

reasonable transition state is the eclipsed form (IV) analogous to ethane. The positive ΔS^\ddagger for rotation in I and II may reflect in part a stretching of the nitrogen-boron bond in the transition state for rotation (IV) and slight concomitant rehybridization of nitrogen toward sp^2 .

It is interesting to note that within experimental error the substitution of deuterium (II) for hydrogen (I) does not change the barrier to *tert*-butyl rotation (Table II) and that hydrogen and deuterium possess essentially the same conformational requirements in systems of this type.

The barrier to *tert*-butyl rotation in I and II is comparable to that for *tert*-butyl rotation in a series of halogenated methylbutanes ($E_a = 10$ –12 kcal/mol).¹⁸

Recent evidence obtained for the 4-*tert*-butyl-1-methylpiperidine boranes indicates little preference for BH_3 axial (~53%) or equatorial (~47%);¹⁹ *i.e.*, BH_3 has approximately the same conformational requirements as CH_3 . Thus, the three vicinal eclipsing interactions in the transition state (IV) for *tert*-butyl rotation in I may be assumed to be approximately equal. The magnitude of one methyl-methyl eclipsed repulsion may be calculated to be one third of ΔH^\ddagger (Table II) for *tert*-butyl rotation or 3.7 ± 0.4 kcal/mol. The potential maximum for *n*-butane involving eclipsing of two methyl groups is estimated to be 4.4–6.1 kcal/mol.²⁰

(18) B. L. Hawkins, W. Bremser, S. Borčić, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4472 (1971).

(19) R. E. Lyle, J. J. Kaminski, and E. W. Southwick, Abstracts, 161st Meeting of the American Chemical Society, Los Angeles, Calif., March 29–April 2, 1971, abstract no. 146 (ORGN).

(20) W. G. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

Subtracting the two H–H eclipsing interactions (~2 kcal/mol), the methyl-methyl eclipsed repulsion in *n*-butane is estimated to be 2.4–4.1 kcal/mol.

Experimental Section

The nmr spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe. Spectral calibrations were performed by the audio-modulation technique using a Hewlett-Packard 651-A audio-oscillator and 5221B electronic counter.

Temperature measurement was performed using a calibrated copper-constantan thermocouple permanently in place in the probe and is done simultaneously with the recording of the spectrum. Temperature measurement is accurate to $\pm 0.3^\circ$ at the sample.

The error ($\pm 5\%$) associated with the rate constants (Table I) obtained by matching theoretical to experimental spectra by superposition is a maximum error established by obviously poor fits at higher and lower values of the rate constant giving the best fit.

tert-Butyldimethylaminoborane (I) and *tert*-butyldimethylamino-*deuterio*borane (II) were prepared by the method of Shore and Parry²¹ using $LiBH_4$ and $LiBD_4$, respectively. The nmr, ir, and mass spectral data for I and II are entirely consistent with their respective structures.

Registry No.—I, 31121-07-0; II, 31819-36-0.

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(21) S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 8 (1958).

The Thermal Decomposition of Bissilyl Peroxides and Triphenylsilyl Triphenylgermyl Peroxide¹

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The thermal decomposition of bis(triphenylsilyl) peroxide gave an essentially quantitative yield of pentaphenylphenoxydisiloxane. Bis(*p*-tolylidiphenylsilyl) peroxide and bis(*p*-anisylidiphenylsilyl) peroxide were synthesized and analysis of the products of their thermal rearrangements gave a migratory aptitude series: *p*-anisyl, 6.0; *p*-tolyl, 1.1; phenyl, 1.0. These figures are consistent with a free-radical mechanism for the rearrangement. Triphenylsilyl triphenylgermyl peroxide was synthesized and its thermal decomposition occurs exclusively by phenyl-silicon bond cleavage to yield, ultimately, phenol, 0.62, triphenylgermyl moiety, 0.98, and polymeric diphenylsilyl oxide. Reproducible first-order kinetics were obtained with difficulty for 1 half-life for the thermal decomposition of the silylgermyl peroxide: k_{180} , 0.4; k_{190} , 1.0; k_{200} , $6.0 \times 10^{-6} \text{ sec}^{-1}$.

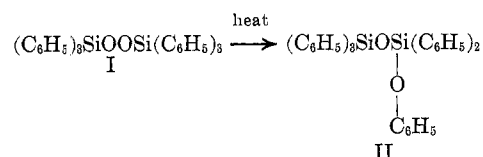
In a previous paper the synthesis of several bissilyl peroxides was described. The present work was planned to study the decomposition of these bis peroxides and to attempt the synthesis of an unsymmetrical organometallic peroxide in which silicon and germanium would be joined by a peroxide link.

Results and Discussion

Bissilyl Peroxides.—Heating bis(triphenylsilyl) peroxide (I)² above its melting point (140–141°) gave an

(1) (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 131. Taken in part from the Ph.D. thesis of A. K. Shubber, Case Western Reserve University, 1970. (b) Supported in part by the National Science Foundation through Grant GP-19018.

essentially quantitative yield (96%) of the rearrangement product II. The isolation of II was unexpected,



for from the thermal decomposition of the analogous bis(triphenylgermyl) peroxide it has been reported³ that

(2) R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

(3) R. L. Dannley and G. C. Farrant, *ibid.*, **34**, 2432 (1969).

only hydrolysis products of the analogous phenoxydiphenylgermyl triphenylgermyl oxide could be recovered.

The structure of II was established from appropriate elemental analyses and a molecular weight determination as well as hydrolysis to a 90.6% yield of phenol. Also, the nmr spectrum of II consisted of one multiplet (τ 3.05–3.60) corresponding to phenoxy hydrogens and a second multiplet (τ 2.30–2.95) corresponding to phenyl hydrogens. The integrated areas under the peaks had the appropriate 1:5 ratio. The assignment of the peaks was confirmed by the nmr spectrum of I which consisted of a single multiplet (τ 2.30–2.90).

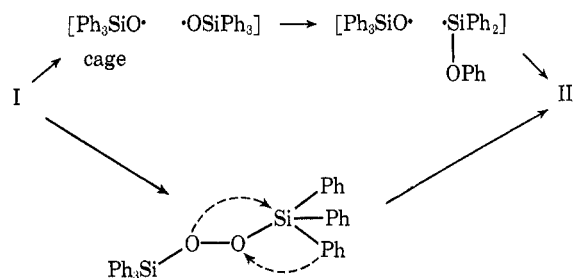
The rearrangement of I to II might proceed by either an ionic or homolytic mechanism. The migratory aptitudes of appropriate aryl groups in the reaction can be used to differentiate between these two alternative mechanisms. Therefore, two new peroxides (III and VI) were prepared in anticipation that the ratios of their isomeric rearrangement products (IV/V and VII/VIII) could be used to calculate the needed relative migratory aptitudes. III and VI were obtained in one-step syntheses from the corresponding triarylsilyl chlorides. In the course of the synthesis of III, *p*-tolylidiphenylsilyl hydroperoxide was obtained. This is the first triarylsilyl hydroperoxide reported containing unlike aryl groups.

The isomeric rearrangement products of the bis peroxides could not be separated conveniently, but two analytical methods were available to determine the ratios of IV to V and VII to VIII. First, in each pair of isomers there were two types of methyl groups (*p*-tolyl *vs.* *p*-tolylloxy and *p*-anisyl *vs.* *p*-anisylloxy) which gave characteristic peaks in the nmr spectra permitting analysis. The assignment of the peaks was obtained by comparison to the nmr spectra of the corresponding peroxides. Second, alkaline hydrolysis of the isomer mixtures produced phenols which were analyzed by glpc. The results of the analysis are given in Scheme I. The nmr figures are the more accurate because the glpc analyses are based upon only a partial (74, 83%) recovery of the phenols, apparently due to some loss of

the more volatile unsubstituted phenol. The glpc values serve to confirm the applicability of the nmr analysis, however.

The relative migratory aptitudes of the aryl groups are phenyl, 1.0; *p*-tolyl, 1.1; *p*-anisyl, 6.0. These low values are characteristic of a free radical but not an ionic rearrangement. For example, the analogous rearrangement of germanium hydroperoxides³ led to the migratory aptitudes *p*-anisyl, 1.98; *p*-trifluoromethylphenyl, 1.36; phenyl, 1.0. Also, the rearrangement of bisgermanium peroxides gave the migratory aptitudes *p*-trifluoromethylphenyl, 1.25; phenyl, 1.0. A *p*-nitrophenyl/phenyl migratory ratio of 4.0–4.4:1 was reported for both the homolytic decomposition of diphenyl-*p*-nitrophenylmethyl hydroperoxide⁴ and the oxidation of diphenyl-*p*-nitrophenylcarbinol with lead tetraacetate.^{5,6} In contrast, for ionic processes such as the cleavage of aryltrimethylsilanes with mineral acid,⁷ relative cleavage aptitudes are *p*-anisyl, 1500; *p*-tolyl, 21; phenyl, 1.0. Therefore, these data are consistent with a free-radical mechanism for the rearrangement of the bissilyl peroxides.

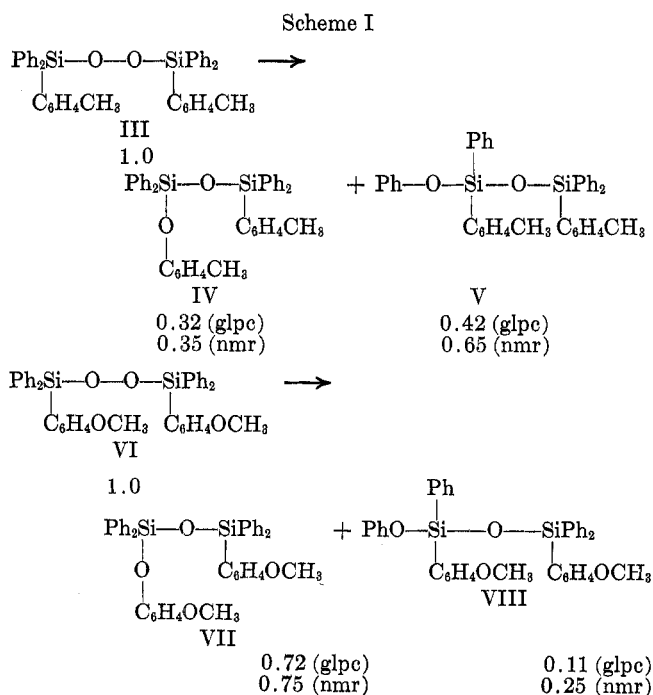
The quantitative formation of II from I must involve either a concerted process or a cage reaction to prevent the formation of some diphenoxytetraphenyldisilane as



a coupling product. The high viscosity of the molten neat peroxide could be expected to give cage reactions, but a concerted process is not excluded. In a concerted reaction there could be a preferred conformation which would account for the migratory aptitudes.

The bissilyl peroxides do not respond to any of the conventional analysis for peroxide content and, in high boiling solvents, an overlap of the nmr peaks occurred. Therefore no kinetic measurements of the bissilyl peroxides decompositions were obtained.

Silylgermyl Peroxides.—When the present work was initiated, no covalent peroxides were known in which two metals were joined by a peroxide link. However, recently the synthesis of trimethylsilyltriphenylgermyl peroxide and triphenylsilyltriphenylgermyl peroxide (IX) have been reported.⁸ These authors obtained IX from the silylamine and the germyl hydroperoxide in ether solution at 0–5°. The same procedure had been attempted in the present work without success. However, triphenylsilylamine and triphenylgermyl hydroperoxide were found to react slowly in refluxing methylene chloride to yield the desired peroxide IX.



(4) P. D. Bartlett and J. Cotman, *J. Amer. Chem. Soc.*, **72**, 3095 (1950).

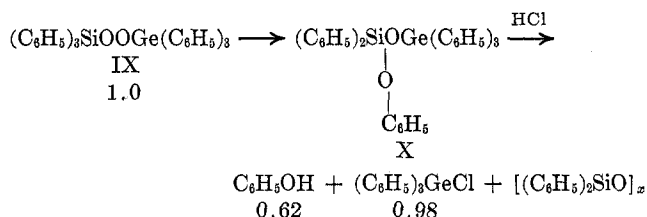
(5) W. H. Starnes Jr., *ibid.*, **89**, 3368 (1967).

(6) W. H. Starnes Jr., *ibid.*, **90**, 1807 (1968).

(7) C. Eaborn and R. W. Bott, "The Bond to Carbon," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 410.

(8) A. P. Tarabarina, V. A. Yablokov, and N. V. Yablokova, *Zh. Obshch. Khim.*, **40** (5), 1094 (1970).

The thermal decomposition of IX either neat or in 1,2,4-trichlorobenzene yielded a new material (X) which, after treatment with anhydrous hydrogen chloride,³ gave the following products. The essentially



quantitative recovery of triphenylchlorogermane proves that the migration of phenyl group occurs exclusively from the silicon atom. Although it has already been reported³ that migration of a phenyl group from germanium to oxygen is possible, the rate of such a rearrangement may be too slow to compete here and the corresponding rearrangement of the silicon moiety is observed exclusively.

The thermal decomposition of IX in 1,2,4-trichlorobenzene was followed kinetically by iodometric titration. The unusual solvent was chosen because of its high boiling point as well as its solubility characteristics for the peroxide. The high stability of the peroxide necessitated temperatures of 180° or higher to give reasonable rates of decomposition. It was very difficult to get reproducible kinetics and reasonably good first-order plots were observed for only a single half-life. Therefore, the rate constants (Table I) should be con-

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS (SEC⁻¹) FOR THE FIRST HALF-LIFE DISAPPEARANCE OF TRIPHENYLSILYL TRIPHENYLGERMANYL PEROXIDE (0.01 M) IN TRICHLOROBENZENE

T, °C	k × 10 ⁶ , expt 1	k × 10 ⁶ , expt 2	k × 10 ⁶ , av
180	0.4 ± 0.05	0.4 ± 0.05	0.4
190	1.1 ± 0.1	0.9 ± 0.1	1.0
200	6 ± 1	7 ± 2	6

sidered initial rates and are not precise enough for an E_a calculation.

Experimental Section

***p*-Tolyldiphenylchlorosilane.**—The addition of *p*-bromotoluene (85.5 g, 0.5 mol) in anhydrous ether (500 ml) to magnesium (12 g, 0.5 g-atom) in ether (500 ml) produced the ethereal Grignard reagent which was filtered and the filtrate was added dropwise to a warm solution of diphenyldichlorosilane (252 g, 1 mol) in dry toluene (500 ml). The ether distilled during the addition and the residual toluene solution was refluxed (4 hr). The toluene was then removed under reduced pressure and the residue was vacuum distilled to give relatively pure *p*-tolyldiphenylchlorosilane [74 g, bp 150–160° (5 mm)] and *p*-tolyldiphenylbromosilane [44 g, bp 205–210° (5 mm), mp 61–62°]. The nmr and ir spectra corresponded to these assigned structures. Hydrolysis of the two fractions produced the same silanol.

***p*-Tolyldiphenylsilyl Hydroperoxide.**—Using the procedure previously described for silyl hydroperoxides,² *p*-tolyldiphenylchlorosilane (5.0 g, 0.016 mol) in ether (200 ml) with 98% hydrogen peroxide (5.0 ml, 0.2 mol) gave *p*-tolyldiphenylsilyl hydroperoxide (3.1 g, 62.5%) which melted at 75° after recrystallization from ether–petroleum ether (bp 30–60°). *Anal.* Calcd for C₁₉H₁₉O₂Si: C, 74.5; H, 5.93; Si, 9.15; active oxygen, 5.21. Found: C, 74.8; H, 6.04; Si, 9.07; active oxygen, 5.20.

Bis(*p*-tolyldiphenylsilyl) Peroxide.—Anhydrous ammonia was bubbled (3 min) through a solution of *p*-tolyldiphenylchloro-

silane (5 g) in anhydrous ether (150 ml), the solution stirred for 5 min, and 98% hydrogen peroxide (1.3 g) was added. After 3 min the precipitated ammonium chloride was removed by filtration, the ether solution washed three times with water, and the ether solution dried with magnesium sulfate. Evaporation of the ether solution gave an oily material which when recrystallized from petroleum ether at –20° gave bis(*p*-tolyldiphenylsilyl) peroxide (3.5 g, mp 135°). *Anal.* Calcd for C₃₈H₃₈O₂Si₂: C, 78.87; H, 5.92; Si, 9.68. Found: C, 78.95; H, 5.89; Si, 9.82. The nmr spectrum consisted of a multiplet (τ 2.4–3.0) and a singlet (τ 7.7).

***p*-Anisyldiphenylchlorosilane.**—*p*-Bromoanisole (47 g) in anhydrous tetrahydrofuran (50 ml) was added to magnesium (6 g) in tetrahydrofuran (250 ml). After refluxing, the Grignard reagent was filtered and added to diphenyldichlorosilane (73 g) in anhydrous benzene (300 ml) kept at a temperature high enough to distil the tetrahydrofuran. After all the tetrahydrofuran was distilled, the residue was refluxed (120 hr). After filtration to remove metallic salts, the solution was distilled to give 60 g of a mixture of *p*-anisyldiphenylchlorosilane [bp 180–195° (0.4 mm)] and *p*-anisyldiphenylbromosilane [bp 195–205° (0.4 mm)].

Bis(*p*-anisyldiphenylsilyl) Peroxide.—By a procedure identical with that for bis(*p*-tolyldiphenylsilyl) peroxide, *p*-anisyldiphenylchlorosilane (5g) in ether (150 ml) and 98% hydrogen peroxide (0.32 g) produced 2.8 g of bis(*p*-anisyldiphenylsilyl) peroxide (mp 112°). *Anal.* Calcd for C₃₈H₃₄O₂Si₂: C, 74.71; H, 5.62. Found: C, 74.59; H, 5.78. The nmr spectrum consists of a multiplet (τ 2.45–3.3) and a singlet (τ 6.4).

Thermal Decomposition of Bis(triphenylsilyl) Peroxide.—The peroxide (1 g, 0.0018 mol) in a sealed tube was heated (200°) for 4 hr. The cooled reaction mixture was extracted with petroleum ether and the extract was cooled to produce pentaphenylphenoxydisiloxane, mp 128–129° (0.96 g, 96% yield). *Anal.* Calcd for C₃₈H₃₀O₂Si₂: C, 78.50; H, 5.49; Si, 10.19; mol wt, 551. Found: C, 78.46; H, 5.64; Si, 10.45; mol wt, 575.

To prove the structure, the rearranged product (0.96 g) was refluxed with 20% potassium hydroxide in 50:50 aqueous methanol (25 ml) and benzene (10 ml) for 5 hr. The mixture was cooled and acidified with dilute hydrochloric acid, water was added, and the phenol was extracted with ether. The ether extract was dried and evaporated to dryness. Gas chromatographic analysis using a 15-ft column of 20% SE-30 on Chromosorb W AW/DMCS treated 80–100 mesh at 150° with *p*-cresol as an internal standard gave 0.906 mol of phenol produced per mole of rearrangement product. An identical hydrolysis procedure applied to the parent peroxide produced a negligible quantity of phenol.

Thermal Decomposition of Bis(*p*-tolyldiphenylsilyl) Peroxide.—After the peroxide (2.75 g) had been heated in an oil bath for 3 hr, it was transferred to a volumetric flask (25 ml) and benzene was added. Gas chromatographic analysis of an aliquot of the benzene solution showed no free phenol or *p*-cresol to be present, even after bubbling hydrogen chloride through the solution for 1 hr. Using the hydrolysis procedure previously described for pentaphenylphenoxydisiloxane, glpc analysis of an aliquot of the benzene solution with a 15-ft column of 20% SE-30 on 80–100 mesh Chromosorb W AW/DMSC at 145° and 2,5-xyleneol as an internal standard showed 0.415 mol of phenol and 0.316 mol *p*-cresol per mole of peroxide or a *p*-tolyl/phenyl migratory aptitude of 1.52.

From the 4.7 ratio of the τ 7.35 singlet (*p*-tolyl-Si) to the τ 7.5 singlet (*p*-tolyl-Si) in the nmr, the tolyl/phenyl migratory aptitude is 1.1.

Thermal Decomposition of Bis(*p*-anisyldiphenylsilyl) Peroxide.—After heating the peroxide (250 mg) at 135° for 4 hr, the product exhibited two singlets (τ 6.3 and 6.4) in the nmr spectrum for the methoxy protons. The rearrangement product was refluxed with benzene (10 ml) and 20% methanolic potassium hydroxide (20 ml) for 4 hr. Water was added and the solution was acidified with dilute hydrochloric acid. The phenolic products were extracted with three portions (10 ml each) of ether. The ether extracts were dried, evaporated to dryness, and analyzed by glpc using the same conditions as for the cresol-phenol mixture except that *p*-cresol was used as an internal standard. In duplicate runs, the percentage yields were determined to be *p*-methoxyphenol, 78 and 65.5%, and phenol, 11.1 and 9.8%, for a migratory aptitude of *p*-anisyldiphenyl of 14. From the relative intensities of the τ 6.3/6.4 peaks in the nmr, the relative migratory aptitude of *p*-anisyldiphenyl is 6.

Triphenylsilyl Triphenylgermyl Peroxide.—A solution of triphenylsilylamine (2.1 g), triphenylgermyl hydroperoxide,⁹ and methylene chloride (150 ml) was refluxed overnight, at the end of which time the evolution of ammonia had ceased. Removal of the solvent using a rotary evaporator and recrystallization of the residue from methylene chloride produced triphenylsilyl triphenylgermyl peroxide (4 g), mp 155° (lit.⁹ mp 142–142.5°). *Anal.* Calcd for C₃₆H₃₀SiGeO₂: C, 72.7; H, 5.08. Found: C, 72.37; H, 5.04. Active oxygen titration showed a purity of 94%.

Thermal Decomposition of Triphenylsilyl Triphenylgermyl Peroxide.—After heating (165°) the asymmetric peroxide (0.2 g) for 16 hr, the product (mp 126°) had a different ir spectrum from that of the starting material. It was dissolved in methylene chloride and hydrogen chloride was bubbled through for 10 min. Triphenylmethane and *p*-cresol were added as internal standards

and glpc analysis³ showed a 98% yield of triphenylchlorogermane and a 62% yield of phenol.

Kinetics of the Decomposition of Triphenylsilyl Triphenylgermyl Peroxide.—The thermal decomposition of a trichlorobenzene solution of the peroxide (0.01 *M*) was followed iodometrically to give the first-order rates in sec⁻¹ × 10⁵ in Table I.

Registry No.—I, 2319-39-3; II, 31952-39-3; III, 31952-40-6; VI, 31999-36-7; IX, 27526-19-8; *p*-tolylidiphenylchlorosilane, 13868-70-5; *p*-tolylidiphenylbromosilane, 31952-43-9; *p*-tolylidiphenylsilyl hydroperoxide, 31952-44-0; *p*-anisylidiphenylchlorosilane, 18670-55-8.

Acknowledgment.—We wish to thank Dr. George Jalics for the first isolation of pentaphenylphenoxydisiloxane from the rearrangement of bis(triphenylsilyl) peroxide.

(9) R. L. Dannley and G. C. Farrant, *J. Org. Chem.*, **34**, 2428 (1969).

A Thermal Two-Carbon Ring Expansion. 2-Cyclopentenones from 3-Cyclopropyl-3-oxopropanoates

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Pyrolysis of 3-cyclopropyl-3-oxopropanoates **1a–d** (**a**, R₁ = R₂ = H; **b**, R₁ = CH₃, R₂ = H; **c**, R₁ = H, R₂ = CH₃; **d**, R₁ = R₂ = CH₃) at 500–600° (1–3 mm) gave the corresponding 2-cyclopentenones **2a–d** in 50–80% yields. The resultant substitution patterns in **2a–d** led to the conclusion that the oxo group was extruded from **1a–d**. Pyrolysis of **1a** at 760 mm gave pyrandione **10b** (R = *c*-C₂H₅). Pyrolysis of **10b** at 1–3 mm gave 2-cyclopentenone (**2a**). This is presented as evidence for the existence of an acylketene intermediate **11b**. The rearrangement of **1** to **2** represents a novel two-carbon ring expansion reaction of cyclopropane derivatives.

Several two-carbon thermal ring expansion reactions of cyclopropanes are known.^{1–11} Of these, only the vinylcyclopropane–cyclopentene rearrangement has received more than passing interest.^{1–3,12} We wish to report¹³ a new thermal rearrangement of 3-cyclopropyl-3-oxopropanoate esters **1a–d** to cyclopentenones **2a–d** in moderate yields (Table I) which may prove to be of synthetic interest.

Results and Discussion

The products of pyrolysis of keto esters **1** near 500° at 1–3 mm included cyclopentenones **2**, ketones **3**,

(1) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapters IX, X.

(2) R. Breslow, "Molecular Rearrangements, Part I," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 4.

(3) G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 53 (1966).

(4) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).

(5) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).

(6) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loesch, and H. E. Wright, *ibid.*, **91**, 6857 (1969).

(7) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969).

(8) W. C. Agosta, A. B. Smith, III, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Lett.*, 4517 (1969).

(9) G. E. Cartier and S. C. Bunce, *J. Amer. Chem. Soc.*, **85**, 932 (1963).

(10) G. E. Cartier and S. C. Bunce, *Diss. Abstr.*, **25**, 826 (1964).

(11) J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

(12) There has been considerable interest, however, in the subject of homoconjugative participation of cyclopropyl systems in developing carbonium ion centers which does not usually result in ring expansion. See, e.g., M. Hanack and H. M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **92**, 6557 (1970), and references cited therein.

(13) Preliminary report: W. F. Berkowitz and A. A. Ozorio, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 22, 1970, ORGN 142.

TABLE I
PYROLYSIS OF KETO ESTERS **1a–d**

Starting material	R ₁	R ₂	T, ° C ^a	% yield of 2a–d , glpc ^b	T, ° C	% yield of 2a–d isolated ^c
1a	H	H	565	51	540	47
1b	CH ₃	H	500	65	500	60
1c	H	CH ₃	585	65	585	58
1d	CH ₃	CH ₃	535	81	570	68

^a Pyrolysis temperature affording greatest glpc yield. ^b Glpc yields based upon unrecovered starting material. ^c Isolated yields based upon weight of product recovered by distillation.

carbon monoxide, carbon dioxide, ethanol, and ethylene (eq 1).

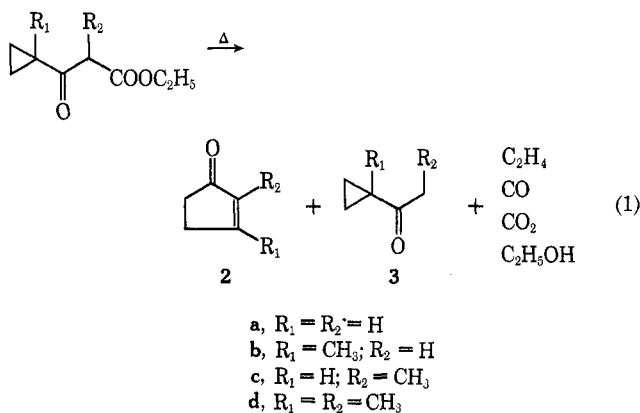


Table II presents evidence that the ratio of ketone **2a** and **3a** increased dramatically with an increase in the surface area of the pyrolysis packing material. This