0.1320 ± 0.0003 cm$^{-1}$. The cell was kept in a bath which was maintained at 25.0 ± 0.2 °C. A Beckman RC-18A bridge was used to measure conductance.

The kinetic runs were made by two different techniques. Preliminary runs (1 and 2) were made by making up a large volume of stock solution from which dilutions were made. The diluted solutions were stored in a thermostated Dewar flask and their conductances were measured periodically by transferring samples into the conductance cell. All manipulations were made in the air. Later runs (run 3) were made by accurately weighing samples of the salt into 25-ml volumetrics and transferring the volumetrics into a nitrogen-flushed glove box. Acetonitrile was added and the salt rapidly dissolved. The cell was rinsed with three small portions (~3 ml each) of the solution and the remaining solution was just sufficient to fill the cell. The cell was closed with its ground glass thermometer, taken out of the glove box, and placed in the thermostated bath. The first conductance measurements were made approximately 15 min after adding solvent and the sample was monitored continuously for up to 1500 min without disruption. While the preliminary runs showed some scatter in the results, the latter technique produced a very consistent set of data.

**Registry No.**—Triphenyl(methyl)stibonium bromide, 58074-28-5; triphenyl(methyl)stibonium tetrafluoroborate, 3802-09-3; triphenylstibine, 603-36-1; trimethyloxonium tetrafluoroborate, 420-37-1.

## References and Notes

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# Photocyclization of 3-(3-Methyl-2-butenyloxy)- and 3-(3-Methyl-2-butenylamino)-5,5-dimethyl-2-cyclohexen-1-ones to 7-Oxa- and 7-Azabicyclo[4.3.0]nonan-2-ones

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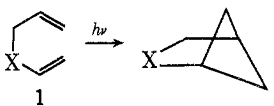
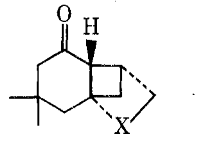
*Received June 23, 1975*

In a preceding paper,[1] we have shown that the photocycloaddition reaction of 1,5-hexadienes to bicyclo[2.1.1]hexanes[2] [**1** (X = $CH_2$) → **2**] can be extended to the syntheses of 2-oxa- and 2-azabicyclo[2.1.1]hexane ring systems [**1** (X

= O or NR) → 2]; e.g., compounds **3** were synthesized from 3-allyloxy- and 3-allylmethylamino-5,5-dimethyl-2-cyclohexen-1-ones. In continuation of our studies directed toward the utilization of this reaction in the syntheses of the heterocyclic compounds, we have examined the photochemical behavior of 3-(3-methyl-2-butenyloxy)- and 3-(*N*,3-dimethyl-2-butenylamino)-5,5-dimethyl-2-cyclohexen-1-ones (**4** and **10**), and found the exclusive formation of 7-oxa- and 7-azabicyclo[4.3.0]nonan-2-one ring systems (**5** and **11**).



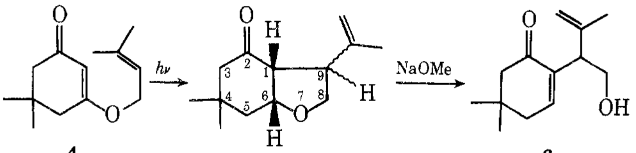
**1** **2**



**3**, X = O or NMe

Compound **4** was prepared by the procedure used to synthesize 3-(3-methyl-2-butenyloxy)-2-cyclohexen-1-one:[3] treatment of the silver salt of dimedone with 1-bromo-3-methyl-2-butene in refluxing anhydrous benzene gave 18% yield of **4**.

Irradiation of a 0.7% cyclohexane solution of **4** with a 350-W high-pressure mercury lamp in a Pyrex tube for 15 h resulted in the formation of an oily isomeric ketone **5** in 69% yield. The assignment of structure **5** is based on its composition, spectra, and subsequent transformation.



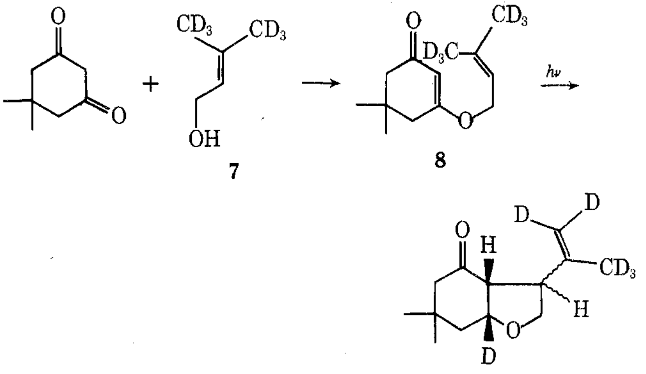
**4** **5** **6**

Compound **5** shows ir bands at 3080, 1710 (six-membered ketone), 1645, and 900 cm$^{-1}$ (C=CH$_2$) and a well-resolved NMR spectrum (see Experimental Section). The assignments were confirmed by spin decoupling experiments and deuterium labeling experiments (vide infra). Irradiation of 6-H at $\tau$ 5.56 caused the doublet of doublets of 1-H at $\tau$ 7.28 to collapse to a doublet, $J$ = 6.0 Hz, and the doublet of 5-H at $\tau$ 8.17 to a singlet, and irradiation of 1-H at $\tau$ 7.28 converted the doublet of triplets of 6-H into a broad triplet, $J$ = 5.6 Hz, and the doublet of triplets of 9-H at $\tau$ 6.64 into a broad triplet, $J$ = 8.0 Hz. Irradiation of 9-H converted triplets of 8-H at $\tau$ 5.94 and 6.42 to doublets, $J$ = 8.0 Hz, the signal of 1-H to a doublet, $J$ = 7.0 Hz, and the broad signal of olefinic protons to a sharp signal. The ketone **5** was cleaved by sodium methoxide in methanol to enone **6**, whose structure was assigned on the basis of its composition and spectral evidence (see Experimental Section).

The stereochemistry of 1-H and 6-H was tentatively assigned on the basis of the spin-coupling pattern (7.0 Hz). This value appears to be reasonable if these protons were cis to each other. In this orientation the dihedral angle between the two protons is 25–30°. If the protons were trans oriented the resulting dihedral angle (~170°) would require larger spin interaction.

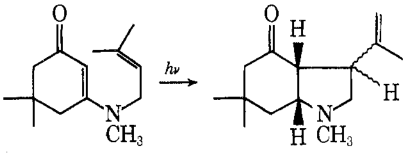
The formation of **5**[4] may be considered as a photochemical intramolecular "ene" reaction,[5] and only two examples of this type of reaction are known: transformations of citral[6,7] and 6-methyl-1,5-heptadien-3-one[8] into 2-isopropenyl-5-methylcyclopentan-1-aldehyde (18% yield) and 3-isopropenylcyclopentanone (10% yield), respectively.

The intramolecularity of this reaction was unequivocally proved by the following deuterium labeling experiments. Deuterated compound **8** was prepared by treating dimedone with dimethylallyl-*3,3-d$_6$* alcohol (**7**) which was in turn synthesized by the reaction of acetone-*d$_6$* and ethoxycarbonylmethylenetriphenylphosphorane followed by lithium aluminum hydride reduction of the resulting ethyl dimethylacrylate-*3,3-d$_6$*. Irradiation of **8**, carried out as described for **5**, afforded **9**, whose NMR spectrum (see Experimental Section) clearly indicated the absence of the signals due to 6-H and the isopropenyl group.

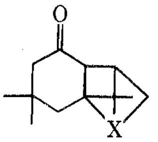


**7** **8** **9**

Under the similar conditions described for **5**, irradiation of **10**, prepared by treating dimedone with *N*,3-dimethyl-2-butenylamine, gave a 66% yield of an oily amine **11** as a sole product, which was characterized as the picrate, mp 142–143 °C. The gross structure of **11** was assigned on the basis of the spectral comparison with **5**. Thus, its ir spectrum displays 3080, 1705 (six-membered ketone), 1640, and 895 cm$^{-1}$ (C=CH$_2$) and its NMR spectrum (see Experimental Section) is well resolved; the coupling constant between 1-H and 6-H is 7.5 Hz, and that between 1-H and 9-H is 5.0 Hz, which are consistent with those of **5**, suggesting that **11** has a stereochemical arrangement identical with that of **5**.



**10** **11**



**12a**, X = O
**12b**, X = NCH$_3$

Finally, it should be noted that 2-oxa- and 2-azabicyclo[2.1.1]hexane derivatives **12a** and **12b** were not detected by the NMR spectra and GLC analyses of the crude products after the photoirradiation of **4** and **10**.

## Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were determined with a Varian HA-100 (for **5** and **11**), and a Hitachi R-20A spectrometer (for the other compounds). Ir spectra were recorded with a Hitachi EPI-G2 spectrophotometer and uv spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6D with a direct inlet system operating at 70 eV. Preparative TLC was carried out on Merck alumina PF$_{254}$. Photoirradiation was carried out in a Pyrex tube using an Eikosha 350-W high-pressure mercury lamp.

**3-(3-Methyl-2-butenyloxy)-5,5-dimethyl-2-cyclohexen-1-one (4).** A suspension of the silver salt of dimedone (prepared from 7.7 g of AgNO$_3$ and 2.7 g of dimedone by application of the method of Woods and Tucker[9]) and 4.47 g of 1-bromo-3-methyl-2-butene in 40 ml of anhydrous benzene was refluxed for 20 min with vigorous stirring. The insoluble material was filtered off and the filtrate was washed with 10% sodium hydroxide and a saturated NaCl solution and dried (MgSO$_4$). The solvent was removed and the residual liquid distilled to give 1.1 g (18%) of **4** as a colorless oil: bp 100–102 °C (0.12 mm); ir (CHCl$_3$) 1640, 1605 cm$^{-1}$; uv max (EtOH) 251 nm (log $\epsilon$ 4.19); NMR (CDCl$_3$) $\tau$ 4.45–4.80 [m, 1, –CH=C(CH$_3$)$_2$], 4.64 (s, 1, 2-H), 5.65 (bd, 2, $J$ = 7 Hz, OCH$_2$), 7.77

(s, 2, 6-H), 7.84 (s, 2, 4-H), 8.25 and 8.33 (s × 2, 3 × 2, $CH{=}C(CH_3)_2$], 8.95 [s, 6, $CH_2C(CH_3)_2$]; mass spectrum *m/e* 208 ($M^+$).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.64; H, 9.47.

**4,4-Dimethyl-9-isopropenyl-7-oxabicyclo[4.3.0]nonan-2-one (5).** A solution of 265 mg of 4 in 40 ml of cyclohexane was irradiated for 15 h. The solvent was removed and the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (3:2) as solvent to give 182 mg (69%) of 5 as a colorless oil: bp 85–90 °C (bath temperature) (0.03 mm); ir ($CHCl_3$) 3080, 1710, 1645, 1060, 900 $cm^{-1}$; NMR ($CDCl_3$, 100 MHz) $\tau$ 5.16 (s, 2, $C{=}CH_2$), 5.56 (dt, 1, $J$ = 7.0 and 5.6 Hz, 6-H), 5.94 (t, 1, $J$ = 8.0 Hz, 8-H), 6.42 (t, 1, $J$ = 8.0 Hz, 8-H), 6.64 (td, 1, $J$ = 8.0 and 6.0 Hz, 9-H), 7.28 (dd, 1, $J$ = 7.0 and 6.0 Hz, 1-H), 7.77 (center of AB q, 2, $J$ = 14.0 Hz, 3-H), 8.17 (d, 2, $J$ = 5.6 Hz, 5-H), 8.26 [t, 3, $J$ = 2.0 Hz, $C(CH_3){=}CH_2$], 8.97 and 8.99 [s × 2, 3 × 2, $C(CH_3)_2$]; mass spectrum *m/e* 208 ($M^+$).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.66; H, 9.47.

**2-(1-Hydroxymethyl-2-methyl-2-propenyl)-5,5-dimethyl-2-cyclohexen-1-one (6).** A solution of 100 mg of 5 and 10 mg of sodium methoxide in 2 ml of methanol was refluxed for 1 h. After the solvent was removed, anhydrous ether was added. The insoluble material was filtered off, and the filtrate was dried ($MgSO_4$) and concentrated. The residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C) as solvent to give 64 mg (64%) of 6 as a colorless oil: ir ($CHCl_3$) 3450, 1660, 900 $cm^{-1}$; uv max (EtOH) 235 nm (log $\epsilon$ 3.91) (calcd for 2-alkyl-2-cyclohexen-1-one, 237 nm); NMR ($CDCl_3$) $\tau$ 3.30 (t, 1, $J$ = 5 Hz, 3-H), 5.05 and 5.22 (bs × 2, 2, $C{=}CH_2$), 6.20–6.50 (m, 3, $CHCH_2OH$), 7.73 (s, 2, 6-H), 7.79 (s, 1, OH), 8.15–8.40 [m, 5, 4-H and $CH_2{=}C(CH_3)$], 9.00 [s, 6, $C(CH_3)_2$]; mass spectrum *m/e* 208 ($M^+$).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.66; H, 9.47.

**Ethyl Dimethylacrylate-*3,3-d*$_6$.** The procedure of Fodor and Tömösközi[10] was employed. A mixture of 1.92 g of acetone-$d_6$ and 10.44 g of ethoxycarbonylmethylenetriphenylphosphorane was heated in a sealed tube at 120 °C for 24 h. To the reaction mixture was added anhydrous petroleum ether and insoluble triphenylphosphine oxide was filtered off. The filtrate was concentrated and distilled to give 860 mg (21%) of ethyl dimethylacrylate-*3,3-d*$_6$: bp 62–63 °C (30 mm); ir ($CHCl_3$) 2200, 1705, 1640, 1165 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 4.36 [s, 1, $CH{=}C(CD_3)_2$], 5.88 (q, 2, $CH_2CH_3$), 8.77 (t, 3, $CH_2CH_3$); mass spectrum *m/e* 134 ($M^+$).

**Dimethylallyl-*3,3-d*$_6$ Alcohol.** A solution of 700 mg of ethyl dimethylacrylate-*3,3-d*$_6$ in 3 ml of anhydrous ether was slowly added to a suspension of 200 mg of lithium aluminum hydride in 5 ml of anhydrous ether. The reaction mixture was refluxed for 12 h. After an usual work-up procedure, dimethylallyl-*3,3-d*$_6$ alcohol was obtained in 48% yield (250 mg): bp 55–60 °C (15 mm); ir ($CHCl_3$) 3580, 2200, 1660 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 4.60 [t, 1, $J$ = 7.0 Hz, $CH{=}C(CD_3)_2$], 5.90 (d, 2, $J$ = 7.0 Hz, $CH_2OH$), 8.00 (s, 1, OH); mass spectrum *m/e* 92 ($M^+$).

**3-(Dimethylallyloxy-*3,3-d*$_6$)-5,5-dimethyl-2-cyclohexen-1-one (8).** A solution of 80 mg of dimedone and 160 mg of dimethylallyl-*3,3-d*$_6$ alcohol in 5 ml of benzene containing of 3 mg of *p*-toluenesulfonic acid was refluxed for 7 h using a Dean-Stark water separator. After removal of the solvent, the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (1:1) as solvent to give 70 mg (57%) of 8 as a colorless oil: ir ($CHCl_3$) 2230, 2180, 1640, 1605 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 4.58 [t, 1, $J$ = 7.0 Hz, $CH{=}C(CD_3)_2$], 4.64 (s, 1, 2-H), 5.65 (d, 2, $J$ = 7.0 Hz, $OCH_2$), 7.77 (s, 2, 6-H), 7.84 (s, 2, 4-H), 8.95 [s, 6, $C(CH_3)_2$]; mass spectrum *m/e* 214 ($M^+$).

**Irradiation of 8.** A solution of 60 mg of 8 in 10 ml of cyclohexane was irradiated for 12 h. The solvent was removed and the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (3:2) as solvent to give 37 mg (62%) of 9 as a colorless oil: ir ($CHCl_3$) 2180, 2120, 1710, 1605 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.00 (t, 1, $J$ = 8.0 Hz, 8-H), 6.44 (t, 1, $J$ = 8.0 Hz, 8-H), 6.70 (ddd, 1, $J$ = 8.0, 8.0, and 6.0 Hz, 9-H), 7.35 (d, 1, $J$ = 6.0 Hz, 1-H), 7.81 (s, 2, 3-H), 8.23 (s, 2, 5-H), 9.04 [s, 6, $C(CH_3)_2$]; mass spectrum *m/e* 214 ($M^+$).

**3-(*N*,3-Dimethyl-2-butenylamino)-5,5-dimethyl-2-cyclohexen-1-one (10).** A solution of 140 mg of dimedone and 220 mg of *N*,3-dimethyl-2-butenylamine in 5 ml of benzene was heated in a sealed tube at 100 °C for 7 h. The solvent was removed and the residual liquid distilled to give 206 mg (93%) of 10 as a yellow oil: bp 160–170 °C (bath temperature) (0.08 mm); ir ($CHCl_3$) 1605, 1550 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 4.47–5.38 [m, 1, $CH{=}C(CH_3)_2$], 4.88 (s, 1, 2-H), 6.18 (bd, 2, $J$ = 7.0 Hz, $CH_2CH{=}$), 7.18 (s, 3, $NCH_3$), 7.79 (s, 2, 6-H), 7.91 (s, 2, 4-H), 8.30 and 8.36 [bs × 2, 3 × 2, $CH{=}C(CH_3)_2$], 8.97 [s, 6, $C(CH_3)_2$]; mass spectrum *m/e* 221 ($M^+$).

Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.71; H, 10.55; N, 6.10.

**4,4,7-Trimethyl-9-isopropenyl-7-azabicyclo[4.3.0]nonan-2-one (11).** A solution of 102 mg of 10 in 25 ml of cyclohexane was irradiated for 5 h. The solvent was removed and the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (3:2) as solvent to give 67 mg (66%) of 11 as a colorless oil: ir ($CHCl_3$) 3080, 1705, 1640, 895 $cm^{-1}$; NMR ($CCl_4$, 100 MHz) $\tau$ 5.30 (bs, 2, $C{=}CH_2$), 6.60–6.85 (m, 1, 9-H), 6.93 (t, 1, $J$ = 8.0 Hz, 8-H), 7.32 (td, 1, $J$ = 7.5 and 4.8 Hz, 6-H), 7.53 (dd, 1, $J$ = 7.5 and 5.0 Hz, 1-H), 7.82 (s, 3, $NCH_3$), 7.87 (s, 2, 3-H), 8.00 (t, 1, $J$ = 8.0 Hz, 8-H), 8.30 [bs, 3, $C(CH_3){=}CH_2$], 8.33 (d, 2, $J$ = 4.8 Hz, 5-H), 8.96 and 8.98 [s × 2, 3 × 2, $C(CH_3)_2$]. Spin decoupling experiments show the following results. Irradiation of 6-H at $\tau$ 7.32 caused the doublet of 5-H at $\tau$ 8.33 to collapse to a singlet, and irradiation of the multiplet of 9-H converted the doublet of doublets of 1-H at $\tau$ 7.53 to the doublet, $J$ = 7.5 Hz, and triplets of 8-H at $\tau$ 6.93 and 8.00 to doublets, $J$ = 8.0 Hz. Irradiation of 1-H converted the signal of 9-H to a broad triplet, $J$ = 8.0 Hz; mass spectrum *m/e* 221 ($M^+$).

It formed a picrate, mp 142–143 °C (from EtOH).

Anal. Calcd for $C_{20}H_{26}N_4O_8$: C, 53.33; H, 5.82; N, 12.44. Found: C, 53.76; H, 6.06; N, 12.53.

**Registry No.**—**4**, 57969-26-3; **5**, 57969-27-4; **6**, 57969-28-5; **7**, 53439-16-0; **8**, 57969-29-6; **9**, 57969-30-9; **10**, 57969-31-0; **11**, 57969-32-1; **11** picrate, 57969-33-2; dimedone, 126-81-8; 1-bromo-3-methyl-2-butene, 870-63-3; ethyl dimethylacrylate-*3,3-d*$_6$, 53439-15-9; *N*,3-dimethyl-2-butenylamine, 29151-30-2.

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(2) For a review, see W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

(3) Y. Tamura, Y. Kita, M. Shimagaki, and M. Terashima, *Chem. Pharm. Bull.*, **19**, 571 (1971).

(4) Energy transfer experiments using piperylene showed that the reaction **4** → **5** was not quenched even by high concentration. For example, when a solution of 0.1 M of piperylene and 0.01 M of **4** in ether was irradiated, product **5** was obtained at a similar rate to that of the reaction without piperylene. The result is in contrast to the case of the formation of **3** (X = NMe),[1] and suggests that this reaction involves a singlet excited state of the enone **4**.

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# Photochemical Studies on Alkyl Amides

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*Received September 17, 1975*

Although there are numerous studies reported on the photochemistry of aldehydes and ketones,[2] there have been only a few reports on the photochemistry of esters[3] and amides.[4–6] In the case of amides in particular the two major reports are contradictory.

Booth and Norrish[4] studied the photochemistry of a series of alkyl amides by examination of the gaseous products from the reaction in dioxane and hexane. They observed alkenes from the $C_4$, $C_5$, and $C_6$ amides and inferred that they were ethylene, propene, and butene. On the basis of these results they suggested that the type II process (eq 1) was the major one occurring. Chemical tests indicated that primary amines but no aldehydes or diketones were present, and, although CO was isolated in all instances, no