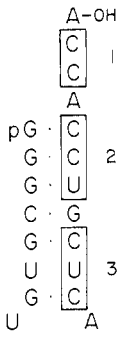

Figure 1. Aminoacyl acceptor stem of $tRNA^{Ala}_{Iab}$. Dimer targets in this area of the molecule are shown in the boxes.

$tRNA^{Ala}_{Iab}$ has 37 individual targets that can react when 254-nm light is absorbed. Although it has been possible to show that formation of a dimer in target 2 or 3 (Figure 1) is sufficient to inactivate the acceptor activity of $tRNA^{Ala}_{Iab}$, it has not been possible to isolate a dimer from either of these target regions.[10] One of the major difficulties in locating the actual photoproduct responsible for inactivation arises from the fact that dimers reverse during continued exposure to 254-nm light and photohydrates form in these areas. Thus, even though formation of a dimer is the initial inactivating event, photohydrates represent the major photoproducts at the end of the irradiation. Since we find no evidence of photohydrate formation by acetone-sensitized inactivation of $tRNA^{Ala}_{Iab}$ at 310 nm, the photochemistry should be much less complex than that produced by irradiation at 254 nm because there are only six areas that can form dimers in $tRNA^{Ala}_{Iab}$ (three of these are shown in Figure 1), and the dimers, once formed, should be stable. Therefore, it may be possible to isolate the actual photoproduct responsible for inactivation by first locating the inactivation target using the approach already developed for this purpose[10] and then isolating the photoproducts from the target oligonucleotide.

Further studies on the position of the inactivation targets, the nature of the photoproducts, and the use of acetone-sensitized photochemistry as a structure–action probe in tRNA are in progress.

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Photochemical Preparation of a Stable Oxetene

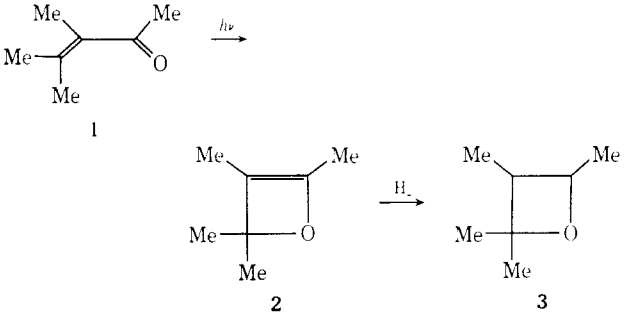
Sir:

We wish to report a significant result encountered in connection with our studies on oxabicyclobutanes. Irradiation[1] of 3,4-dimethylpent-3-en-2-one (**1**) in hexane solution through a Pyrex filter gave no observable reaction after 35 hr. Yang[2] and his coworkers have previously observed the same photochemical stability of compound **1** and other α,β-unsaturated ketones. The stability may result from the possible existence of a lowest energy $\pi-\pi^*$ triplet state[2,3] which is not prone toward hydrogen abstraction or other reactions familiar to $n-\pi^*$ triplet states.

When a 0.16 *M* solution of **1** in pentane was irradiated with Vycor-filtered ultraviolet light, however, the absorption maximum of the α,β-unsaturated ketone at 238 mμ rapidly disappeared with the simultaneous increase in end absorption at 215 mμ. The nmr spectrum of the crude product is greatly simplified if an unknown white solid is removed which precipitates when the pentane solution is cooled to −78°, followed by the evaporation of the solvent at 0°. The spectrum then shows mainly the presence of a small amount of starting material in addition to strong absorptions at δ 1.72 (narrow multiplet, $J < 1$ Hz), 1.58 (narrow multiplet, $J < 1$ Hz), and 1.38 (singlet) in a ratio 1:1:2. The low-field multiplet is partially obscured by a similar narrowly split absorption of the starting ketone at δ 1.75. The infrared spectrum shows an unresolved medium absorption centered at 1700 cm^{-1} accompanied with a shoulder at 1685 cm^{-1} attributed to the starting material.

Heating this partially purified photoproduct in carbon tetrachloride or pentane leads to a reappearance of starting material absorptions in the nmr, ir, and uv spectral regions. Silicone vpc chromatography showed only one major peak corresponding to starting material. Silica gel chromatography of the colorless product gave a red band on the column which would not elute with hexane. Our attempts at vacuum distillation gave only starting material. We estimate the product is formed in *ca.* 50% isolable yield and approximate the thermal half-life of the material in refluxing pentane to be 12 hr.

The structure of the suspected photochemically generated oxetene **2** was proved by hydrogenation over 5% palladium on calcium carbonate to give one major reduced material (vpc analysis) in *ca.* 60% yield based on vpc integration. The vpc collected product showed the following: nmr (δ, CCl_4) 4.47–4.94 (1 H, narrowly split pentet), 2.62 (1 H, pentet, $J = 6.5$ Hz), 1.38 (3 H, s), 1.18 (3 H, s), 1.17 (3 H, d, $J = 6.5$ Hz), 1.00 (3 H, d, $J = 6.5$ Hz);[4] ir (CCl_4) 958 cm^{-1}. Thus absorptions



(1) All radiations were performed with purified solvents in the usual immersion-well apparatus with a Hanovia 450-W medium-pressure lamp. In some cases, base-washed equipment was used, although to our knowledge it appears unnecessary.

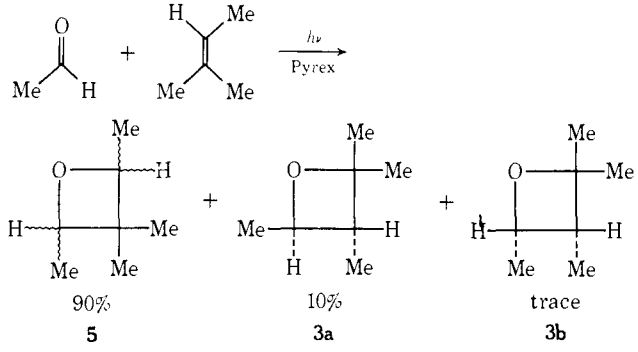
(2) N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964).

(3) S. Kuwata and K. Schaffner, *Helv. Chim. Acta*, 52, 173 (1969).

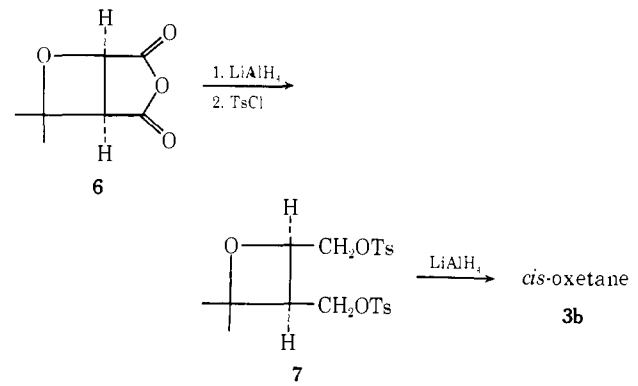
(4) Double-resonance studies at 100 MHz fully confirm these assignments.

and a carbon–hydrogen analysis[5] demand the hydrogenated photoproduct to be one of the two *cis–trans* isomers of oxetane **3**.

Attempts to synthesize oxetane **3** by base-catalyzed hydrogen chloride or bromide elimination from a diastereomeric mixture of 4-halo-2,3-dimethylpentan-2-ols were unsuccessful. Irradiation of a cooled pentane solution of acetaldehyde and 2-methylbut-2-ene, however, did give approximately a 10% yield (vpc collected) of oxetane **3**,[5] but it is evidently the other *cis–trans* isomer: nmr (δ, CCl_4) 4.19 (1 H, pentet, J = 6.5 Hz), 2.17 (1 H, multiplet), 1.30 (3 H, s), 1.27 (3 H, d, J = 6.5 Hz), 1.22 (3 H, s), 1.00 (3 H, d, J = 6.5 Hz).[4] A major easily observable ir spectral difference between the two oxetanes was the absence of a small peak at 1029 cm^{-1} for the Patterno–Büchi reaction product. The major (2 + 2) addition photoproduct (*ca.* 90% yield) appears to be a *cis–trans* mixture of oxetane **5**[5] which shows a two-proton multiplet centered at δ 4.37 in the nmr in addition to the other expected absorptions for this material. Significantly, the vpc-collected oxetane **5** which showed a symmetrical peak on several vpc columns exhibited weak-impurity nmr absorptions due to the hydrogenated photoproduct from ketone **1**. We subsequently determined that the hydrogenated photoproduct has the same vpc retention time as oxetane **5**.



Proof that the hydrogenated photoproduct has structure **3b** was finally obtained by a simple stereospecific synthesis of the *cis*-oxetane. Photochemical (2 + 2) addition of acetone to maleic anhydride gave the known adduct **6**.[6] Reduction and ditosylate formation gave **7**,[5] mp 106–107°, which was reduced in a low yield to



3b. No trace of the *trans* isomer **3a** was observed by vpc analysis. The major reduction product of **7** was shown to be 2,3-dimethylpentan-2-ol[7] which was independently synthesized by a Grignard reaction of 2-bromobutane and acetone.

To our knowledge this is the second report in which a simple unfluorinated stable oxetene product has been definitely verified by spectral data and hydrogenation to an oxetane. The first reported simple oxetene was prepared by photoisomerization of cyclooctatetraene oxide.[8]

The rapid formation of oxetene **2** is most likely facilitated by a significant cisoid population of ketone **1**.[9] This aspect plus the fact that the reaction is initiated by irradiation of the π–π^* absorption is reflected in similar features of the substituted acrylic acids studied by Chapman.[10] In the latter case nonisolable oxetene formation was postulated upon irradiation. The possibility exists, therefore, that oxetene formation may be a general photochemical reaction of α,β-unsaturated carbonyl compounds just as cyclobutene formation is a general reaction from conjugated dienes.[11] We are investigating this possibility plus the questions concerning the multiplicity of this photochemical reaction.

Acknowledgments. The authors are grateful for Research Grant GP-8878 from the National Science Foundation.

(5) A satisfactory carbon and hydrogen analysis was obtained.
(6) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967).
(7) L. Schmerling and E. Meisinger, *ibid.*, 75, 6217 (1953).
(8) J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *ibid.*, **90**, 5041 (1968). See also D. F. Bowman and F. R. Hewgill, *Chem. Commun.*, 524 (1964); D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); H. J. T. Bos and J. Boleiji, *Rec. Trav. Chim. Pays-Bas*, **88**, 465 (1969).
(9) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).
(10) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).
(11) R. Srinivasan, *ibid.*, **85**, 4045 (1963).
(12) To whom inquiries should be addressed.

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Reversal of the Anhydropenicillin Rearrangement

Sir:

Conversion of the carboxyl group of a penicillin (**1**) into an acid chloride or mixed anhydride and treatment with base result in rearrangement to an anhydropenicillin (**2**).[1] The process has been represented[1] as a reverse Michael opening of the thiazolidine ring (**3** → **4a**), followed by recyclization at the acyl carbon (**4a** → **2**). Reversal of the sequence, *i.e.*, **2** → **4b,c** → **1**, is of interest because of its synthetic and biosynthetic implications, but there are several stages at which the reaction might fail. It is necessary to hydrolyze selectively an α,β-unsaturated γ-thiolactone in the presence of a β-lactam; the resulting sulfhydryl grouping must then effect a conjugate addition to a double bond whose reactivity toward nucleophilic attack is uncertain because, if viewed as an α,β-unsaturated acid, it is activated, and, as an enamine, it is deactivated;[2] if con-

(1) S. Wolfe, J. C. Godfrey, C. T. Holdrege, and Y. G. Perron, *Can. J. Chem.*, **46**, 2549 (1968); S. Wolfe, *ibid.*, **46**, 459 (1968); S. Wolfe, U. S. Patent 3,311,638 (1967).
(2) The unusual chemical and spectroscopic properties of anhydropenicillins have been explained[1] in terms of partial enamine character of the exocyclic double bond. The attendant decreased basicity of the β-lactam nitrogen could then have the opposing effects of permitting