

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 α -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.⁸ Inversion of reactivity due to inclusion of an isokinetic temperature in the experimental temperature range⁹ 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^{1a} 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

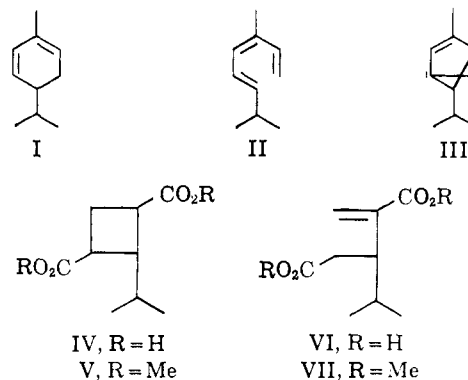
Sir:

The recent photoisomerization of 1,5-hexadiene to bicyclo[2.1.1]hexane¹ suggests a new general approach to the synthesis of this interesting ring system.² This communication records a cognate preparation of the first unsaturated member (III) of the series.

Ultraviolet irradiation of α -phellandrene (I) was reported to give a mixture of trienes (II), which disappeared on prolonged irradiation.³ In the present work a 3% ethereal solution of this terpene (80%) was irradiated with light above 250 m μ until it showed no absorption in this region. The crude product showed only a weak maximum at 1950 cm.⁻¹ due to allenic photoproducts⁴ 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 μ . The presence of the $-\text{HC}=\text{CMe}-$ group is indicated by the n.m.r.⁵ maxima at τ 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.⁻¹ of the anhydride and confirmed by a reverse Michael reaction.⁶ 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°, λ_{max} 206 m μ (ϵ 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 synthetic⁷ 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% platinized 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 Goldman⁸ 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 $m/e = 43$.⁹ It is thus surprising that the n.m.r. spectra of neither IV nor V show splitting of the isopropyl peak at τ 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 CDCl₃ 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.

(6) Cf. L. Crombie, J. Crossley, and D. A. Mitchard, *J. Chem. Soc.*, 4957 (1963).

(7) P. A. S. Smith and J. P. Horowitz, *J. Am. Chem. Soc.*, **71**, 3418 (1949).

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(2) For a review see J. Meinwald, *Record Chem. Progr.*, **22**, 39 (1961).

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(4) K. J. Crowley, *Proc. Chem. Soc.*, 17 (1964).

The other portions of these spectra are in accord with the assigned structures.¹⁰

(10) Satisfactory carbon and hydrogen analyses were obtained for all new compounds.

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Interconversion of the Aspidospermine Skeleton to the Refractine Type¹

Sir:

In the course of our work² on the structure of minosine³ (= minovincine⁴) I, an alkaloid isolated from *Vinca minor*,^{3,4} we discovered a reaction which made possible an experimentally facile transformation of a skeleton of the aspidospermine type⁵ into the pleiocarpine⁶-refractine⁷ class of alkaloids, an interconversion of considerable biogenetic interest.

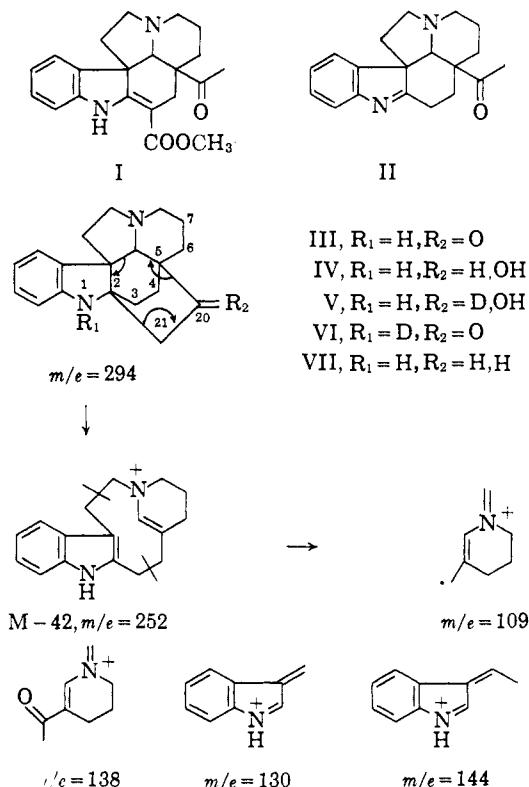
While our approach as well as the conclusions regarding the structure of I had closely paralleled those published at about that time by Janot, Djerassi, and their collaborators,⁴ we realized that an unexpected cyclization had occurred during one of the degradation reactions.

On heating of I in constant-boiling hydrochloric acid a crystalline compound (m.p. 176–177°, mol. wt. 294) was obtained to which we assign the hexacyclic structure III, a skeleton of the pleiocarpine type. Aside from its biogenetic significance, this observation contradicts the report⁴ cited above in which the apparently identical substance (same melting point and molecular weight, also obtained by acid decarboxylation of I) was considered—without citing much experimental evidence—to be the isomeric indolenine II, the product expected *a priori* in the hydrolysis of a carbomethoxymethyleneindole such as I.

The mass spectrum of the decarbomethoxylation product cannot be reconciled with structure II (it is very different from the one exhibited by the carbonyl-free analog of II⁸) and all our results are consistent with structure III instead: the ultraviolet spectrum is typically that of a dihydroindole: $\lambda_{\max}^{\text{EtOH}}$ 241 (ϵ 7110) and 292 $m\mu$ (ϵ 3080), and from the infrared absorption at 1706 and 3350 cm^{-1} ketone and amino functions can be inferred. The molecular ion at $m/e = 294$ in the mass spectrum of III confirms the loss of the ester function and all other peaks are readily interpreted in terms of the assumed structure: loss of both 28 and 42 mass units from the molecular ion, the former representing carbon monoxide and ethylene,⁹ the

latter a ketene fragment resulting from the familiar retro Diels-Alder-type of fragmentation (see arrows), common for alkaloids of the aspidospermine¹⁰ and refractine classes.¹¹ The $M - 42$ fragment ($m/e = 252$) can then undergo simple bond fission as indicated to yield an ion of $m/e = 109$, a very characteristic phenomenon for systems such as III. Other important ions are the indole fragments of $m/e = 130$ and 143, 144, as well as the one at $m/e = 138$ which arises from the alicyclic part *via* a variation¹¹ of the general pathway outlined above. Further proof of the conversion of $\text{CH}_3\text{CO}-$ to $-\text{CH}_2\text{CO}-$ is derived from the base-catalyzed exchange of the α -hydrogens. Two atoms of deuterium were exchanged (under conditions leading to incorporation of three deuterium atoms into I) as judged from the mass spectrum of the product which also agrees with the above interpretation of the spectrum of III (peaks at $m/e = 109, 130, 140, 143, 144, 252, \text{ and } 296$).

Chemical transformations of III support the assignment: lithium aluminum hydride reduction produced a dihydroindole alcohol IV (mol. wt. 296), the mass spectrum of which had the expected peaks at $m/e = 252$ ($M - 44$), 140 ($= 138 + 2$), and 109. Similarly, reduction with lithium aluminum deuteride furnished the C-20 deuterated derivative V, whose mass spectrum showed the appropriate shifts $M = 297$, $m/e = 252$ ($M - 45$), 141 ($= 138 + 3$), and 109. Partial exchange of the active hydrogen on nitrogen in III for deuterium led to a compound (VI) which showed doublets in its mass spectrum at $m/e = 295, 294$ (M^+), 267, 266 ($M - 28$), 252, 253 ($M - 42$), 145, 144, and



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