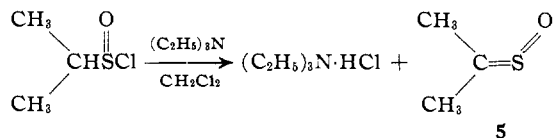


and a stoichiometric yield of triethylamine hydrochloride was separated by filtration. Concentration of the cold filtrate gave a straw-colored liquid characterized as isopropylidene sulfine (**5**, thioacetone S-oxide) by spectral analysis (chemically nonequivalent



methyl groups were noted in the n.m.r. spectrum). On warming to room temperature, this product underwent a mildly exothermic rearrangement or self-condensation. Compound **5** was trapped with chlorine to give 2-chloroisopropyl sulfinyl chloride, but efforts to isolate **5** or any rearrangement product by distillation and crystallization or by trapping with reactive olefins or dienes have not been successful.

A full account of the preparation and properties of the sulfines will be published in the near future.

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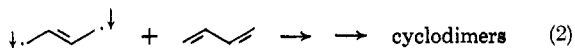
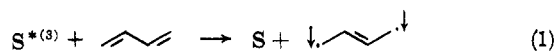
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JURGEN DIEKMANN

RECEIVED MARCH 2, 1964

Photosensitized Cyclization of Myrcene: The Problem of Addition of Dienes to Alkenes¹

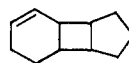
Sir:

We believe that photosensitized cycloaddition reactions of conjugated dienes involve transfer of triplet excitation from the sensitizer to the diene, followed by addition of diene triplets to a molecule of diene in its ground state.³



Unconjugated olefinic compounds might reasonably be expected to play the role of the ground-state diene molecule in eq. 2 albeit with reduced reactivity. We have attempted to carry out a number of crossed addition reactions with very limited success. No cross adducts were obtained when solutions containing cyclopentadiene or 1,3-cyclohexadiene and 2-acetonaphthone in olefins such as cyclohexene, norbornene, and 1,5-hexadiene were irradiated with light absorbed by the sensitizer. However, irradiation of a solution of a 15:1 cyclopentene-1,3-cyclohexadiene mixture containing 0.02 *M* acetone naphthone led to formation of three new compounds in addition to the photodimers of cyclohexadiene.⁴ The new compounds were formed in the ratio 4:2:1. The major component was isolated by vapor chromatography in sufficient amount to permit measurement of its n.m.r. and infrared spectra. A mixture of the major product and the second most abun-

dant material was also isolated. The spectra of the mixture were essentially identical with that of the pure material and hydrogenation of the mixture gave a single product having a v.p.c. retention time identical with that of the product from hydrogenation of the major product. The n.m.r. spectra showed poorly resolved, broad absorption between τ 7.5 and 8.7 and an unresolved signal in the vinyl proton region centered at τ 4.22. There is no significant absorption between 7.0 and 7.5, the region in which we would expect to find the allylic proton attached to the cyclobutane ring of a structure such as **1**. Consequently we believe that the compounds are the two stereoisomers of structure **2**.

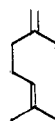


1

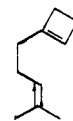


2

Although the crossed addition reaction is of some theoretical interest, it does not seem to offer great synthetic promise because of competition from dimerization of the diene even when the concentration of the latter is rather low. A much more promising situation was encountered when we attempted to effect intramolecular cycloaddition of a diene unit to an unconjugated double bond. Myrcene (**3**) seemed an appropriate material with which to attempt such experiments.



3

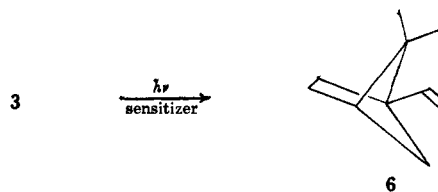


4



5

Crowley⁵ has reported that direct irradiation of myrcene gives a complex mixture in which **4** is a major product. β -Pinene (**5**) is a minor product. In contrast, irradiation of 5% solutions of myrcene in *n*-hexane or benzene containing benzophenone, β -acetone naphthone, or fluorenone leads to formation of a single new product with a quantum yield of 0.05 in the case of benzophenone. For reasons outlined below, the reaction is formulated as follows.



The photoproduct is easily isolated by preparative vapor chromatography. The structure is clearly indicated by the n.m.r. spectrum. The low-field signals have a relative area of 3.0 and fall into the ABC pattern characteristic of vinyl groups. Two strong, unsplit signals at τ 8.86 and 9.25 have relative areas of 3.1 and 2.9 (tetramethylsilane as an internal standard). The signals obviously belong to two isolated methyl groups and have chemical shifts virtually identical with those of the corresponding methyl groups in **7**⁶ (τ 8.89 and 9.30). A doublet with total relative area 1.1 is centered at 9.03 with a coupling constant of 8.0 c.p.s. This signal is

(1) Mechanisms of Photochemical Reactions in Solution. XXVII.²

(2) Part XXVI: G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Am. Chem. Soc.*, in press.

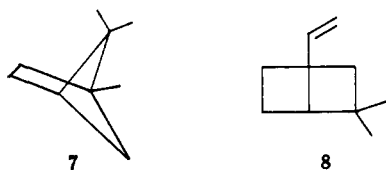
(3) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(4) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, submitted.

(5) K. J. Crowley, *Proc. Chem. Soc.*, 245, 334 (1962).

(6) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

probably the most definitive feature of the spectrum. Structures **6** and **8** are the only products of internal cycloaddition which would have intact vinyl groups. There is no precedent for the expectation that any of the single protons of **8** would absorb at very high field. On the other hand the spectra of bicyclo[2.1.1]cyclohexane⁶ and its derivatives^{6,7} have high-field signals (τ 9.13 in the parent compound and 9.11 in **8**) attributed to the *endo* protons on methylene bridges. A slightly distorted A_2B_2 group (relative area 4.0) centered at about τ 8.35 is assigned to the protons attached to the two-carbon bridge of **6** and an unresolved broad signal (relative area 2.0) centered at τ 7.96 must include the *exo*-methylene and bridgehead protons. The only surprising feature of the spectrum is the relatively high-field position of the latter signal. However, the spectrum of **7** shows a signal at τ 8.01, probably due to the proton attached to the bridgehead, and the bridgehead protons in tricyclo[3.3.0.0^{2,6}]octane occur at τ 8.18.⁸



Since myrcene is converted smoothly to 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane (**6**) in the sensitized reaction, we conclude that in the direct irradiation⁵ the excited diene system does not cross, or at best, inefficiently crosses, to the triplet manifold prior to cyclization. In view of the simplicity of the procedure and the current interest in highly strained, polycyclic systems, we suggest that this and similar sensitized cyclization reactions may have significant synthetic utility.

- (7) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).
 (8) R. Srinivasan, *ibid.*, **85**, 819 (1963).

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RECEIVED MARCH 3, 1964

Mechanisms of Esterification of 2-Benzoylbenzoic Acids¹

Sir:

From the fact that methyl 2-benzoyl-6-methylbenzoate (I) underwent alkaline hydrolysis more rapidly than methyl 2-benzoylbenzoate (II), the conclusion was drawn that the mechanism of hydrolysis of I involved mainly attack of the hydroxyl ion on the ketonic function and that the 6-methyl group provided steric assistance in the subsequent intramolecular hydrolysis.² However, it was not possible to estimate the amount of hydrolysis which took place by attack at the ketonic and ester functions in methyl 2-benzoylbenzoate (II) if, indeed, both mechanisms were competitive in this case.

On acid-catalyzed esterification with methanol, 2-benzoylbenzoic acids are converted into normal and/or pseudo-methyl esters.³ Accordingly we turned to this

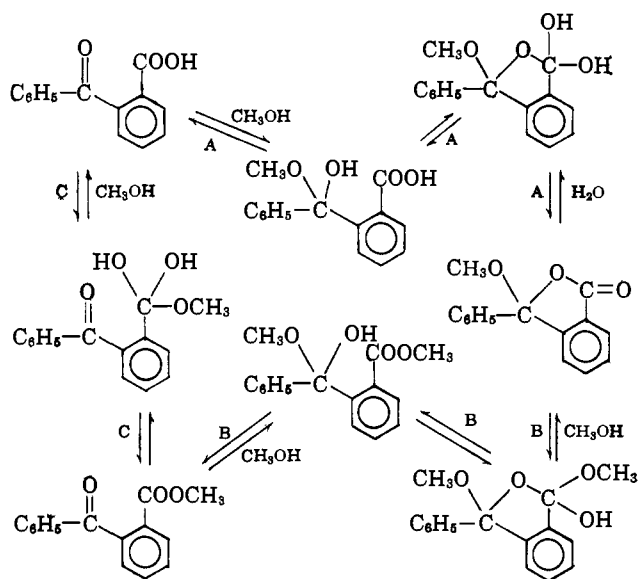
(1) This research was supported by grant GP 718 of the National Science Foundation.

(2) M. S. Newman and S. Hishida, *J. Am. Chem. Soc.*, **84**, 3582 (1962). See also M. L. Bender and M. S. Silver, *ibid.*, **84**, 4589 (1962), and F. Ramirez, B. Hansen, and N. B. Desai, *ibid.*, **84**, 4588 (1962).

(3) For references and results see M. S. Newman and C. W. Muth, *ibid.*, **73**, 4627 (1951).

reaction to find out if it proceeded by attack at the carboxy or the keto functions. We now report that 2-benzoylbenzoic acid first forms pseudo-methyl 2-benzoylbenzoate. The pseudo-ester is then rapidly converted to the normal ester under esterification conditions.

The reason 2-benzoylbenzoic acid has always been reported³ to form normal ester on esterification is that previous workers allowed the reaction to proceed long enough to ensure that equilibrium was attained. The following scheme illustrates the processes involved (no attempt is made to locate the protons involved in catalysis).



Pseudo-ester is first formed by route A. The pseudo-ester is then rapidly transformed into normal ester by route B. Some normal ester is probably formed directly *via* route C, but the following experiments show that little is so formed. When 2-benzoylbenzoic acid in methanol (0.2 *N* in hydrochloric acid) was held at 55.5° for 15 min., 13.5% was converted into ester of composition 70.5% normal–29.5% pseudo.⁴ When an exactly comparable solution of pseudo-methyl ester was held at 55.5° for 15 min., the ester obtained was 94% normal. Thus the rate of conversion of pseudo to normal ester is much greater than the rate of esterification. At equilibrium the esters are 98% normal–2% pseudo. From these results one can readily see that little normal ester is formed from 2-benzoylbenzoic acid by route C. Kinetic studies are under way to determine just how much.

Turning to 3,6-dimethyl-2-benzoylbenzoic acid, an acid which forms 85% pseudo–15% normal ester at equilibrium,³ we find another surprising result: after 15 min. the ester formed in 6.7% yield is over 80% normal. This result is explained by noting that this acid exists mainly (86%) as the hydroxylactone form³ which is esterified as shown in Scheme I.

Thus we see that 2-benzoylbenzoic acid, which is present mainly in the keto acid form³ and whose normal methyl ester is more stable, forms pseudo-ester preferentially under kinetic control, whereas 3,6-dimethyl-2-benzoylbenzoic acid, which is present mainly in the

(4) The analysis was carried out by n.m.r. The normal methyl ester had τ 6.56 and the pseudo had τ 6.84, following the lead of P. T. Lansbury and J. F. Bieron [*J. Org. Chem.*, **28**, 3564 (1963)].