

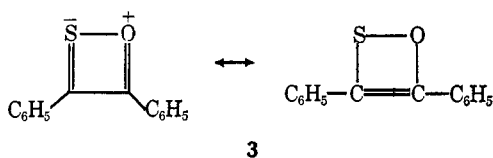
(2; 55%) and benzil (56%). This photochemical decomposition of dibenzoylstilbene episulfoxide is the first such decomposition of an episulfoxide, a relatively new class of compounds.⁴

Solutions of about 0.3 g of episulfoxide in 500 ml of benzene were irradiated with a water-cooled, internal mercury arc lamp (Hanovia Type L, 450 w) with or without a Pyrex filter. Purified nitrogen was passed through the solution and reaction vessel for at least 30 min before irradiation, and a positive pressure of nitrogen was maintained during the reaction.

Monothiobenzil was obtained as a blue oil after column chromatography on silicic acid which separated it from the benzil. Monothiobenzil forms the same 2,4-dinitrophenylhydrazone, mp 188–190° (lit.⁵ mp 189°), and dioxime, mp 238° dec (lit.⁶ mp 238° dec) as benzil. Hydrogen sulfide is evolved in the preparation of these derivatives. Ultraviolet and visible spectra in chloroform [λ 247, 325, 606 m μ ($\epsilon \sim 30$)] were similar to those of thiobenzophenone in chloroform [λ 248, 329, 598 m μ ($\epsilon^7 \sim 167$)]. Monothiobenzil exhibits in the mass spectrum a molecular ion at m/e 226 and ions at m/e 198, 178, 121, and 105 formed by the loss of CO, SO, C₆H₅CO, and C₆H₅CS radicals, respectively. The thioketone is a labile compound, and a satisfactory analysis has not been obtained.

The infrared and ultraviolet spectra, melting point and mixture melting point (95°), and 2,4-dinitrophenylhydrazone (mp 185–189°) of the benzil produced in the irradiation are identical with those of authentic benzil.

Monothiobenzil is of interest because of the possibility of interaction between sulfur as an electron acceptor and oxygen as an electron donor as indicated in 3. The interaction of two sulfur atoms on adjacent



carbon atoms in the dianion *cis*-dimercaptomaleonitrile has been considered.⁸ No definite evidence for or against interaction between sulfur and oxygen has been obtained, but the mass spectrum of monothiobenzil indicates no ion is formed by loss of sulfur alone, whereas in the mass spectrum of thiobenzophenone an important fragment corresponds to the parent ion minus sulfur.⁹

A possible mechanism for the photochemical de-

didesyl sulfide and of a dibenzyl thioketal: A. Schönberg and O. Schütz, *Ann.*, **454**, 53 (1927); A. Schönberg and Y. Iskander, *J. Chem. Soc.*, 90 (1942).

(4) In addition to dibenzoylstilbene episulfoxide, several other episulfoxides have been prepared recently and thermochemical loss of sulfur monoxide from them has been observed: G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, **88**, 2616 (1966); G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967). Thermochemical decomposition of dibenzoylstilbene episulfoxide, observed by us, gives a complex mixture of products, among which are benzil, benzoic acid, and *trans*-dibenzoylstilbene.

(5) N. R. Campbell, *Analyst*, **61**, 391 (1936).

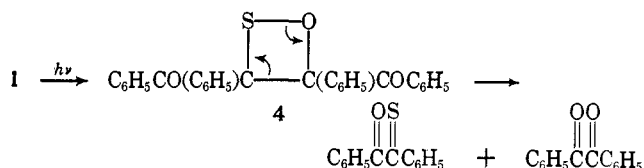
(6) G. Ponzio and L. Avogadro, *Gazz. Chim. Ital.*, **53**, 317 (1923); J. Meisenheimer and W. Lamparter, *Ber.*, **57**, 276 (1924).

(7) R. H. Abeles, R. F. Hutton, and F. H. Westheimer, *J. Am. Chem. Soc.*, **79**, 712 (1957).

(8) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *ibid.*, **84**, 4756 (1962).

(9) Determination of whether monothiobenzil has an *s-cis* or *s-trans* structure would be pertinent to the question of the importance of 3.

composition of 1 involves rearrangement to the oxathietane, 4.



Work is in progress on the mechanism of photochemical and thermochemical rearrangements of episulfoxides.

(10) National Science Foundation Undergraduate Research Scholar.

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A Novel Method for the Reduction of α,β -Unsaturated Ketones

Sir:

We wish to report a novel method for the selective reduction of only those double bonds which are conjugated with the carbonyl group as in an α,β -unsaturated ketone under the nonreducing conditions. This method involves the condensation of a ketone with benzylamine to give the corresponding Schiff base (I), which on treatment with a base (0.1–1 mole) such as potassium *t*-butoxide undergoes rearrangement to II (*cf.* the isomerization of β,γ -unsaturated ketones \rightarrow α,β -unsaturated ketone analogs). The rearrangement can be carried out with or without any solvent. Various solvents used are benzene, monoglyme, diglyme, dimethyl sulfoxide, hexamethylphosphoramide, *t*-butyl alcohol, and other protic and aprotic solvents. Hydrolysis of II with dilute acetic acid furnishes the corresponding saturated aldehyde or a ketone with the concomitant formation of benzaldehyde. Rearrangement can also be effected with an acid catalyst such as *p*-toluenesulfonic acid, but the yields are unsatisfactory in this case.

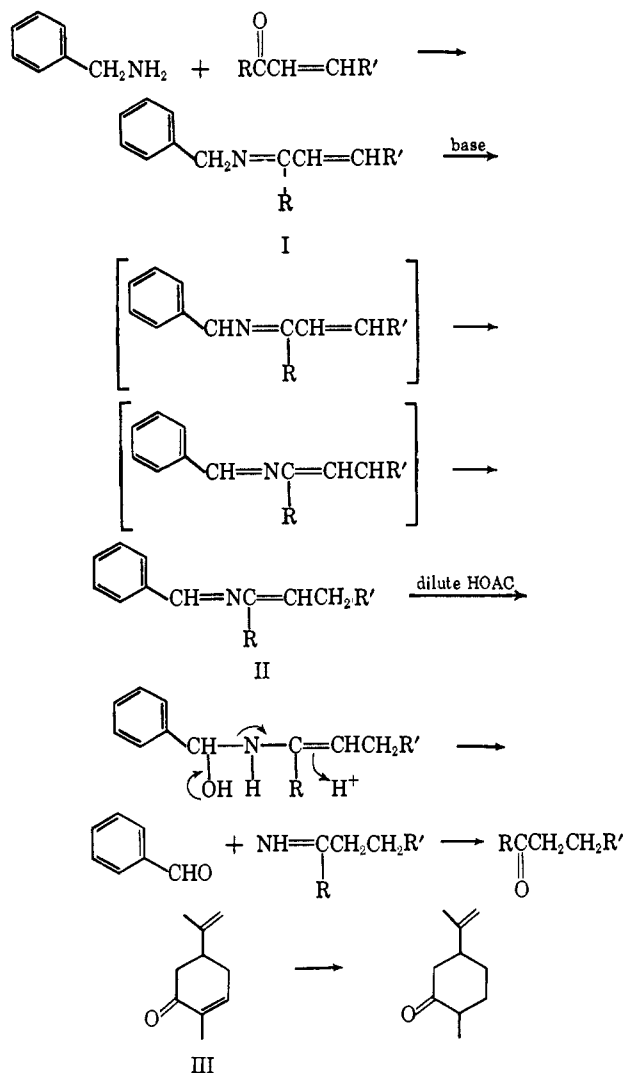
The method may be illustrated by the reduction of a typical α,β -unsaturated ketone such as *d*-carvone (III), as described below.

A mixture of 20 g (0.084 mole) of the benzylamine Schiff base of *d*-carvone (bp 113° (0.02 mm); *Anal.* Found: C, 85.67; H, 8.60) and 0.93 g (0.0084 mole) of potassium *t*-butoxide in 75 ml of anhydrous diglyme was stirred at room temperature and under nitrogen for 20 min. To the resulting solution 30 ml of 50% acetic acid was added and stirring was continued for another 20 min. After the usual work-up, the product, dihydrocarvone, bp 90–92° (15 mm) (oxime mp 88°; lit.¹ mp 88–89°) was obtained in 75% yield.

Other monocyclic ketones reduced by this method are 3-methyl- Δ^2 -cyclohexenone, 3,5-dimethyl- Δ^2 -cyclohexenone, 3,4-dimethyl- Δ^2 -cyclohexenone, 2,4-dimethyl- Δ^2 -cyclohexenone, and isophorone, the overall yields being 40–70%.

The I–II rearrangement was found to be slower for the ketones with alkyl groups at the β position than for those lacking such substitution. For instance, the

(1) J. L. Simonson, "The Terpenes," Vol. I, 2nd ed, The University Press, Cambridge, England, 1953, p 352.

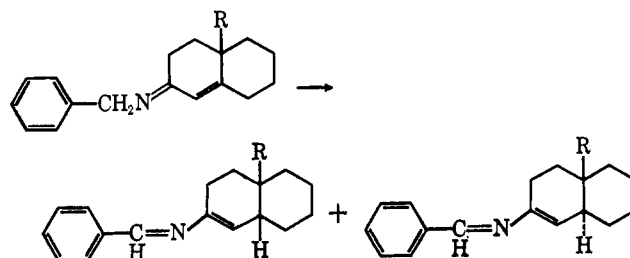


room temperature rearrangement of the Schiff base of 3,5-dimethyl- Δ^2 -cyclohexenone with 0.1 mole of potassium *t*-butoxide in hexamethylphosphoramide solution proceeded to the extent of only 56.7% in 1 hr.² On the other hand, under similar conditions the rearrangement of the Schiff bases of 2,4-dimethyl- Δ^2 -cyclohexenone and *d*-carvone was complete within 5 min. The slowness is most likely due to (a) the intermediacy of a tertiary carbanion in contrast to the secondary carbanion arising from the Schiff's bases of ketones lacking substitution at the β position, and (b) hyperconjugative and inductive effects of the alkyl groups enhancing the ground-state stability of the Schiff bases of the β -substituted ketones. The rate of the rearrangement could, however, be accelerated by increasing the amount of base and the reaction temperature. For instance, the rearrangement of the Schiff base of 3,5-dimethyl- Δ^2 -cyclohexenone with 1 equiv of KO-*t*-Bu was complete within 40 min at 100°.

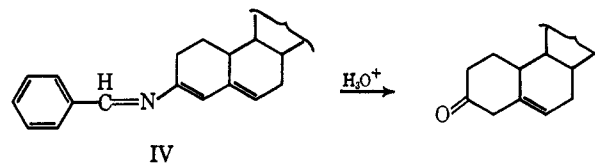
Reduction of bicyclic ketones, e.g., $\Delta^{1(9)}$ -2-octalone and 10-methyl- $\Delta^{1(9)}$ -2-octalone, when the rearrangement of their Schiff bases was stopped after 30–40% completion, led to the corresponding *trans*-decalones. These results indicate that, in this mode of reduction,

(2) The extent of the rearrangement of the Schiff base was followed by the disappearance of bands due to benzylic protons in the nmr spectrum and by the determination of saturated and unsaturated ketones in the hydrolyzed product by glpc.

the transition state for the kinetic protonation at the β -carbon atom is analogous to that involved in the metal-ammonia reduction of these ketones.³ It is, however, obvious that under equilibrating conditions the rearrangement of these Schiff bases would lead to a thermodynamic mixture of the *cis* and *trans* isomers and thus provide a direct method for the determination of the thermodynamic stabilities of various substituted Δ^1 -octalins.⁴ Further work along these lines is in progress.



Reduction of steroidal Δ^4 -3-ketones, e.g., testosterone and cholestenone, proceeded in relatively poor yields in our hands, due to the formation of side products. Pregna- $\Delta^{5,16}$ -dien-3 β -ol-20-one was reduced to pregnenolone in 40% yield. Reduction of cholest- $\Delta^{4,6}$ -dien-3-one led to a mixture of cholest- Δ^4 - and Δ^5 -en-3-ones in 50% yields.⁵



(3) G. Stork and S. D. Darling, *J. Am. Chem. Soc.*, **86**, 1761 (1964); M. J. T. Robinson, *Tetrahedron*, **21**, 2475 (1965).

(4) The Schiff base of $\Delta^{(9)}$ -2-octalone on heating with 0.1 mole of potassium *t*-butoxide at 130° for 19 hr gave a 1:4 mixture of *cis*- and *trans*-decalones.

(5) The formation of Δ^5 -3-one is due to the protonation of IV at C-4 which is analogous to the protonation of $\Delta^{3,5}$ -enolate. Also see S. K. Malhotra and H. J. Ringold, *J. Am. Chem. Soc.*, **87**, 3228 (1965), and references cited therein.

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Chlorine(III) Oxide, a New Chlorine Oxide

Sir:

There are four known stable oxides of chlorine: Cl_2O , ClO_2 , Cl_2O_6 (which dissociates to ClO_3 in the vapor), and Cl_2O_7 . These compounds have been known and characterized for a long time and they are discussed in inorganic textbooks. In the course of a study of the decomposition of chlorine dioxide¹ we have discovered a new oxide of empirical formula $\text{ClO}_{1.5}$. We believe this chlorine(III) oxide to be Cl_2O_3 , and we wish to report its synthesis and behavior in this communication.

When gaseous ClO_2 is admitted from a Pyrex storage vessel at room temperature to another Pyrex vessel at a temperature above about 50°, it explodes after an induction period. We found that the induction period

(1) E. T. McHale and G. von Elbe, to be published.