of phenyl *trans-β*-phenylthiolglycidate is supported by the clear example of thiol ester group migration during the rearrangement of phenyl α-methyl-*trans-β*-phenyl-thiolglycidate where substitution of a methyl group at the α carbon atom would be expected to assist phenyl migration in preference to thiol ester group migration during the rearrangement.[9,10] The biosynthesis of tropic acid in *Datura stramonium* has been extensively studied by Leete,[18] who has demonstrated carbonyl group migration in the transformation of phenylalanine to tropic acid *via* some as yet unknown intermediate.

We are presently investigating other synthetic methods for the preparation of thiolglycidic esters and exploring their chemistry and biogenetic significance.

James Wemple

Department of Chemistry, University of Detroit
*Detroit, Michigan 48221*
Received June 22, 1970

Synthesis and Reactions of 5,6-Dimethylenebicyclo[2.2.0]hexene-2. "Dewar *o*-Xylylene"

Sir:

o-Xylylene has never been isolated nor even characterized except by Diels–Alder trapping experiments.[1–5] We wish to report that its "Dewar" analog, the highly strained molecule **4**, is not nearly so elusive, as the success of the synthesis formulated in Scheme I demonstrates.

Scheme I
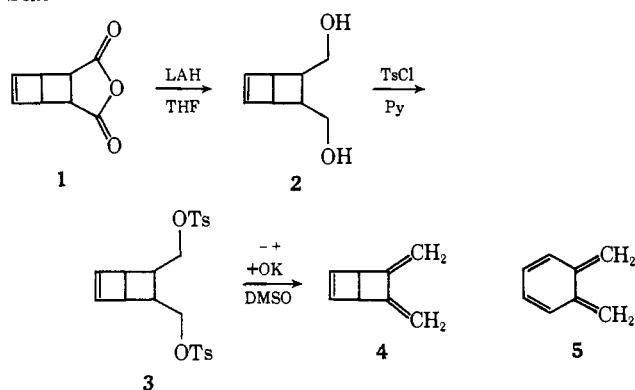
Anhydride **1**[6,7] was first converted to the diol **2** by LAH–THF reduction (inverse addition, 1.5-hr reflux). In our hands, better yields were obtained when the crude anhydride photolysate[6,7] was reduced

(1) L. A. Errede, *J. Amer. Chem. Soc.*, **83**, 949 (1961).
(2) M. P. Cava and A. A. Deana, *ibid.*, **81**, 4266 (1959).
(3) D. A. Ben-Efrain and F. Sonaheimer, *Tetrahedron Lett.*, 313 (1963).
(4) K. Sisido, K. Tani, and H. Nozaki, *Tetrahedron*, **19**, 1323 (1963).
(5) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.*, 15 (1962).
(6) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).
(7) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

directly and the diol partially purified by distillation or column chromatography: bp 90–105° (5 × 10⁻³ Torr); 20–27% composite yield of *ca.* 90% pure diol in the photolysis and reduction steps; nmr (CDCl₃) τ 3.66 (t, 2 H, *J* = 1 Hz), 5.36 (s, 2 H), 6.1–6.5 (m, 2 H), 7.20 (m, 2 H), 7.5–7.8 (m, 2 H). Several attempts to convert **2** to a dibromide (PBr₃) failed, but tosyl chloride–pyridine (0°, overnight) gave ditosylate **3**: mp 146–147° (MeOH); 18–34%; nmr (CDCl₃) τ 2.1–2.8 (q, *J* = 8.5), 3.73 (t, 2 H, *J* = 1 Hz), 5.8–6.0 (m, 4 H), 7.03 (m, 2 H), 7.56 (s, 8 H). Elimination by *tert*-butoxide–DMSO (ambient, 10⁻⁶ Torr) gave **4** isolated from the −78° trap: 40%, nmr (CCl₂=CCl₂, HA-100) τ 3.83 (t, 2 H, *J* = 1.0 Hz), 4.88 (d, 2 H, *J* = 1.0 Hz), 5.24 (s, 2 H), 6.27 (s, 2 H) (*J*₁₃C-H = 156 (bridgehead) and 169 (cyclobutene) Hz; uv (EtOH) λmax 234 mμ (sh), 242 (ε 6100), 253 (sh); mass spectrum *m/e* 104, 103 (P, P − 1); ir (vapor) ν 3050, 3000, 1770, 1650, 883, 800, 730, 670 cm⁻¹.

Note that the uv spectrum of **4** is virtually identical with that of 1,2-dimethylenecyclobutane[8] (**6**, λmax 237, 246, 255 mμ) suggesting no interaction between the ene and diene moieties, even in the excited state of **4**. The ¹³C–H splittings are also in conformity with the structure assigned to **4**.

In sharp contrast to its fully conjugated counterpart (**5**), **4** is thermally stable at room temperature (evacuated sealed tube), although the decomposition rate is perceptible at 60°. As is the case with Dewar benzene,[6] the thermal disrotatory ring opening of **4** is symmetry forbidden, and it is, no doubt, at least partly to this circumstance that **4** owes its modicum of stability. However, because of the high exothermicity of the transformation **4** → **5**, one might suspect that it will nevertheless manage to transpire and, under mild conditions, furnish **5** in either its ground or, more interestingly, one of its excited states. Pertinent studies are underway.

Scheme II summarizes our results in reactions of **4** with dienophiles. The hyperreactive dienophile 2-phenyl-2,4,5-triazoline-1,3-dione converts **4** to a

Scheme II
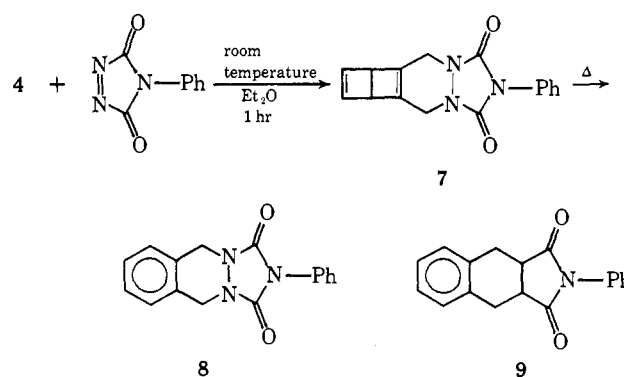
Dewar benzene adduct (**7**), thus providing a new approach to this class of molecules. The crude **7** is nearly pure, but does contain a small amount of the benzenoid isomer (**8**). Brief warming of **7** in methanol, followed by recrystallization or column chromatography, yields pure **8**: **7** has nmr (CDCl₃) τ 2.4–2.8 (m, 5 H), 3.40 (s, 2 H), 5.8 (m, 4 H), 5.96 (s, 2 H); **8** has mp

(8) A. T. Blomquist and J. A. Verdol, *J. Amer. Chem. Soc.*, **77**, 1809, (1955).

185–187° (MeOH); nmr (CDCl₃) τ 2.35–2.65 (m, 5 H), 2.7 (broad, 4 H), 5.2 (s, 4 H); mass spectrum m/e 279 (P); ir (CHCl₃) ν 1770, 1720, 910, 705, 650 cm⁻¹. The reaction with N-phenylmaleimide necessitates heating (DME, 80°, 15 min) and so leads directly to the ring-opened adduct **9**: nmr (CDCl₃) τ 2.6–2.85 (m, 9 H), 6.5–7.1 (m, 6 H).

In addition to its novel structure and potential as a source for *o*-xylylene, **4** was of interest because of the possibility that its anion radical would rearrange to **5·⁻**, a reaction which should be even more exothermic than the **4 → 5** transformation. Under conditions which readily afforded esr spectra of the anion radicals of **6** and other 1,2-diexocyclic dienes[9] (*intra muros* electrolysis in THF at −90° with *n*-Bu₄N⁺ClO₄⁻ electrolyte), **4** produced no esr signal at all. Since the conditions are sufficient for reduction (and current does flow) and since diene anion radicals are usually stable under these conditions, it may be that **4·⁻** does indeed rearrange to **5·⁻** which is unable to survive long enough to be detected. Alkali metal reductions also failed to yield esr signals. That Birch reduction (Scheme III)

Scheme III
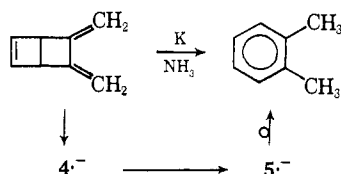
gives *o*-xylene but no 2,3-dimethyl Dewar benzene would also be in accord with the hypothetical rearrangement of **4·⁻**.

(9) N. L. Bauld, F. Farr, and G. R. Stevenson, *Tetrahedron Lett.,* 9, 625 (1970).
* Address correspondence to this author.

Frank R. Farr, Nathan L. Bauld*
*Department of Chemistry, The University of Texas
Austin, Texas 78712*
Received July 21, 1970

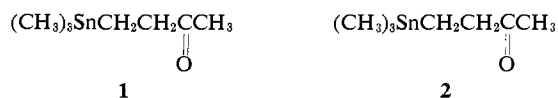## Intramolecular Energy Transfer in the Photochemistry of Keto Organotins

Sir:

Our knowledge of the photochemistry of aliphatic ketones has increased greatly as a result of recent elegant investigations, and we are thus provided much insight into the behavior of photoexcited 2-alkanones with γ hydrogens.[1] Chemical consequences of photoexcitation may be cleavage of one of the carbon–carbon bonds at the carbonyl group (type I cleavage) or abstraction of a γ hydrogen by the carbonyl oxygen, followed by fragmentation to olefin and enol (type II process) or cyclobutanol formation.[2] In each case the atoms of the carbonyl group participate in the reaction. We have been interested in the question of whether the excitation

energy can be transferred from the carbonyl group to another site in the molecule at which reaction might occur.[3] A promising reactive site would have one or more bonds weaker than the C–C or C–H bonds. Our first efforts involved the photochemistry of some keto organosilanes.[4] None of the compounds investigated (in which the carbonyl carbon and the silicon were separated by more than one carbon) showed special reactions which could be attributed to the presence of the silicon atom. We now report extension of these studies to keto organotins in which we do, in fact, find photoinduced reactions profoundly different from those of the ketosilanes and simple *n*-alkanones.

3-Oxobutyltrimethyltin (**1**) was prepared by treating the adduct of trimethyltin hydride with acrylonitrile (2-cyanoethyltrimethyltin) with methylmagnesium bromide. 4-Oxopentyltrimethyltin (**2**) was prepared similarly by treating the adduct of trimethyltin hydride with allyl cyanide (2-cyanopropyltrimethyltin) with methylmagnesium bromide.[5] Carbonyl absorptions of **1** were at 1710 cm⁻¹ and 280 nm (ϵ 26) and those of **2**

$$(CH_3)_3SnCH_2CH_2\underset{\substack{\|\\O}}{C}CH_3 \qquad (CH_3)_3SnCH_2CH_2\underset{\substack{\|\\O}}{C}CH_3$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

were at 1710 cm⁻¹ and 280 nm (ϵ 35), indicating no significant perturbations due to the presence of the trimethyltin group.

Cyclohexane solutions of **1** in quartz vessels were degassed and irradiated with a medium-pressure lamp. A gas identified as methane by its infrared spectrum was evolved. The reaction solution contained no volatile products. When the solvent was removed, a viscous polymeric product remained which reacted rapidly with iodine. Subsequent addition of sodium hydroxide caused precipitation of dimethyltin oxide, which also precipitated when the reaction product mixture was treated directly with hydrogen peroxide. These observations indicate the presence of dimethyltin as a reaction product. Yields of methane ranged from 0.54 to 0.69 mol/mol of ketone reacted and yields of dimethyltin oxide collected ranged from 0.38 to 0.64 mol/mol of ketone. Results obtained with **2** under similar conditions yielded 0.39–0.41 mol of methane and 0.21–0.23 mol of dimethyltin oxide/mol of ketone reacted. When the nitriles from which the ketones were prepared were irradiated under similar conditions no methane was evolved and only a trace of precipitate which might be dimethyltin oxide was formed upon treatment of the photolysis product mixture with hydrogen peroxide. Neither methane nor dimethyltin was formed when tetramethyltin was irradiated with 2-butanone, benzaldehyde, acetophenone, or benzophenone in cyclohexane, nor when trimethyl-3-cyanopropyltin was irradiated with 2-butanone in the same solvent. Thus a substantial fraction of the tin atoms in each keto organotin suffers cleavage of two carbon–tin bonds, and

(1) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.,* 91, 7551 (1969).
(2) P. J. Wagner and G. S. Hammond, *Advan. Photochem.,* 5, 21 (1968).

(3) For other recent approaches to the problem of intramolecular transfer see: (a) H. Morrison, *J. Amer. Chem. Soc.,* 87, 932 (1965); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.,* 87, 2322 (1965); P. A. Leermakers, J. Montillier, and R. D. Rauh, *Mol. Photochem.,* 1, 57 (1969); D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.,* 92, 2153 (1970).
(4) H. G. Kuivila and P. L. Maxfield, *J. Organometal. Chem.,* 10, 41 (1967).
(5) All compounds had satisfactory elemental analyses, and nmr and infrared spectra were consistent with the assigned structures.