Tetrahedron Letters No.31, pp. 3671-3675, 1966. Pergamon Press Ltd.
Printed in Great Britain.

PHOTOCHEMISTRY OF ISOMESITYL OXIDE*

N. C. Yang and Do-Minh Thap

Department of Chemistry, University of Chicago, Chicago, Ill. 60637

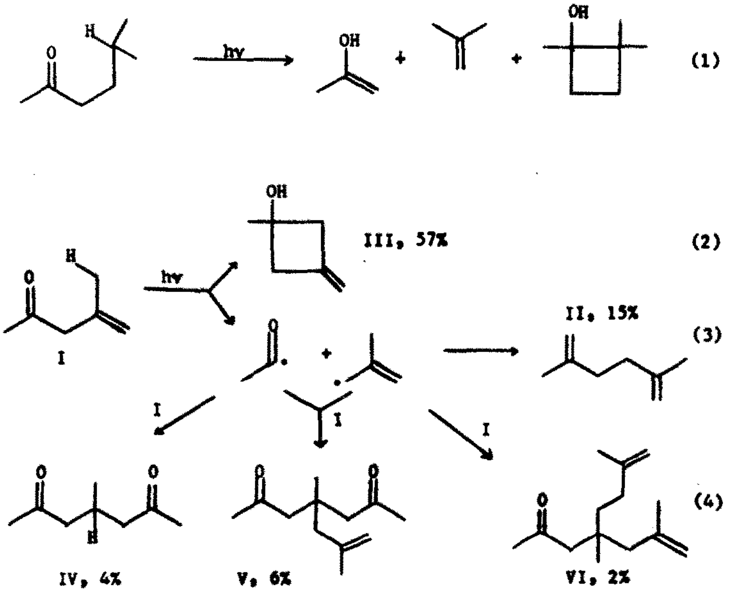
(Received 30 April 1966)

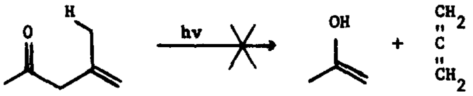
Acyclic unsaturated carbonyl compounds are usually considerably less reactive photochemically than their saturated analogs.[1,2,3] The photostability of these compounds has been at least in part attributed to the energy transfer from the excited carbonyl to the double bond which then may undergo cis-trans isomerization or deactivation to the ground state without chemical reactions. Photochemical reactions of carbonyl compounds frequently occur from the triplet state and the energy transfer from the triplet state of the carbonyl group to the double bond is energetically favorable. However, the intramolecular type II process of ketones and cyclobutanol formation (reaction 1) cannot be entirely quenched even in the presence of high concentrations of piperylene, an efficient triplet state quencher, and may proceed through the singlet excited state.[4] Since the energy transfer from the $\underline{n} \rightarrow \pi^*$ singlet excited state of the carbonyl group to the unsaturated system is unfavorable energetically, it will be interesting to investigate the photochemical reactions of non-conjugated unsaturated ketones which may undergo type II process and cyclobutanol formation.

---

*The authors wish to thank the U. S. Atomic Energy Commission for a contract, AT(11-1)-1043, to support this work. The authors also wish to acknowledge the National Science Foundation and the Louis Block Fund of the University of Chicago for their support to purchase the A-60 n.m.r. spectrometer and the MS-9 high resolution mass spectrometer used in this work.

Isomesityl oxide (I), a β,γ-unsaturated ketone with allylic γ-hydrogens, was prepared by the acid catalyzed isomerization of mesityl oxide,[5] b.p. 121.5° or 53.0°(60 mm); $\underline{n}_D^{20}$ 1.4205; $\lambda_{max}^{isooctane}$ 283mμ(ε=72); γ_{max} 1720 cm^{-1}; τ_{max}, 8.30τ(doublet, 3H), 7.95τ(singlet, 3H), 6.97τ(singlet, 2H), 5.10-5.30τ(multiplet, 2H). In contrast to the unusual stability of mesityl oxide,[6] isomesityl oxide reacts readily in light to give one major and many minor products. A solution of I in pentane (10 g in 200ml) was irradiated with a Hanovia medium pressure mercury arc (550 watts) in a quartz immersion well and the reaction was complete within 90 minutes. After the solvent was removed by evaporation under reduced pressure, the reaction mixture was fractionally distilled to give: 2,5-dimethyl-1,5-hexadiene (II, 1.5 g, 15%),[7] b.p. 116°, $\underline{n}_D^{20}$ 1.4294, 1-methyl-3-methylenecyclobutanol (III, 5.7 g, 57%), b.p. 151-2° or 60-2° (25 mm), $\underline{n}_D^{20}$ 1.4559, and a higher boiling residue. Compound III was characterized by its analysis, found C, 73.35 and H, 10.42, a phenylurethane derivative, m.p. 75°, and its physical data: γ_{max} 3380, 3080, 1680 and 890 cm^{-1}; τ_{max}, 8.52τ(singlet, 3H), 7.25τ(multiplet, 4H), 5.38τ (singlet, 1H) and 5.12τ(multiplet, 2H). The higher boiling residue from the previous distillation was distilled under reduced pressure (0.1 mm) to give a volatile fraction (1.7 g) and a non-volatile residue (0.8g). Both fractions exhibited strong carbonyl absorption in the infrared region. The volatile fraction was separated by v.p.c. on a 10 ft Carbowax column at 200°, and five components were isolated. Three of these components were tentatively identified as Compound IV, V and VI and the other two were not identified. Since all these components were isolated in relatively small amount, no microanalyses were performed, and the yields were estimated from the v.p.c. analysis. Compound IV (4%), was tentatively identified as 4-methyl-2,6-heptadione. It exhibits: mol. wt., 142.208 (mass spec., calcd. for $C_8H_{14}O_2$, 142.200); γ_{max} 1720 cm^{-1}; τ_{max}, 9.20τ(doublet, 3H), 8.45τ(multiplet, 1H), 8.05τ (singlet, 6H) and 7.75τ(broad singlet, 4H). Compound V (6%) exhibits: mol. wt., 196.294 (mass spec., calcd. for $C_{12}H_{20}O_2$, 196.292); γ_{max} 3080, 1720, 1640 and 900 cm^{-1}; τ_{max}, 9.05τ(singlet, 3H), 8.37τ(doublet, 3H), 8.06τ(singlet, 6H), 7.90τ(singlet, 2H), 7.42τ(singlet, 4H), 5.20τ and 5.40τ(two multiplets, 2H). Compound VI (2%) exhibits: mol. wt., 208.344 (mass spec., calcd. for $C_{14}H_{24}O$, 208.347); γ_{max} 3080, 1720, 1650 and 895 cm^{-1}; τ_{max}, 9.10τ(singlet, 3H), 8.25-8.40τ(multiplet, 8H), 8.05τ(singlet, 4H), 7.95τ(singlet, 2H), 5.18 and 5.48τ(two multiplets, 4H).





(5)

The ease of the reaction and comparatively high yield of cyclobutanol formed may be at least in part attributed to the reactivity of γ-allylic hydrogens. The products formed may be readily rationalized by two concurrent primary steps, the intramolecular cyclobutanol formation (reaction 2) and the α-cleavage to give an acetyl and a methallyl radical (reaction 3). The methallyl radical formed may dimerize to give 2,5-dimethyl-1,5-hexadiene (II) or it may add with the acetyl radical to isomesityl oxide to give Compounds IV, V and VI (reaction 4). Since no acetone or allene was detected in the reaction mixture, the competing type II process (reaction 5) which usually accompanies the cyclobutanol formation did not occur with isomesityl oxide. The suppression of type II process may be attributed to the fact that a β-cleavage would involve the breaking of a relatively strong sp^2 C-C bond in isomesityl oxide rather than a sp^3 bond in saturated ketones.

The quantum yield of photo-decomposition of isomesityl oxide in pentane was found to be 0.33 at 313mμ using a ferri-oxalate actinometer, which is comparable to that of saturated ketones and is much higher than the other unsaturated ketones. The quenching of this reaction with piperylene[4] was then investigated, and we found that piperylene with concentration up to 4M in pentane had no measurable effect on the quantum yield of formation of II (0.22 ± 0.02) but decreased the quantum yield of formation of III somewhat from 0.05 ± 0.005 to 0.038 ± 0.005. The results indicate that the photochemical reaction of isomesityl oxide proceeds mainly through the $\underline{n} \rightarrow \pi^*$ singlet state or an exceedingly short-life triplet state. Our experiments bear out our prediction that the energy-transfer from the excited carbonyl group to the unsaturated system in a β,γ-unsaturated ketone with allylic γ-hydrogens is relatively unimportant, and the compound will undergo photochemical reaction in appreciable quantum yield. The reaction also provides a new route for the synthesis of methylenecyclobutanols, a group of interesting compounds, which are not readily accessible from conventional chemical synthesis.

REFERENCES

1. R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1959).
2. H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 932 (1965).
3. N. C. Yang, M. Nussim and D. R. Coulson, *Tetrahedron Letters*, 1525 (1965).
4. P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1248 (1966) and references therein.
5. F. S. Stross, J. M. Monger and H. de V. Finch, *ibid.*, **69**, 1627 (1947).
6. N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).
7. A. L. Henne, H. Chanan and A. Turk reported: b.p. 114.3°, n_D^{20} 1.4293, *J. Am. Chem. Soc.*, **63**, 3473 (1941). The compound also exhibited the expected i.r. and n.m.r. spectra.