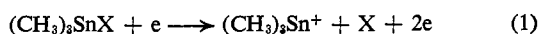


Table I. Appearance Potentials of the $(\text{CH}_3)_3\text{Sn}^+$ Ion from Some $(\text{CH}_3)_3\text{SnX}$ Compounds

X	A.P., e.v.	ΔH_f° , kcal. mole ⁻¹	
		$(\text{CH}_3)_3\text{SnX}$	$(\text{CH}_3)_3\text{Sn}^+$
CH_3	9.72 ± 0.06	-4.6^a	186 ± 2
C_2H_5	9.47 ± 0.15	-7.1^a	186 ± 4
$n\text{-C}_3\text{H}_7$	9.50 ± 0.12	-11.6^b	187 ± 4
$\text{Sn}(\text{CH}_3)_3$	9.84 ± 0.09	-5.4^a	35 ± 4^c

^a Reference 7. ^b Calculated by the method described in ref. 7. ^c ΔH_f° of the $(\text{CH}_3)_3\text{Sn}$ radical.

of the trimethylstannium from $(\text{CH}_3)_4\text{Sn}^{120}$ with that of Hobrock and Kiser⁹ from $(\text{CH}_3)_4\text{Sn}^{116}$ (9.9 ± 0.15), and the similarity of the relative intensities of the isotopic $(\text{CH}_3)_3\text{Sn}^+$ species from all the molecular sources with the isotopic abundances of the tin isotopes, leads us to conclude that interference from carbon-hydrogen bond rupture is not significant. This would be especially true near the low threshold values observed. The heats of formation of the trimethylstannium ion were calculated from the appearance potentials and the assumption that we are observing the simple dissociation process (eq. 1) involving no excess



energy. The agreement of the ionic heats of formation from the three molecular sources supports this assumption and attests to the precision of the data. Combining the heat of formation of the trimethylstannium ion with the appearance potential from hexamethyldistannane, and again assuming no excess energy, leads to the value shown in Table I for the heat of formation of the trimethylstannyl radical. These data can then be combined to give a value of 6.54 e.v. for the ionization potential of the trimethylstannyl radical.

Taking the heat of formation of $(\text{CH}_3)_3\text{Sn}$ from Table I and the molecular heats of formation of trimethylstannane derivatives from Davies, Pope, and Skinner,⁷ we arrive at the bond dissociation energies shown in Table II. In computing these dissociation energies we have used the following radical heats of formation: $\Delta H_f^\circ(\text{CH}_3) = 33 \pm 1$,^{10,11} $\Delta H_f^\circ(\text{C}_2\text{H}_5) = 25.5 \pm 2$,^{10,11} $\Delta H_f^\circ(\text{C}_3\text{H}_7) = 20.5 \pm 2$,¹² $\Delta H_f^\circ(\text{C}_6\text{H}_5) = 72 \pm 2$,¹³ $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 42 \pm 3$,¹⁴ $\Delta H_f^\circ(\text{C}_2\text{H}_3) = 65 \pm 3$.¹⁵ The bond dissociation energies are compared in Table II to the average bond energy values derived from the molecular heats of formation and heats of atomization. It is obvious that the average bond energies reflect very poorly the actual bond dissociation energies in the trimethylstannane derivatives and therefore very little reliance should be placed on the average bond energies in reaction mechanism considerations. However, the rather remarkably constant difference of 20–21 kcal. mole⁻¹ between *D* and *E* as shown in the last column of Table II provides a means of correcting average bond energies. If *D* – *E* be viewed as an energy of “reorganization” of the $(\text{CH}_3)_3\text{Sn}^\cdot$ radi-

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cal, which occurs on rupture of the $(\text{CH}_3)_3\text{Sn-X}$ bond,¹⁶ then on rupture of the $(\text{CH}_3)_3\text{Sn-Sn}(\text{CH}_3)_3$ bond this “reorganization” must occur twice. This will, of course, lead to a doubling of *D* – *E* as is borne out in the last column of Table II.

Table II. Bond Dissociation Energies in Some Trimethylstannane Derivatives

Bond	<i>D</i> , kcal. mole ⁻¹	\bar{E} , ^a kcal. mole ⁻¹	<i>D</i> – \bar{E} , kcal. mole ⁻¹
$(\text{CH}_3)_3\text{Sn-CH}_3$	73 ± 4	52	21
$(\text{CH}_3)_3\text{Sn-C}_2\text{H}_5$	68 ± 4	48	20
$(\text{CH}_3)_3\text{Sn-}n\text{-C}_3\text{H}_7$	68 ± 6	48	20
$(\text{CH}_3)_3\text{Sn-Br}$	94 ± 4	74	20
$(\text{CH}_3)_3\text{Sn-I}$	80 ± 4	59	21
$(\text{CH}_3)_3\text{Sn-C}_6\text{H}_5$	81 ± 5	61	20
$(\text{CH}_3)_3\text{Sn-CH}_2\text{C}_6\text{H}_5$	57 ± 5	36	21
$(\text{CH}_3)_3\text{Sn-C}_2\text{H}_3$	78 ± 5	57	21
$(\text{CH}_3)_3\text{Sn-Sn}(\text{CH}_3)_3$	76 ± 6	35	41

^a Reference 1.

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(16) We are grateful to Dr. H. A. Skinner for this interpretation.

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Photochemical Transformations of a β,γ -Epoxy Ketone¹

Sir:

The light-induced α,β -epoxy ketone rearrangement to the corresponding 1,3-diketone was studied as early as 1918² and has been re-explored extensively in recent years.³ The photoisomerization has been described by two consecutive steps: a cleavage of the $\text{C}_\alpha\text{-O}$ bond of the oxide ring followed by a 1,2-shift of the β -hydrogen to the α position.^{3b} The driving force for the fission of the epoxide ring was attributed to the tendency of the excited $n\text{-}\pi^*$ state to eliminate α substituents as odd electron or anionic species according to the reaction medium.^{3b} In contrast to the exhaustive studies concerned with the photochemistry of α,β -epoxy ketones there has been no attempt, to date, to examine the phototransformations of the related β,γ -acyl oxide system. We now wish to demonstrate that, although a formally analogous rearrangement occurs,

(1) Photochemical Transformations of Small Ring Carbonyl Compounds, part V. For Part IV, see A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **87**, 1821 (1965).

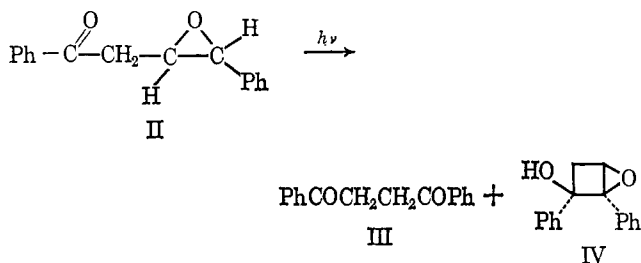
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the mechanism of the transformation is markedly different.

trans-1,4-Diphenyl-3-buten-1-one (I) was prepared by refluxing a benzene solution of *trans*-1,4-diphenyl-2-butene-1,4-diol⁴ with *p*-toluenesulfonic acid, m.p. 92–93^o; λ_{\max} (KBr) 5.98 and 10.31 μ ; $\lambda\lambda_{\max}$ (95% ethanol) 249, 277, and 287 $m\mu$ (ϵ 28,600, 4100, and 2300); n.m.r. τ 6.12, 3.42, 2.51, 1.89, ratio 1:1:4:1. *Anal.* Calcd. for C₁₆H₁₄O: C, 86.45; H, 6.35. Found: C, 86.41; H, 6.30. Treatment of I with *m*-chloroperbenzoic acid afforded, in essentially quantitative yield, *trans*-1,4-diphenyl-3,4-epoxy-butan-1-one (II), m.p. 112–113^o, λ_{\max} (KBr) 5.93 and 11.25 μ ; $\lambda\lambda_{\max}$ (95% ethanol) 243 and 277 $m\mu$ (ϵ 14,000 and 1000); n.m.r. τ 6.62, 6.26, 2.62, 2.01, ratio 3:1:8:2. *Anal.* Calcd. for C₁₆H₁₄O₂: C, 80.64; H, 5.89. Found: C, 80.66; H, 5.92.

The irradiation of II was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w.) with a Pyrex filter to eliminate wave lengths below 280 $m\mu$. The photolysis was followed by withdrawal of small samples at fixed intervals and examination of these by thin-layer chromatography. Upon irradiation of 500 mg. of II in benzene for 8 hr., the spot on a thin-layer plate due to II had completely disappeared and three new spots had appeared in its place. Chromatography of the crude photolysis mixture on Woelm basic alumina (Activity II) afforded 2,5-diphenylfuran (27%) and dibenzoyl-ethane (III, 30%) as the only isolable products. The formation of 2,5-diphenylfuran was shown, by control experiments, to be the result of a ground-state acid-catalyzed rearrangement of II.⁶ By using scanning liquid-liquid partition chromatography⁷ the crude photolysis mixture could be resolved into two major components. In addition to dibenzoyl-ethane (III, 18%), an alcohol, m.p. 142–143^o (23%), was obtained whose structure is assigned as IV on the basis of chemical and physical data cited.



The elemental analysis of this component (*Anal.* Calcd. for C₁₆H₁₄O₂: C, 80.64; H, 5.92. Found: C, 80.47; H, 5.90) indicates that it is an isomer of II. The molecular weight (calcd. 238, found 226) is consistent with a monomeric unit. The high-dilution infrared spectrum (CHCl₃) of IV shows a sharp strong intramolecular hydrogen bond (3559 cm.⁻¹); the infrared band corresponding to a non-bonded hydroxyl stretching frequency was absent. Increasing the concentration by factors up to fifty causes little change in the peak shape or position.⁸

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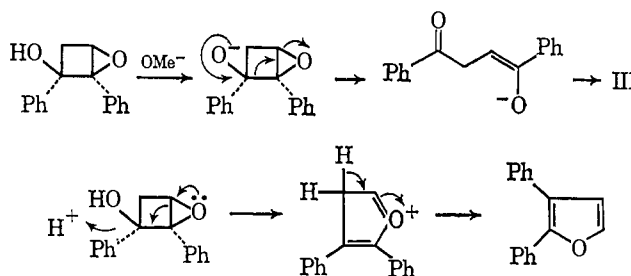
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The fact that absorption due to this bond is strong and is invariant with concentration suggests that the hydroxyl group of IV is *cis* to the oxide ring. The ultraviolet spectrum (95% ethanol) with maxima at 260 and 265 $m\mu$ (ϵ 525 and 440) is characteristic of two isolated benzene rings. The n.m.r. in deuteriochloroform shows the methylene hydrogens as a pair of doublets at τ 7.87 and 7.32 ($J = 13$ c.p.s.), the hydroxyl proton as a singlet at τ 6.51, the tertiary hydrogen as a broad singlet at τ 5.40, and the aromatic hydrogens as a multiplet centered at τ 2.69. The peak areas are in the ratio of 1:1:1:10.

We found that IV is converted rapidly to dibenzoyl-ethane by chromatography on Woelm base-washed alumina but can be recovered unchanged from liquid-liquid partition chromatography. Further evidence for the cyclobutanol oxide structure was provided by the observation that IV was quantitatively converted with base to dibenzoyl-ethane, whereas treatment with acid gave 2,3-diphenylfuran⁹ as the major product. A reasonable mechanism for these transformations is presented below.



The possibility that IV may be an intermediate in the formation of III was eliminated by the finding that IV can be recovered unchanged when subjected to the same photolytic conditions that were used for II. The formation of IV may be considered to be analogous to the formation of cyclobutanols from the irradiation of aliphatic ketones containing γ -hydrogens.¹⁰ Two mechanisms have been considered to account for the photochemical formation of cyclobutanols, one a concerted mechanism¹¹ and the other a stepwise process.¹² On the basis of the previously existing experimental data, these two mechanisms have not yet been differentiated. The isolation of both III and IV in the present investigation, however, adds strong support for Yang's stepwise mechanism.¹³

The multiplicity of the state involved in the abstraction step has not been established. Experiments designed to demonstrate that each of the products arises from the diradical formed from the $n-\pi^*$ triplet are in progress.

(8) The infrared spectrum of related model systems, in which the tertiary hydroxyl group has a similar steric environment, revealed the presence of extensive polymeric association.

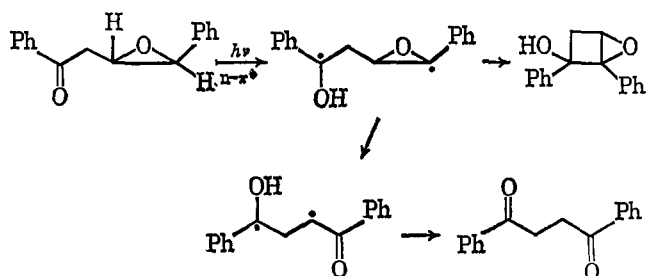
(9) A. Padwa, *Tetrahedron Letters*, No. 16, 1049 (1965).

(10) O. L. Chapman, *Advan. Photochem.*, **1**, 371 (1963).

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(13) An alternate mechanism which is based on intramolecular energy transfer from the excited carbonyl chromophore to the epoxide ring followed by hydrogen migration is not favored, primarily because intermolecular energy transfer of propiophenone or benzophenone to styrene oxide does not produce acetophenone.



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Radical Skeletal Rearrangement of Butylbenzenes over Chromia-Alumina Catalyst¹

Sir:

The catalytic skeletal isomerization of butylbenzenes via a cationic mechanism is well established in the literature.²⁻⁴ We wish now to report skeletal rearrangement of butylbenzenes catalyzed by a nonacidic chromia-alumina-B which is of a radical type. This will become evident from the reactions of *t*-butylbenzene and from 2-phenyl-2-¹⁴C-butane.

The catalyst was prepared from an alumina, obtained from potassium aluminate,⁵ which was impregnated with chromic acid according to the method described previously.⁶ It was shown that this catalyst does not contain acidic sites which can cause skeletal isomerization of hydrocarbons via a cationic mechanism.⁶

***t*-Butylbenzene.** This hydrocarbon underwent rearrangement when passed over chromia-alumina-B at 481° and an hourly liquid space velocity of 0.77. The extent of reaction was 11.3% and the product consisted of 30.5% isobutylbenzene (1), 49.4% β,β-dimethylstyrene (2), and 20.1% isobutenylbenzene (3). The reaction was highly selective, as less than 0.1% of secondary products was obtained. The fact that benzene and isobutylene were not produced is an indication that the chromia-alumina-B did not contain catalytic acidic sites.

The course of the reaction can be explained as shown in Scheme I. The chromium-carbon bond ruptures, under the influence of temperature, to generate a radical which can then rearrange. Radical rearrangement of *t*-butylbenzene in solution was reported by one of us previously.⁷ The mechanism of the removal of a hydrogen atom in an alkane system was proposed by Burwell and co-workers.⁸ No rearrangement of *t*-butylbenzene was detected over alumina as such under similar conditions.

(1) This work was supported by the Atomic Energy Commission, Contract AT(11-1)-1096.

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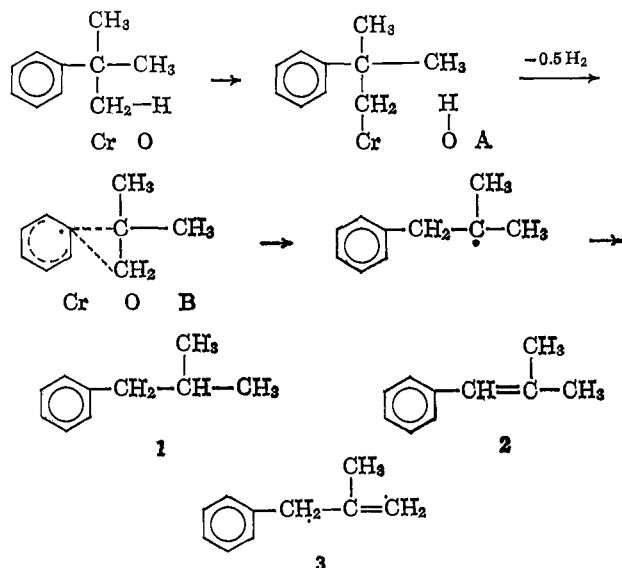
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(7) H. Pines and C. N. Pillai, *ibid.*, **82**, 2921 (1960).

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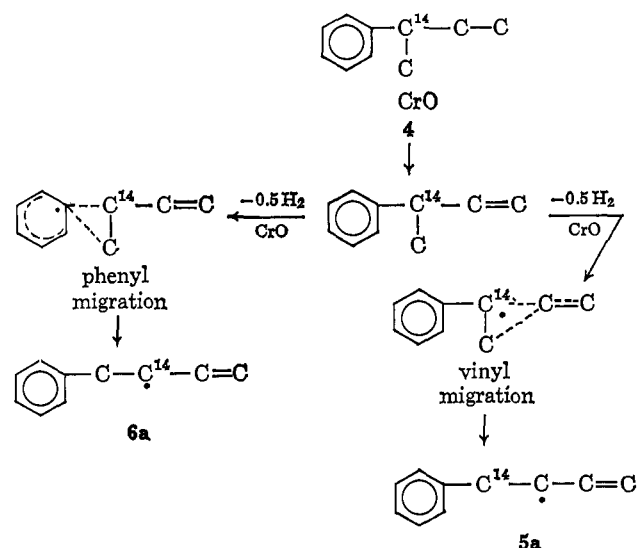
Scheme I



2-Phenyl-2-¹⁴C-butane (4). At 487° about 15% of this hydrocarbon underwent reaction of which 35% rearranged to aromatics, which after selective hydrogenation consisted of *n*-butylbenzenes composed of about equal amounts of C₆H₅¹⁴CH₂CH₂CH₂CH₃ (5) and C₆H₅CH₂¹⁴CH₂CH₂CH₃ (6). This novel rearrangement to compound 5 can be explained by a radical mechanism involving methyl-carbon insertion (vinyl migration), while the formation of compound 6 can be explained by a phenyl migration. The distribution of the ¹⁴C in *n*-butylbenzene was determined by measuring the total radioactivity of the molecule and the radioactivity of benzoic acid, obtained from the oxidation of the butylbenzene with potassium permanganate.

The course of the reaction is presented in Scheme II.

Scheme II



The methyl-carbon insertion (vinyl migration) via a radical mechanism has been recently reported by Raley and co-workers using iodine.⁹

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