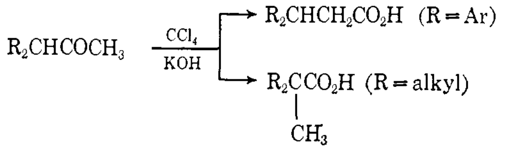
acids expected to be formed from the corresponding α-chloro ketones *via* the Favorskii reaction (eq 1).[2]



$$R_2CHCOCH_3 \xrightarrow[KOH]{CCl_4} \begin{cases} R_2CHCH_2CO_2H \ (R = Ar) \\ R_2\underset{\displaystyle CH_3}{\underset{|}{C}}CO_2H \ (R = alkyl) \end{cases} \qquad (1)$$

Alcohols. Primary alcohols (class I) are oxidized to the corresponding aldehydes. The latter may subsequently undergo aldol condensations leading to polymers or the Cannizzaro reaction leading entirely to carboxylic acids. Aldehydes that are more resistant to strong alkali (*viz.*, salicylaldehyde, pivalaldehyde)[3] can be isolated. Secondary alcohols (class II) are oxidized to the corresponding ketones. If the latter possess α hydrogens they react further (*vide supra*); those bearing no α hydrogens can be isolated. Tertiary alcohols are essentially unreactive.

Sulfones. Aryl alkyl sulfones (class I) are quantitively α-chlorinated, di- and trichlorination proceeding at increased rates. Trichloromethyl sulfones are prone to nucleophilic cleavage under these alkaline conditions (eq 2).[4]

$$ArSO_2CH_3 \xrightarrow[KOH]{CCl_4} ArSO_2CH_2Cl \longrightarrow \longrightarrow ArSO_2CCl_3 \longrightarrow ArSO_3H \qquad (2)$$

Dibenzyl sulfones (class II) are rapidly converted *in situ* into the stilbenes expected to be formed from the corresponding α-chloro sulfones *via* the Ramberg–Bäcklund reaction (eq 3).[5] These reactions can be highly stereospecific, *dl* sulfones being converted mainly into *trans* stilbenes, and *meso* sulfones into *cis* stilbenes,[6] in accord with the geometries predicted and observed in Ramberg–Bäcklund reactions.[5d,e]

$$(Ar(R)CH)_2SO_2 \xrightarrow[KOH]{CCl_4} Ar(R)C{=}C(R)Ar \quad (R = H \text{ or alkyl}) \qquad (3)$$

Di-*sec*-alkyl sulfones (class III) are converted into alkenes as well as the alkene-dichlorocarbene adducts (1,1-dichlorocyclopropanes). The latter are often the major products, which suggests that most of the dichlorocarbene (generated in the reaction of sulfonyl carbanion with CCl_4) may react with the rapidly formed episulfone or alkene in a common transition envelope before diffusing into and reacting with the *t*-BuOH, H_2O, or KOH.[7]

Hydrocarbon anions[8] as well as *t*-BuOK[9] react with CCl_4 presumably by direct attack on chlorine, dichlorocarbene being generated. Solid KOH, even in the presence of *t*-BuOH or H_2O, reacts only slightly with CCl_4 under reflux. When appropriate ketones, alcohols, or sulfones are added a vigorous reaction occurs and an abundance of chloride ion is produced.

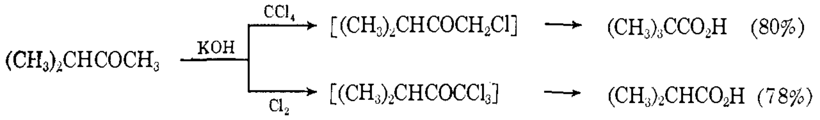
These observations, and the fact that the products we isolated are either the chlorinated substrates or compounds expected to be formed from them under these conditions, suggest that these reactions also involve attack by the substrate anion on chlorine of CCl_4. These chlorinations with CCl_4 are relatively slow, allowing subsequent (or concerted) reactions to occur *before* multiple chlorinations (eq 4–7). In contrast, more common halogenating agents react rapidly with anions to yield polyhalogenated species and products derived from them. The type of product ultimately formed can be significantly controlled by the difference in these relative rates,[10] *e.g.*, eq 8.

$$Nu\text{-}H \overset{:B^-}{\rightleftarrows} Nu:^- + B\text{-}H \qquad (4)$$

$$Nu:^- \ Cl{-}CCl_3 \longrightarrow Nu\text{-}Cl + :CCl_3^- \rightleftarrows :CCl_2 + Cl^- \qquad (5)$$

$$Nu\text{-}Cl \xrightarrow[(CCl_4)]{:B^-} \text{products} \qquad (6)$$

$$:CCl_2 \xrightarrow[\text{solvent}]{\text{products}} \text{other products} \qquad (7)$$



$$(CH_3)_2CHCOCH_3 \xrightarrow{KOH} \begin{cases} \xrightarrow{CCl_4} [(CH_3)_2CHCOCH_2Cl] \longrightarrow (CH_3)_3CCO_2H \ (80\%) \\ \xrightarrow[Cl_2]{} [(CH_3)_2CHCOCCl_3] \longrightarrow (CH_3)_2CHCO_2H \ (78\%) \end{cases} \qquad (8)$$

Acknowledgment. We are grateful to the University's Office of Research and Projects for supporting this study.

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(2) Favorskii reaction mechanism studies are of current interest: (a) F. G. Bordwell and M. W. Carlson, *J. Amer. Chem. Soc.*, **91**, 3951 (1969), and preceding papers; (b) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *ibid.*, **90**, 514 (1968).

(3) T. A. Geissman, *Org. Reactions*, **2**, 94 (1944).

(4) This was also observed by W. V. Ferrar, *J. Chem. Soc.*, 508 (1956).

(5) Synthetic and mechanistic aspects of the Ramberg–Bäcklund reaction have been reported recently: (a) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969); (b) L. A. Paquette and R. W. Houser, *ibid.*, **91**, 3870 (1969); (c) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969); (d) F. G. Bordwell and E. Doomes, 157th National Meeting of the American Chemical Society, ACS, Minneapolis, Minnesota, April 1969, Abstract ORGN 55; (e) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968).

(6) Configurational assignment to *dl* and *meso* sulfones by means of nmr was reported by C. Y. Meyers and A. M. Malte, *ibid.*, **91**, 2123 (1969).

(7) Generally, yields of alkene–:CCl_2 adducts similar to those we observed are realized from reactions carried out with :CCl_2 generated under strictly anhydrous conditions, in the alkene as solvent; *cf.* W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

(8) (a) W. T. Miller and C. S. U. Kim, *J. Amer. Chem. Soc.*, **81**, 5008 (1959); (b) C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

(9) (a) W. G. Kofron, F. B. Kirby, and C. R. Hauser, *ibid.*, **28**, 873 (1963); (b) C. Y. Meyers and J. A. Tykal (Midwest Regional Meeting of the American Chemical Society, Manhattan, Kans., Oct 1968, Abstracts, p 32) suggested that *t*-BuOCl is initially formed and rapidly converted into isobutylene oxide, which they isolated. This mechanism gains support by the observation of C. Walling and J. Kjellgren (*J. Org. Chem.*, **34**, 1487 (1969)) that isobutylene oxide is a major product from the exothermic reaction of *t*-BuOCl with *t*-BuOK.

(10) C. Y. Meyers and W. S. Matthews (manuscript in preparation) have also found that Favorskii and haloform reactions can be competitive when certain methyl ketones are treated with alkaline hypohalite.

(11) (a) Southern Illinois University Foundation Postdoctoral Fellow, 1968–1969; (b) University Predoctoral Fellow, 1968–1969.

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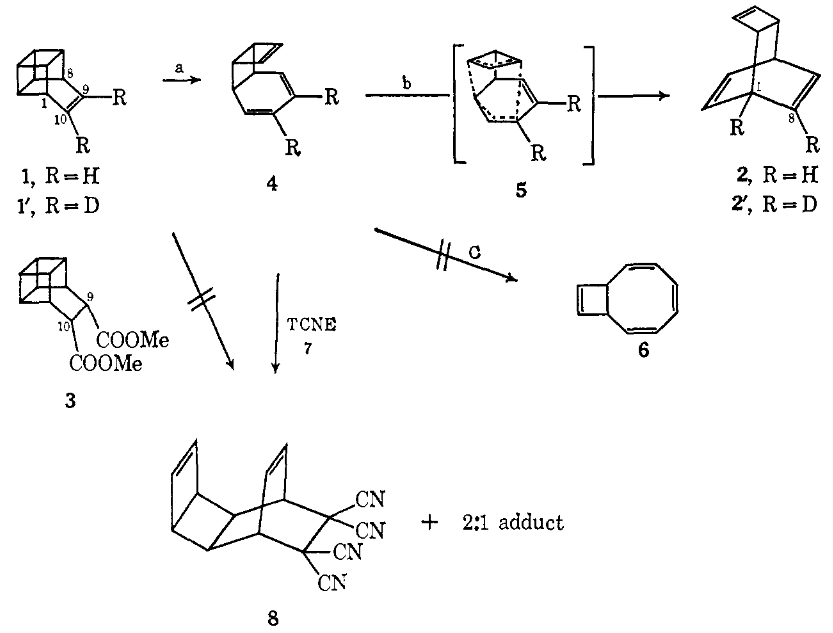
Thermolysis of Pentacyclo[4.4.0.0.^{2,5}0.^{3,8}0^{4,7}]dec-9-ene

Sir:

Thermal conversion of pentacyclic hydrocarbon **1** to Nenitzescu's hydrocarbon **2** is a well-known reaction.[1]

Scheme I



Certain experimental observations have led us to believe that this thermal process is not a straightforward cyclobutane ring cleavage caused by the strain involved in the system but rather a sequence of thermally allowed reactions. (i) Compound **1** decomposed to **2** with a half-life of 34 min at 110.1° (*vide infra*), whereas a structurally similar diester (**3**) was recovered unchanged after heating at 220° for 1 hr.[2] (ii) During the rearrangement of **1** to **2** in a temperature range of 140 to 170°, we failed to observe emission and absorption due to chemically induced dynamic polarization in the olefinic protons of **2**,[2] a phenomenon expected if a diradical species is involved in the process.[3] We wish to demonstrate that the thermolysis of **1** is a thermally allowed two-step process, involving a new (CH)$_{10}$ hydrocarbon (**4**) as the intermediate.

cis Dimethyl ester **3** was converted to the *trans*-9,10-dideuteriodimethyl ester[1] by heating for 2 hr in methanol-d_1 containing sodium methoxide. Hydrolysis of this diester in D$_2$O (NaOD) and subsequent electrolytic bisdecarboxylation[4] of the diacid provided 9,10-dideuterio pentacyclo compound **1′** (deuterium incorporation >98% by nmr analysis). Compound **1′** was thermally isomerized (110°, 8 hr) to the tricyclic dideuterio derivative **2′** in which one of the deuterium atoms was attached to bridgehead C-1 and the other to position C-8. This assignment was made by comparing an nmr spectrum (100 MHz, CCl$_4$) of **2′** [τ 3.72 (br d, 1 H), 4.02 (s, 2 H), 4.12 (d, 2 H), 6.69 (m, 1 H), 7.60 (d, 2 H)] with that of nondeuterated **2** [τ 3.72 (sextet, 2 H), 4.02 (s, 2 H), 4.12 (sextet, 2 H), 6.69 (m, 2 H), 7.60 (m, 2 H)]. The mechanism consistent with this deuterium distribution is readily conceivable. Compound **1′** undergoes a retro-Diels–Alder reaction to provide **4** which rapidly rearranges to **2′** *via* a Cope process, as indicated by dotted lines in **5**.[5] Relief of strain serves as the driving force for step a, while step b is an example of the well-known conversion of *cis*-1,2-divinylcyclobutane to cycloocta-1,5-diene.[6,7] In the present case one would obviously expect that reaction b is greatly facilitated by the favorable orientation of the two double bonds of **4** for the new σ bond formation. An equally likely thermal process of **4** would be the isomerization to bicyclo[6.2.0]deca-2,4,6,9-tetraene (**6**)[8] (path c), as bicyclo[4.2.0]octa-2,4-diene is known to isomerize to cycloocta-1,3,5-triene.[9] However, it is not unreasonable to assume that path b is favored over c by only a few kilocalories per mole in free energy of activation and the formation of **6** is negligible. **2′** was recovered unchanged in more than 90% yield after heating at 180° for 23 hr. During this process, **2′** was completely equilibrated with **4**, as evidenced by a new distribution of deuterium at C-1 (0.75 D), C-8 (0.75 D), and C-9 (0.5 D) of **2**.

LeGoff and Oka reported recently[10] that **1** reacted with tetracyanoethylene (**7**) to form adduct **8** and interpreted this process as a $2\pi + 2\sigma + 2\sigma$ cycloaddition across the 1,8 carbons of **1**.[11] However, their interpretation is incompatible with the kinetics of this addition reaction as shown below. Solutions of **1** and **7** in a 1:2 molar ratio in CD$_3$CN were immersed in a constant temperature bath and rates of reaction were measured by nmr spectroscopy. The rate (k_1) of decrease of **1** was first order; consequently the half-life of **1** was independent of the initial concentration (0.1~0.5 *M* **1**) and, further, k_1 was within experimental error the same as the

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(1) E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 98 (1969); S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966); W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966).

(2) H. H. Westberg and S. Masamune, unpublished results.

(3) J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, **91**, 3649 (1969), and references quoted therein.

(4) H. H. Westberg and H. J. Dauben, Jr., *Tetrahedron Letters*, 5123 (1968); P. Radlick, *et al.*, *ibid.*, 5117 (1968). Experimental details of this method will appear in "Organic Photosynthesis," R. Srinivasan, Ed., John Wiley & Sons, Inc., New York, N. Y., in preparation.

(5) Obviously a boat-type transition state rather than chair is demanded for this [3.3]sigmatropic rearrangement (*e.g.*, bullvalene).

(6) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964). $\Delta H^{\ddagger} = 23.1$ kcal/mol, $\Delta S^{\ddagger} = -11.7$ eu.

(7) E. Vogel, *Ann.*, **615**, 1 (1958).

(8) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, **89**, 4804 (1967). Compound **6** isomerizes to 9,10-dihydronaphthalene under the condition that **1** is converted to **2**.

(9) D. S. Glass, J. Zirner, and S. Winstein, *Chem. Commun.*, 620 (1966). $\Delta H^{\ddagger} = 24.7$ kcal/mol, $\Delta S^{\ddagger} = 2$ eu.

(10) E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969).

(11) For a reaction of this type, see C. D. Smith, *ibid.*, **88**, 4274 (1966). Also see H. Prinzbach and J. Rivier, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1069 (1967).

rate of thermolysis of **1** (in CD_3CN without **7**) to **2**: k at 110.1° = $(3.4 \pm 0.2) \times 10^{-4}$ sec^{-1}, k at 90.6° = $(4.2 \pm 0.2) \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 29$ kcal/mol, $\Delta S^{\ddagger} =$ 1 eu. With **7** all of **1** was converted into the adducts described by LeGoff, *et al.*,[10] but in the presence of 2 mol of a weaker dienophile, maleic anhydride, **1** provided **2** and maleic anhydride adducts of **4** in 40 and 60% yield, respectively, although the rate of decrease of **1** remained the same as k_1 (110°). Therefore, we conclude that tetracyanoethylene and maleic anhydride simply intercept intermediate **4**, the latter less efficiently, and that path a is the rate-determining step of the thermolysis of **1**.

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Received October 6, 1969

Fluorescence of Acetone in the Solution Phase

Sir:

The recent report by O'Sullivan and Testa on the fluorescence of acetone excimer and monomer species has created interest in this laboratory, since the gas-phase fluorescence of 2-pentanone[2] has a spectral distribution similar to that which O'Sullivan and Testa attribute to the excimer of acetone. Thus, there exists a possibility that the 2-pentanone emission at 25 Torr is actually due to an excimer. In the process of initiating experiments to study the gas phase emission as a function of pressure we have repeated the O'Sullivan and Testa experiments in the solution phase. As a result of these experiments we conclude that the apparent monomer emission (λ_{max} 345 nm) reported by those workers appears to be due to an impurity in the acetone, whose fluorescence is quenched by acetone in the high acetone concentration region ($\sim 10^{-2}$ *M*).

The fluorescence spectra at varying concentrations of acetone in hexane are shown in Figure 1.[3] The spectra were obtained with a Farrand spectrofluorometer using slits with a 5-nm bandpass. The acetone was "spectroquality" and was purified by preparative gas chromatography just prior to use. The hexane used was a fresh bottle of either spectroquality or chromatoquality (Matheson Coleman and Bell). If a bottle of either grade hexane was used which had been opened several times previously during normal laboratory use, spectra similar to those reported by O'Sullivan and Testa were obtained. However, the short wavelength emission was at 330 nm rather than 345 nm and was more intense than that seen by O'Sullivan and Testa.[4] Careful distillation of this hexane removes the 330-nm emission. It was observed that if the hexane came in contact with plastic stoppers on volumetric flasks or rubber serum caps, the emission at 330 nm was very intense at low ketone concentrations.

Experiments using distilled water and carefully distilled methanol as solvents showed only the 405-nm emission and the concentration dependence agreed with that shown in Figure 1. Experiments with chromatographically purified diethyl ketone gave only the 405-nm emission at concentrations of $\geq 3 \times 10^{-4}$ *M*.

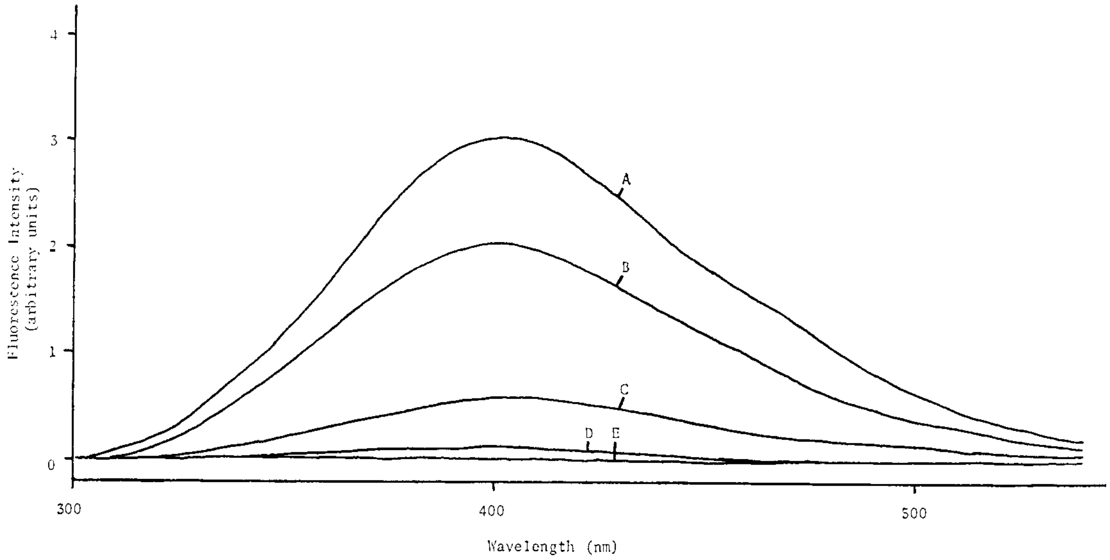

Figure 1. Fluorescence spectra of acetone at varying concentrations (hexane solvent, excitation λ 2850 ± 50 Å): (A) 2.2×10^{-2} *M*, (B) 1.1×10^{-2} *M*, (C) 2.7×10^{-3} *M*, (D) 2.7×10^{-4} *M*, (E) pure hexane.

A plot of the integrated area under the spectral curve *vs.* acetone concentration was linear to 0.03 *M* acetone, beyond which the integrated intensity showed the char-

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(1) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 6245 (1968).

(2) F. S. Wettack, *J. Phys. Chem.*, 73, 1167 (1969).

(3) Professor N. J. Turro's group at Columbia has obtained similar spectra. We thank Mr. J. C. Dalton for communicating these unpublished results to us.

(4) Private communication with Professor Testa indicates that the 330-nm emission seen in our work is definitely not the same as the 345-nm emission seen in their work. The solvents employed by O'Sullivan and Testa were emission-free and, hence, we conclude that the short-wavelength emission seen by those workers was probably due to an impurity in the ketone. We thank Professor Testa for helpful discussions on this matter.