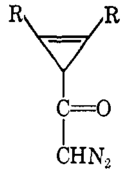
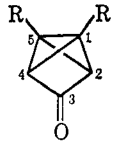
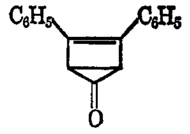


1a, R=C_6H_5
b, R=n-C_3H_7



2a, R=C_6H_5
b, R=n-C_3H_7



3

Crystals of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl p-bromobenzoate, mp 138.5–139°, are triclinic: a = 5.92, b = 8.98, c = 17.85 A, α = 89° 17′, β = 82° 46′, γ = 89° 50′, Z = 2, space group P$\bar{1}$. The structure was determined with visual Cu Kα data from three-dimensional Patterson and electron-density distributions and refined by ten cycles of block-diagonal least-squares, the final R value being 0.16 for 1228 reflections. Sections of the electron-density distribution, and a corresponding diagram of the ring system, are shown in Figure 1, and the dimensions of the tricyclopentane ring system are given in Table I.

Table I. Bond Distances (Angstroms) and Valency Angles (Degrees) in the Tricyclopentane System[a]

C(2)–C(3)	1.50	C(2)–C(3)–C(4)	81.7
C(3)–C(4)	1.54	C(3)–C(4)–C(5)	89.3
C(2)–C(5)	1.53	C(3)–C(4)–C(1)	92.2
C(1)–C(2)	1.54	C(3)–C(2)–C(5)	90.8
C(4)–C(5)	1.53	C(3)–C(2)–C(1)	92.9
C(1)–C(4)	1.52	C(4)–C(5)–C(2)	81.3
Mean	1.53	C(4)–C(1)–C(2)	81.4
		C(5)–C(4)–C(1)	56.3
C(1)–C(5)	1.44	C(5)–C(2)–C(1)	56.1
		C(4)–C(5)–C(1)	61.4
C(2)···C(4)	1.99	C(4)–C(1)–C(5)	62.3
		C(2)–C(5)–C(1)	62.3
		C(2)–C(1)–C(5)	61.6
External angles at C(1) and C(5) = 134.4–142.1 (six angles), mean 138		C(2)–C(3)–O	115.6
		C(4)–C(3)–O	109.5

[a] Standard deviations are 0.05 A and 3°.

The crystal analysis has confirmed the formulation of the compound as a derivative of tricyclo[2.1.0.0^{2,5}]pentane. The great strain in the ring system is indicated by the valency angles given in Table I, there being six C–C–C angles of about 60°, three of about 80°, and four of about 90°. The C(2)···C(4) nonbonded distance is only 1.99 A. The bond distances, however, do not appear to be greatly influenced by the strain. Six of the C–C distances are in the range 1.50–1.54 A, mean value 1.53 A (standard deviation of the mean = 0.02 A), close to the normal single bond length. The bond which is common to the two three-membered rings, C(1)–C(5), measures 1.44 ± 0.05 A, so that this bond does seem to be shortened slightly, although the difference from the other bonds (0.09 A = 1.8σ) cannot be claimed to be definitely statistically significant.

All the dimensions of the substituent groups are normal. The orientations of the two phenyl groups with respect to the tricyclopentane ring system are similar, but not quite identical, and are probably influenced by intermolecular interactions.

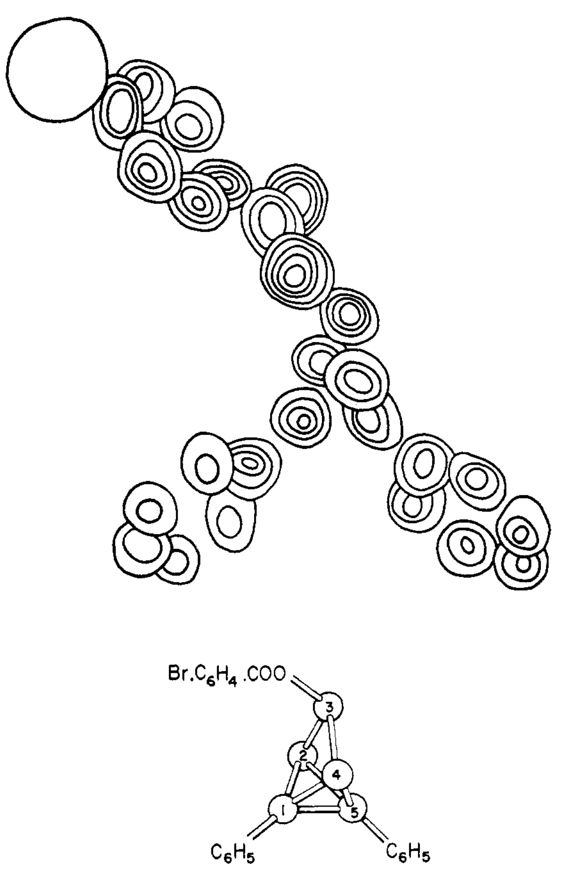


Figure 1.

The geometry of a derivative of **2** now being known, we understand better the unusual spectral behavior of this strained system. It is interesting to note that mass spectra of **2** and the corresponding hydroxy compound exhibited, in addition to their parent peaks, pronounced peaks at M − CO[4] and M − CHO, respectively. The interpretation of these peaks, of course, must await further studies.[6]

(6) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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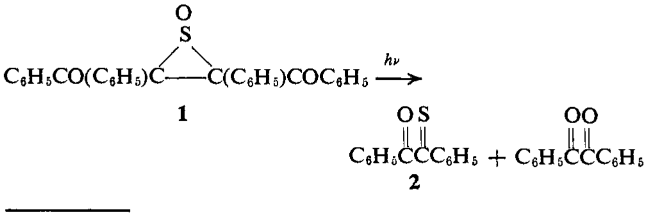
Photolysis of Dibenzoylstilbene Episulfoxide. Formation of Monothiobenzil[1]

Sir:

Irradiation of dibenzoylstilbene episulfoxide[2] (**1**) in benzene at 7–11° gives deep blue monothiobenzil[3]



$$\underset{\mathbf{1}}{C_6H_5CO(C_6H_5)C\overset{\overset{O}{S}}{\diagup\diagdown}C(C_6H_5)COC_6H_5} \xrightarrow{h\nu} \underset{\mathbf{2}}{C_6H_5\overset{O\,S}{\overset{\|\,\|}{CC}}C_6H_5} + C_6H_5\overset{O\,O}{\overset{\|\,\|}{CC}}C_6H_5$$

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(1) This work was supported in part by Grant GP-5513 of the National Science Foundation.

(2) D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965). Its stereochemistry is unknown.

(3) No previous characterization of monothiobenzil has been reported, although it has been suggested as a decomposition product of

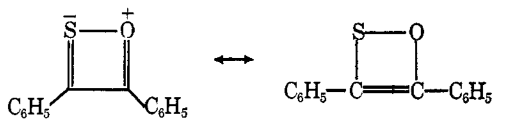
(2; 55%) and benzil (56%). This photochemical decomposition of dibenzoylstilbene episulfoxide is the first such decomposition of an episulfoxide, a relatively new class of compounds.[4]

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 mμ (ϵ $\sim$30)] were similar to those of thiobenzophenone in chloroform [λ 248, 329, 598 mμ (ϵ[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, C_6H_5CO, and C_6H_5CS radicals, respectively. The thioketone is a labile compound, and a satisfactory analysis has not been obtained.

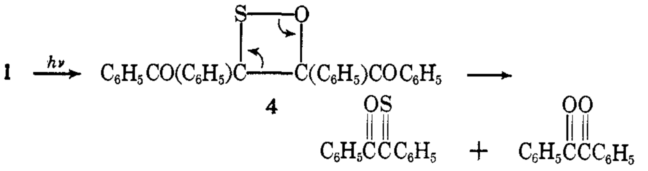
The infrared and ultraviolet spectra, melting point and mixture melting point (95°), and 2,4-dinitrophenylhydrazone (mp 185–189°) of the benzil produced in the irradiation are identical with those of authentic benzil.

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]



3

A possible mechanism for the photochemical decomposition of **1** involves rearrangement to the oxathietane, **4**.



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

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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**.

(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 → 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

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