Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF TECHNOLOGY SYDNEY on 11/10/14
For personal use only.

probably aliphatic tertiary amine *N*-oxides, which are known (see ref. 2) to undergo elimination of the amine group by the action of heat and to give an olefin.

EXPERIMENTAL

The *N*-oxide was mixed with 4 molar equivalents of ferrous oxalate dihydrate and granulated lead (ca. 6 g/g of *N*-oxide), and the mixture ((*a*) in a flask arranged for distillation for *N*-oxides of liquid amines, or (*b*) in a flask fitted with a condenser for *N*-oxides of solid amines) was heated in a metal bath at 300° (bath temperature) for 30 minutes. The product isolated by distillation (in case (*a*)), or by ether extraction of the reaction mixture (in case (*b*)), was dried overnight over potassium hydroxide pellets. The identity of the products was established by comparison of their infrared spectra with those of authentic samples of the bases. The picrates of the products were prepared in the cases of pyridine-, 2-picoline-, 3-picoline-, and 2-phenylpyridine-*N*-oxides, and their identity confirmed by melting point and mixed melting point determinations. 2-Aminopyridine, as isolated from this reaction, was recrystallized from light petroleum (40–60°) and had m.p. 57–59°, which was not depressed on admixture with an authentic sample.

ACKNOWLEDGMENTS

This work was carried out during the tenure (by K. A. H. A.) of a C.I.L. Fellowship, and with the financial support of the National Research Council.

1. R. A. Abramovitch and K. A. H. Adams. Can. J. Chem. In press.
2. A. C. Cope, R. A. Pike, and C. S. Spencer. J. Am. Chem. Soc. **75**, 3212 (1953).

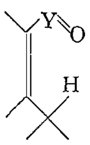
Received July 3, 1961.
Department of Chemistry,
University of Saskatchewan,
Saskatoon, Sask.

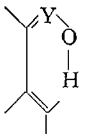
THE IRRADIATION OF β-IONONE

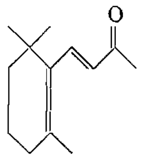
P. de Mayo, J. B. Stothers, and R. W. Yip

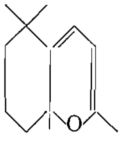
Study of the literature suggests that the irradiation of substances containing the system (I) where Y is carbon and (or) a hetero atom(s) leads to (reversible) hydrogen transfer and the formation of (II) which may then be further transformed. In those cases noted there is the possibility of $n \rightarrow \pi^*$ excitation, though this may not be a requirement. The irradiation of α,β-unsaturated ketones ((I), Y = $C\cdot CH_3$) gives, for example, the β,γ-unsaturated isomer (1). All the requirements of the *o*-nitrobenzaldehyde ((I), Y = NO) – *o*-nitrosobenzoic acid conversion and related changes are met by the postulation of an intermediate ketene formed by hydrogen transfer (2). Recently it has been shown that substituted benzophenones ((I), Y = C·Ph) are enolized by irradiation (3).

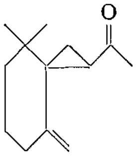
β-Ionone (III) on irradiation has been shown (4) to give (reversibly) the pyran (IV) as main product, together with a by-product which was tentatively attributed the structure (V). The alternative (VI) was considered and rejected on reasonable but negative evidence. Since β-ionone falls into the class of substance under present consideration, by vinylogous extension, (VI) seemed mechanistically much more favored. We have repeated the preparation and determined the n.m.r. spectrum (Fig. 1), which was not available at the time of the earlier work.

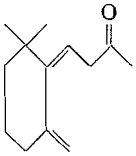

(I)


(II)


(III)


(IV)


(V)


(VI)

At 60 Mc/sec in dilute carbon tetrachloride solution, the following peaks are found (in p.p.m. from internal tetramethylsilane): 1.06 (singlet), $(\mathrm{CH_3})_2\mathrm{C}\!<$; 2.04 (singlet), $\mathrm{CH_3{-}\overset{|}{C}{=}O}$: 3.16 (doublet, $J = 7.1$ cycles/sec), $=\mathrm{CH{-}\underline{CH_2}{-}C{=}O}$; 5.33 (triplet, $J =$

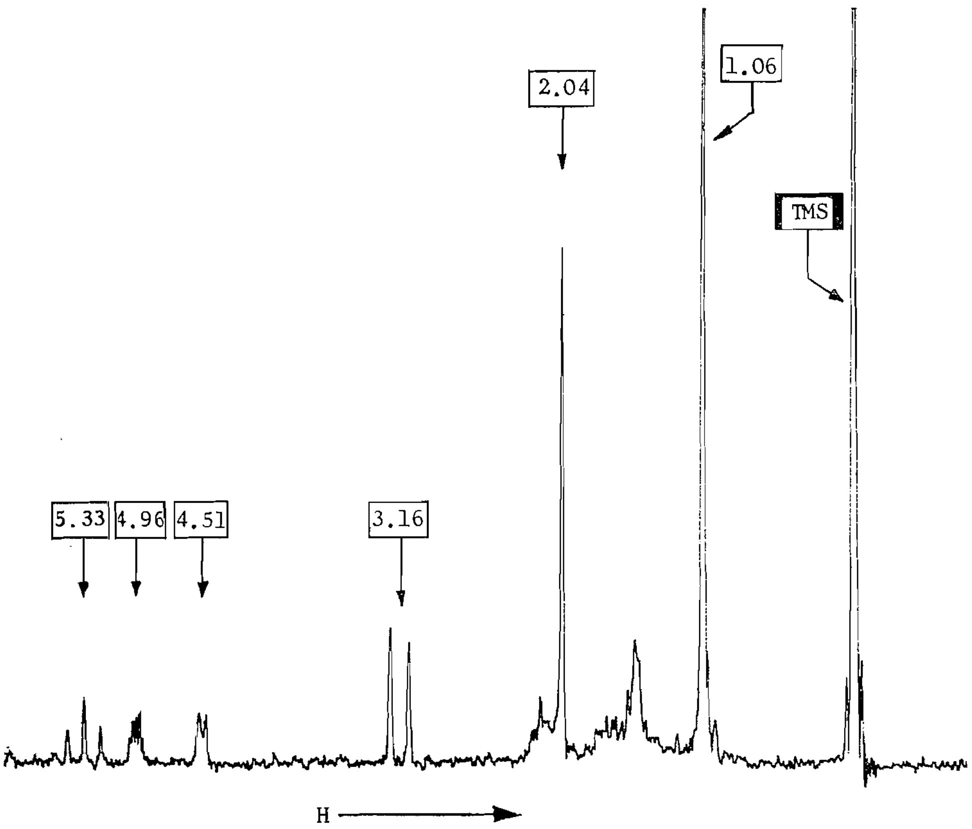


FIG. 1. 60 Mc/sec spectrum of the irradiation product (VI) of β-ionone.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF TECHNOLOGY SYDNEY on 11/10/14
For personal use only.

7.1 cycles/sec), $=\underline{CH}-CH_2-C=O$; 4.51, 4.96 (multiplets), $=CH_2$. From the splitting observed in the latter two bands, it was found that $J = 2.6$ cycles/sec for the geminal coupling, while the lower band clearly showed a long-range interaction with $J = 1.3$ cycles/sec. It is to be noted that no absorption characteristic of the cyclopropane methylene group required by (V) is observed. These results conclusively establish the correctness of (VI).

1. R. Y. Levina, V. N. Kostin, and P. A. Gembitskii. J. Gen. Chem. U.S.S.R. **29**, 2421 (1959).
2. P. de Mayo and S. T. Reid. Quart. Revs. (London). In press.
3. N. C. Yang and C. Rivas. J. Am. Chem. Soc. **83**, 2213 (1961).
4. G. Büchi and N. C. Yang. J. Am. Chem. Soc. **79**, 2318 (1957).

Received July 3, 1961.
Department of Chemistry,
University of Western Ontario,
London, Ont.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIV OF TECHNOLOGY SYDNEY on 11/10/14
For personal use only.