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HYDROCARBONS FROM PYROLYSIS OF 2,2-DIPHENYLPROPYLDIMETHYLAMINE OXIDE

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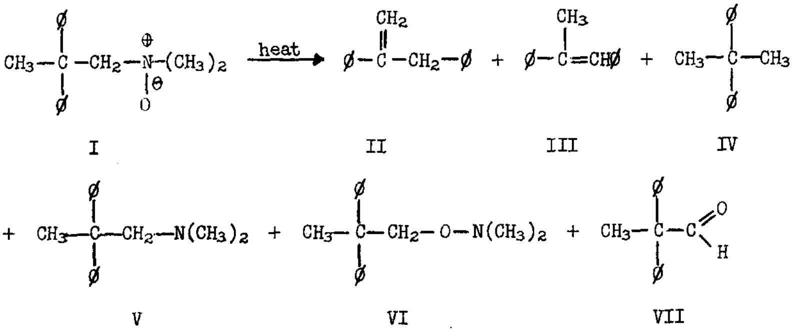
Amine oxides which have at least one hydrogen atom in the position β to the nitrogen atom readily undergo an olefin-forming elimination reaction, a valuable alternate to the Hofmann route for the preparation of olefins and for the degradation of nitrogen-containing compounds (1). Pyrolysis of amine oxides having no β-hydrogen atoms generally produces amines (by deoxygenation of the amine oxide) and substituted hydroxylamines (by migration of an alkyl group from the nitrogen to the oxygen atom) (1).

We have now observed a case where olefins and an alkane are produced from thermal decomposition of an amine oxide which has no β-hydrogen atoms. When a concentrated aqueous solution of 2,2-diphenylpropyldimethylamine oxide (I) was heated under nitrogen from 32° to 194° at 0.5 mm over a period of 90 minutes a complex mixture of products was isolated in 77% yield. The mixture, resolved by fractional distillation and gas chromatography over Carbowax, was found to consist of 2,3-diphenylpropene-1 (II), 1,2-diphenylpropene-1 (III),[*] 2,2-diphenylpropane (IV), 2,2-diphenylpropyldimethylamine (V), O-2,2-diphenylpropyl-N,N-dimethylhydroxylamine (VI), and 2,2-diphenylpropionaldehyde (VII) in the proportions shown in Table 1.



Structural assignments are based on elemental analyses and the n.m.r. data summarized in Table 1. In the case of olefins II and III, an independent synthesis using benzyl phenyl ketone and triphenyl-

$$\phi-\overset{O}{\overset{\|}{C}}-CH_2-\phi \xrightarrow[\text{reaction}]{\text{Wittig}} \text{II} \xrightarrow{\text{base}} \text{III}$$

phosphine methylene provided confirmatory evidence.

The results in Table 1 demonstrate that carbon-to-carbon as well as the established carbon-to-oxygen rearrangements can occur

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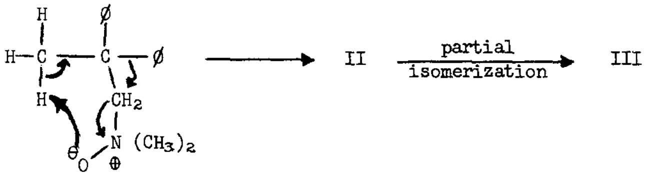
[*] Stereochemistry not determined.

during amine oxide decomposition and that the presence of β-hydrogen atoms is not an absolute requirement for olefin formation. Although a concerted pathway could account for rearranged olefins II and III such a route does not easily provide for the formation of alkane IV.



We therefore interpret the data as support for Schöllfopf's view (2) that amine oxide rearrangements proceed by a cleavage-recombination mechanism rather than in a concerted manner. A plausible reaction scheme for formation of II, III and IV involves homolysis of a C–N bond (2,3), aryl migration, and disproportionation (4).*

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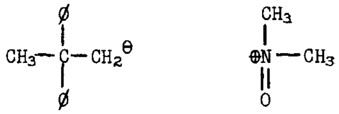
*As a referee pointed out, other pathways such as heterolysis of I to ion pair i (from which IV and possibly II and III can be derived) and α-elimination of I (which can produce III) might be considered. We shall discuss these and other possibilities in the full paper which we hope to publish shortly.



i

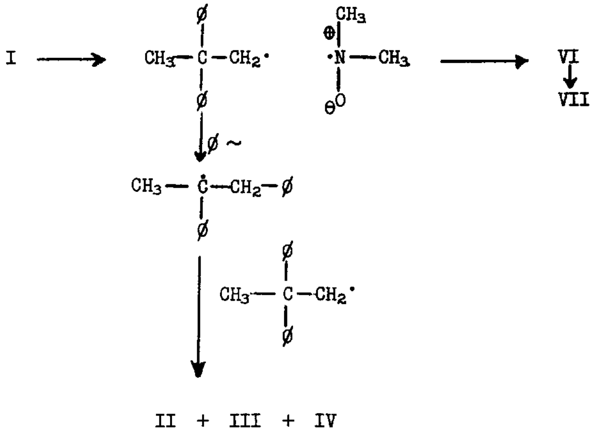

I
CH3—C—CH2·
ø
ø
CH3
⊕
·N—CH3
⊖O
VI
VII
ø ~
CH3—Ċ—CH2—ø
CH3—C—CH2·
II + III + IV

Table I

Products from 2,2-Diphenylpropyldimethylamine Oxide (I)

Compound	NMR Data*	Weight % of mixture
II	7.2 (aromatic) 4.99 (vinyl) 5.45 (vinyl) 3.80 (benzyl)	6.6
III	7.2 (aromatic) 6.80 (vinyl) 2.24 (methyl)	4.4
IV	7.2 (aromatic) 1.68 (methyl)	19.3
V	7.19 (aromatic) 2.99 (methylene) 2.00 (N-methyl) 1.72 (methyl)	21.4
VI	7.18 (aromatic) 4.13 (methylene) 2.46 (N-methyl) 1.68 (methyl)	45.1
VII**	9.90 (aldehydic) 7.2 (aromatic) 1.78 (methyl)	1.5
Unknown		1.7

* Chemical shifts are in p.p.m. downfield from internal TMS. Spectra were obtained using $CDCl_3$ solutions at probe temperature 25° with a Varian Associates HA-100 spectrometer. The type of hydrogen associated with a given signal appears in parenthesis. Ratios of peaks are consistent with the assigned structure in all cases.

**A decomposition product of VI.

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