

0.001 v., which is in excellent agreement with the theoretical slope predicted by eq. 2 for the reversible two-electron dimer-monomer reaction  $1 [(2.303)RT/2\mathcal{F} = 0.0293 \text{ v. at } 25^\circ]$ . A wave analysis plot of  $Q_2$  vs.  $E_{\text{dme}}$  was rectilinear with a reciprocal slope of 0.044 v. This excludes any one-electron transfer process, whether reversible or irreversible, and is not consistent with Nernst control for a two-electron reduction. A Koutecky-type mathematical analysis<sup>8</sup> eliminated the possibility of a two-electron transfer "rate controlled" by slow steps other than diffusion. The remote alternative of spurious slopes,<sup>9,10</sup> due to extraneous effects (e.g., double layer), was ruled out in our results by considerations of internal consistency.

Equation 2 predicts that the half-wave potential of hemin should shift with pH as shown in eq. 3. This

$$\frac{dE_{1/2}}{d(\text{pH})} = -0.059 \quad (3)$$

dependence has been previously reported in the literature.<sup>11</sup> From our data and the applicable expanded form of the Ilkovic equation,<sup>12</sup> the diffusion coefficient of the dimeric hemin ion A was evaluated as  $1.72 \times 10^{-7} \text{ cm.}^2/\text{sec. at } 25^\circ$ . It should be noted that this assignment applies only to the species which controlled the current under the specific experimental conditions prevailing in this investigation, i.e., in a dilute aqueous solution (millimolar in total hemin) containing 0.1 M potassium hydroxide as the sole supporting electrolyte in the absence of any maximum suppressor. It is well known that the degree of polymerization of hemin<sup>4</sup> is highly dependent on environmental conditions. Studies are in progress for elucidating the polarographic properties of iron protoporphyrin aggregates in media of biological significance.

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### The Question of Heterolytic Mechanisms for Gas-Phase Pyrolyses of Alkyl Chlorides

Sir:

At elevated temperatures in the gas phase, in reaction vessels which have been seasoned by prolonged contact with reaction products, monochlorinated hydrocarbons have usually been shown to decompose by homogeneous and unimolecular processes.<sup>1</sup> The prod-

(1) For reviews on pyrolytic elimination reactions see (a) A. Maccoll, "Proceedings of the Kekule Symposium on Theoretical Organic Chemistry,

ucts of such a reaction are hydrogen chloride and an olefin, and relative rates of elimination for a series of chlorides parallel the rates of solvolytic reactions for the same series.<sup>1</sup> Rearrangements during the thermal decomposition of neopentyl chloride<sup>2</sup> and bornyl chloride<sup>3</sup> are also observed, and all of these facts suggest "quasi-heterolytic"<sup>1a</sup> mechanisms analogous to those of solvolytic eliminations. Consequently, very polar transition states<sup>1a</sup> or ionic pair intermediates<sup>4</sup> have been postulated for thermal dehydrohalogenations.

The original analogy was based upon a comparison of primary, secondary, and tertiary halides whose relative rates of elimination at 400° were in the approximate ratio 1:200:40,000, respectively.<sup>1a,c</sup> We choose to compare a series of secondary chlorides which differ greatly in their solvolytic reactivity. Some relative rates of dehydrochlorination in the gas phase compared with solvolytic (SN1 or E1) reactivities are presented in Table I.

TABLE I  
RELATIVE RATES OF THERMAL DEHYDROCHLORINATION

Reactant	400°	500°	Solvolysis <sup>a</sup>
Cyclohexyl chloride	1.00	1.00	1.00
2-Butyl chloride	0.85	1.12	1.51 <sup>b</sup>
Cyclopentyl chloride	1.20	0.93	14.1 <sup>c</sup>
exo-Norbornyl chloride	0.67	0.77	117. <sup>d</sup>
α-Phenylethyl chloride	7.76	6.92	12,500 <sup>e</sup>
t-Butyl chloride	101	71	19,100 <sup>f</sup>

<sup>a</sup> Approximate values for 80% aqueous ethanol at 85°. <sup>b</sup> The quoted value is for isopropyl chloride: A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., New York, N. Y., 1962, p. 96. <sup>c</sup> J. D. Roberts, L. Urbaneck, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 3049 (1949). <sup>d</sup> J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950). <sup>e</sup> Extrapolated from 50°: A. M. Ward, *J. Chem. Soc.*, 445 (1927). <sup>f</sup> Extrapolated from 50°: E. D. Hughes, *ibid.*, 255 (1935).

Relative rates for the secondary chlorides were obtained by pyrolyzing a mixture of the required chloroalkanes in stirred flow reactor systems which have been described previously in detail.<sup>5,6</sup> The relative rate for t-butyl chloride is calculated from the Arrhenius equation since the magnitude of the rate precluded competitive experiments. Flow rates in these experiments were generally varied by a factor of ten and the usual precautions of surface inhibition were followed.<sup>1c</sup> Four to eight runs were made for each pair and the standard deviation of the resulting relative rate was always less than 5%. In the pyrolysis of norbornyl chloride, the corresponding olefin, bicyclo[2.2.1]heptene, was not isolated. As expected, the retro-Diels-Alder reaction of the bicyclic olefin<sup>7</sup> was so rapid that only cyclopentadiene and ethylene could be identified. In all of the other cases secondary processes did not occur to measurable extents.

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The differences in solvolytic reactivities would not be as large at 400 or 500°, but one should find the same order of reactivity. One notes that the reactivity of *exo*-norbornyl chloride is less than that of cyclohexyl or cyclopentyl chloride, although an analogy to carbonium ion reactions in solution requires a greater reactivity. In addition, the reactivity of  $\alpha$ -phenylethyl chloride is comparable to that of the other secondary chlorides. The analogy would predict a rate similar to that of *t*-butyl chloride.

Exner has recently suggested that a parallelism of rates at two different temperatures is sufficient to infer similarity or identity of mechanism in a reaction series.<sup>8</sup> Inversion of reactivity due to inclusion of an isokinetic temperature in the experimental temperature range<sup>9</sup> is discounted. However, as one can see from Table I, isokinetic temperatures do intrude into the ordinary temperature range for thermal dehydrochlorination.

The work reported herein shows clearly that the "quasi-heterolytic" mechanism<sup>1a</sup> for gas-phase thermal dehydrochlorination is not correct in detail, although the parallel reactivities to solvolytic reactions found previously now become more difficult to explain.

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### Synthesis of a Bicyclo[2.1.1]hexene

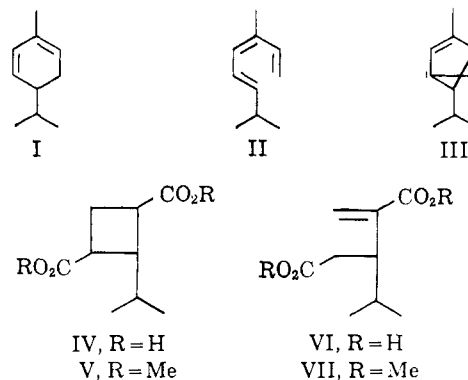
Sir:

The recent photoisomerization of 1,5-hexadiene to bicyclo[2.1.1]hexane<sup>1</sup> suggests a new general approach to the synthesis of this interesting ring system.<sup>2</sup> This communication records a cognate preparation of the first unsaturated member (III) of the series.

Ultraviolet irradiation of  $\alpha$ -phellandrene (I) was reported to give a mixture of trienes (II), which disappeared on prolonged irradiation.<sup>3</sup> In the present work a 3% ethereal solution of this terpene (80%) was irradiated with light above 250 m $\mu$  until it showed no absorption in this region. The crude product showed only a weak maximum at 1950 cm.<sup>-1</sup> due to allenic photoproducts<sup>4</sup> and yielded one principal photoproduct (45%) on distillation.

This compound (III) has b.p. 55° (18 mm.), is optically inactive, and shows no ultraviolet maximum

above 190 m $\mu$ . The presence of the  $-\text{HC}=\text{CMe}-$  group is indicated by the n.m.r.<sup>5</sup> maxima at  $\tau$  8.2



(intensity 3) and 4.5–5.0 (1) and confirmed by ozonolysis followed by hypobromite oxidation to the dicarboxylic acid IV (30%), m.p. 133°. This, with acetic anhydride, yielded the anhydride (m.p. 40–40.5°) and with diazomethane, the ester (V); the infrared, ultraviolet, and n.m.r. spectra of these three compounds indicate the absence of olefinic groups, so that the acid IV is monocyclic. That it is a glutaric acid is suggested by the maxima at 1761 and 1805 cm.<sup>-1</sup> of the anhydride and confirmed by a reverse Michael reaction.<sup>6</sup> Thus, when the ester V was saponified (3 hr. refluxing with 10% potassium hydroxide in methanol) and the product re-esterified, gas chromatography indicated starting material (37.5%) and a new isomer (VII, 56%). The same reaction was effected less cleanly by heating a 6% solution of V in isooctane for 20 hr. at 280°. The corresponding new acid (VI) had m.p. 156–157°,  $\lambda_{\text{max}}$  206 m $\mu$  ( $\epsilon$  15,000), and, when treated with ozone followed by warm 30% hydrogen peroxide, gave isopropylsuccinic acid (45%), identified by infrared spectrum and mixture melting point with a synthetic<sup>7</sup> specimen.

The photoproduct III is thermally stable, having a half-life at 300° of 40 min.; five pyrolysis products, probably isomers of the starting material, are formed. When heated at 240° for 5 hr. with 5% platinumized charcoal, *m*-cymene and *p*-cymene were obtained (8 and 5%, respectively, from a 96% sample); these were isolated by gas chromatography and identified by their infrared spectra. Büchi and Goldman<sup>8</sup> have described the acid-catalyzed aromatization of another bicyclo[2.1.1]hexane.

The mass spectrum of III further confirms the presence of an isopropyl group, having its base peak at  $m/e = 93$  and the complementary ion peak in comparable abundance (58%) at  $m/e = 43$ .<sup>9</sup> It is thus surprising that the n.m.r. spectra of neither IV nor V show splitting of the isopropyl peak at  $\tau$  8.9–9.1, while those of the anhydride of IV and the hydrocarbon III both show this peak as only partially resolved doublets ( $J = 3$  and 1.6 c.p.s., respectively).

(5) Run in CDCl<sub>3</sub> on a Varian A-60. The author is deeply indebted to Drs. L. Stautzenberger and R. M. Geudin, Celanese Corp., Clarkwood Texas, for the n.m.r. and mass spectral data given in this work.

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