

strained,¹⁹ in which the hydrogens at 3 and 5 were placed in their natural positions, following the distortion. Figures 3 and 4 show the computed potential energy curves. Strained cyclopentyl has a minimum

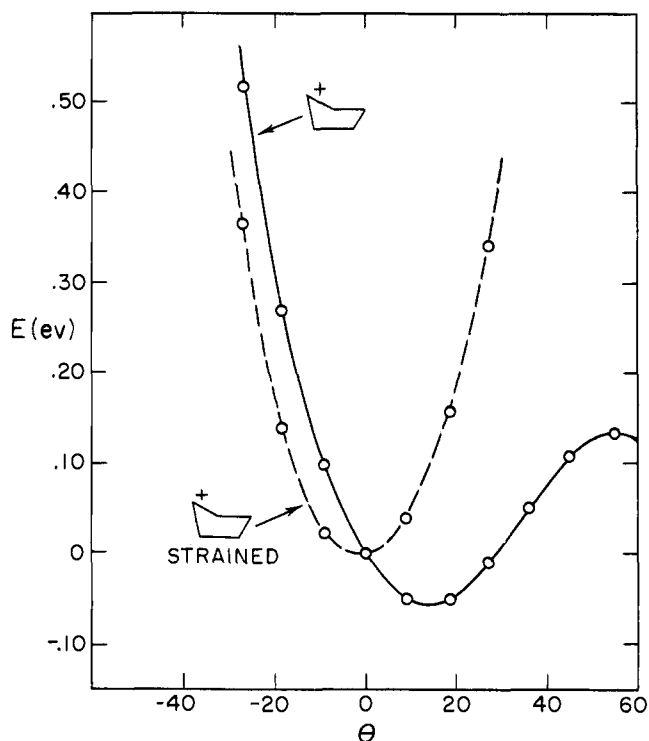


Fig. 3.—Potential energy curves for 4-cyclopentyl cation. Angle θ , measured in degrees from position in norbornane fragment, with zero of energy set at this angle for both forms. Planar molecule at $\theta = 54.5^\circ$. On an absolute scale, the unstrained curve should be displaced down by 1.315 e.v.

very close to the norbornene fragment geometry; the unstrained form, while still preferring a puckered shape, resists less a distortion toward planarity of the carbon framework. The strained cyclopentyl exhibits two minima, one puckered nearly 90° and stabilized by charge transfer to the double bond, the other, nearly planar, stabilized by charge transfer to the adjacent carbons and their hydrogens. Unstrained cyclopentyl, while clearly preferring a planar molecule, still retains a second minimum. Insofar as these factors can be isolated, the favored planarity of cyclopentyl contrasted to the slight puckering of cyclopentyl can be attributed to the absence of eclipsing hydrogen configurations in the former.

Approximate superposition of the strained cyclopentyl and cyclopentyl curves (including an attenuation factor to account for the fact that carbons and not hydrogens are responsible for the strain) results in the energy variation exhibited for 7-norbornenyl in Fig. 1. A superposition of two strained cyclo-

(9) The "unstrained" form still retains in its carbon framework the strain imposed by the norbornane geometry, such as the small CCC angle at C^+

pentenyl moieties gives a reinforcement of the double minima, resulting in the deep wells of 7-norbornadienyl. A distortion in the latter molecule is thus stabilized not only by improved charge transfer to the nearer

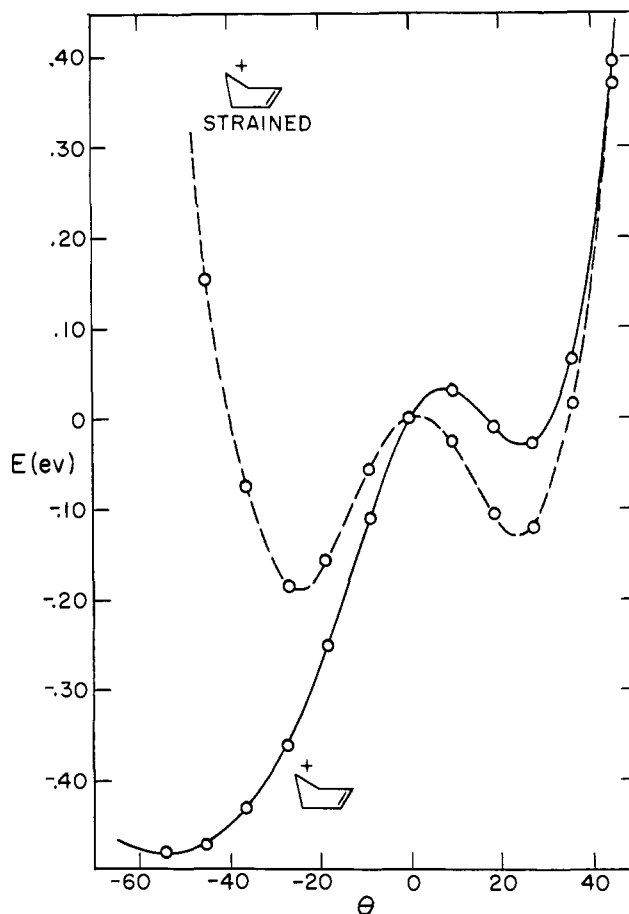


Fig. 4.—Potential energy curves for 4-cyclopentyl cation. Angle θ , measured in degrees from position in norbornane fragment, with zero of energy set at this angle for both forms. Planar molecule at $\theta = -54.5^\circ$. On an absolute scale the unstrained curve should be displaced down by 1.103 e.v.

double bond, but also by the assumption of an advantageous planar geometry with respect to the other double bond. The very interesting feature of the double minimum in the cyclopentyl cation raises the possibility of a new type of isomerism.¹⁰

Acknowledgment.—The author wishes to thank E. J. Corey for numerous discussions.

(10) The nonclassical minimum of unstrained cyclopentyl is probably so energetically unfavorable relative to the planar ion that it does not influence normal reactions. Experimentally, the absence of activation in 4-bromocyclopentene solvolysis was recently demonstrated by P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(11) Junior Fellow, Society of Fellows, Harvard University.

CHEMISTRY DEPARTMENT
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

ROALD HOFFMANN¹¹

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A Dicarbonium Ion as a Solvolysis Intermediate

Sir:

The formation of a stable dipositive carbonium ion from trichloromethylpentamethylbenzene in concen-

trated sulfuric acid has been reported¹; we wish to report kinetic evidence for such a dicarbonium ion intermediate in the solvolysis of trichloromethylpentamethylbenzene in aqueous dioxane.

Reaction rates were followed by the disappearance of the absorption peak at 302 m μ using a Beckman DU spectrophotometer with thermospacers on each side of the cell compartment with water circulated from a Sargent Thermonitor controlled water bath. In 85% by volume dioxane-water the reaction proceeds at a convenient rate at 25° with concentrations of added salts up to 0.100 *M*.

The reaction exhibits the special salt effect² with an increase in k_1 by a factor of over 20 on the addition of 0.005 *M* LiNO₃ and of over 100 on the addition of 0.100 *M* LiNO₃. In a comparable solvolyzing medium, the effects of added salts on the hydrolysis of benzhydryl chloride, which does not show the special salt effect, in 90% (w./w.) aqueous bis(2-ethoxyethyl) ether show an increase in k_1 of only a factor of 2.5 on addition of 0.100 *M* LiClO₄.³

This special salt effect is consistent with the formation of the unusually stable dicarbonium ion¹ and the expected larger dependence upon the ion stabilizing power of the medium than for a monovalent ion. The data appear in Table I.

TABLE I^a

LiNO ₃ , <i>M</i>	$k_1 \times 10^3$, sec. ⁻¹
0.000	6.91
.005	150
.010	261
.020	360
.030	418
.040	573
.050	621
.070	615
.080	797
.100	825

^a 2.87 $\times 10^{-4}$ *M* (CH₃)₅C₆CCl₃, 25.00 \pm 0.05°, 85 vol. % dioxane-water.

Good first-order plots of $\ln(A_t - A_\infty)$ vs. time were obtained for the higher salt concentrations but there was considerable upward curvature in the graphs in the absence of added salt. These results are consistent with an unusually large common ion rate depression, summarized in Table II, and with the mechanism of the special salt effect, in which the added salt displaces the common ion and prevents return.^{2b} For comparison, addition of 0.100 *M* (*n*-Bu)₄NCl to benzhydryl chloride in 90% (w./w.) aqueous bis(2-ethoxyethyl) ether leaves the hydrolysis rate almost unaffected, simply canceling the kinetic salt effect mentioned above.³

Since the chloride ion retardation was measured at constant ionic strength it is possible to evaluate k_1 and k_2/k_3 in the expression

$$\text{rate} = -\frac{d(\text{ArCCl}_2)}{dt} = \frac{k_1(\text{ArCCl}_2)}{1 + k_2/k_3(\text{Cl}^-)^2}$$

which assumes two chloride ions and a dicarbonium ion formed in the reversible rate-determining step and a steady-state concentration of dicarbonium ion.⁴

(1) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 5419 (1960); *ibid.*, **83**, 4460 (1961).

(2) (a) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956); (b) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(3) K. D. McMichael and R. A. Clement, *J. Org. Chem.*, **26**, 620 (1961).

Using initial rates and concentrations with no added chloride ion, k_1 is that from Table II and may be substituted into the expression for the run with initial chloride at 0.030 *M* to give a value of k_2/k_3 of 1.24 $\times 10^3$ l.² mole⁻². These values when applied to the runs of chloride concentration 0.010 and 0.020 *M* gave calculated initial rates which differed from those observed by 2.4% and 1.3%, respectively. The same calculations using an expression assuming a monocarbonium ion and one chloride ion gave a value of k_2/k_3 of 37.2 l. mole⁻¹ and calculated initial rates with discrepancies of 16% and 13%, respectively. Thus the data are consistent within reasonable experimental error with a dicarbonium ion intermediate and in disagreement greater than experimental error if a monocarbonium ion is assumed.

TABLE II^a

LiNO ₃ , <i>M</i>	LiCl, <i>M</i>	$k_1 \times 10^3$, sec. ⁻¹
0.100	0.000	8.25
.090	.010	7.17
.080	.020	5.42
.070	.030	3.91

^a Conditions same as in Table I.

Finally the temperature dependence of the rate constant in the presence of 0.100 *M* LiNO₃ shows a very low enthalpy of activation, 9.7 \pm 0.3 kcal./mole, consistent with considerable relief of strain in a transition state resembling the dicarbonium ion but not with a resonance-stabilized monocarbonium ion requiring both chlorines to lie coplanar with the ring.¹ The entropy of activation is also very low, -36 \pm 3 e.u., reflecting an unusually great amount of extra ordering of solvent molecules in the doubly charged transition state. Activation entropies of some other arylmethyl halide solvolyses are listed in Table III. It is perhaps noteworthy that the only equally large value is for *p*-nitrobenzyl bromide, where the nitrogen bonded to the ring has a formal positive charge so that the carbonium ion would have at least formal dipositive character. Also in comparing it is well to remember that the 0.100 *M* LiNO₃ gives a considerable acceleration so that comparison with a medium of higher water content would be more valid.

TABLE III

Halide	Medium	ΔS^\ddagger , e.u.	Ref.
(CH ₃) ₅ C ₆ CCl ₃	85% dioxane, 0.1 <i>M</i> LiNO ₃	-36 \pm 3	This work
<i>p</i> Nitrobenzyl bromide	70% dioxane 90% dioxane	-36.8 -44.2	<i>a</i> <i>a</i>
PhCH ₂ Cl	50% acetone	-11.1	<i>b</i>
PhCHCl ₂	50% acetone	+0.4	<i>b</i>
PhCCl ₂	50% acetone	-1.0	<i>b</i>
Ph ₃ CCl	85% acetone	-17	<i>c</i>

^a J. W. Hackett and H. C. Thomas, *J. Am. Chem. Soc.*, **72**, 4962 (1950). ^b Calculated from data of J. Hine and D. E. Lee, *ibid.*, **73**, 22 (1951). ^c C. G. Swain and C. B. Scott, *ibid.*, **75**, 246 (1953).

Thus all data obtained to date are consistent with the hypothesis that the solvolysis of trichloromethylpentamethylbenzene proceeds through a dicarbonium

(4) The treatment follows that for the ordinary case as found in S. J. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p. 549 ff.

ion intermediate. Further work investigating substituent and medium effects is planned.

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RAMSTAD RESEARCH LABORATORIES
DEPARTMENT OF CHEMISTRY
PACIFIC LUTHERAN UNIVERSITY
TACOMA, WASHINGTON 98447

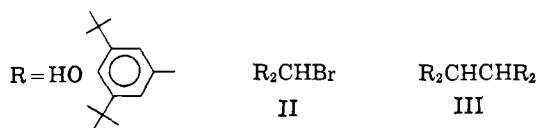
WILLIAM P. GIDDINGS
RICHARD F. BUCHHOLZ

RECEIVED DECEMBER 14, 1963

Bisgalvinoxyl,¹ a Stable Triplet

Sir:

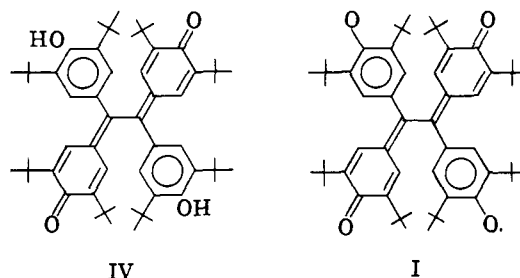
The study of interelectronic interactions in organic biradicals has been of interest in recent years.² We have been interested in systems containing individually stable radicals which may form a triplet electronic state rather than a chemical bond. An unusually stable type of radical has been studied by Coppinger.³ The synthesis⁴ and theoretical considerations⁵ of a potential triplet, based on Coppinger's galvinoxyl system, have been described but no further details have been published. We have synthesized bisgalvinoxyl (I) and found it to be a reasonably stable biradical. Its e.p.r. spectrum, in solid matrices at 77°K. and also in solution at room temperature, is interpretable as the spectrum of a biradical whose electrons are weakly coupled, resulting in a triplet electronic state.



Bromination of bis(3,5-di-*t*-butyl-4-hydroxyphenyl)-methane in benzene gave the benzhydryl bromide II. It was not isolated but its dehydrobromination product, the corresponding quinonemethide, could be obtained. Treatment of the crude benzene solution of II with finely divided copper metal gave the tetraphenylethane III in 70% yield. The assignment of structure III to the colorless crystalline reaction product, m.p. 330–332°⁶, rests on its elemental analysis,⁷ its infrared spectrum (hindered phenol at 2.7 μ , no bands other than CH below the weak phenyl band at 6.24 μ), and its ultraviolet spectrum⁸ ($\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 276 μ (log ϵ 3.89), 283 (3.81)).

It was not possible to oxidize III to a single compound with any of the usual reagents for phenol oxidation. Bromination (8 moles of Br₂) of III in benzene followed by treatment of the reaction mixture with aqueous acidic stannous chloride gave the brick red bisquinonemethide IV (ca. 45%, erratic), m.p. 306–308°^{6,9}. The infrared (λ_{max} 2.75, 6.30 μ) and ultra-

violet spectra⁸ ($\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 385 μ (log ϵ 3.48), 478 (4.26)) of the product are in accord with the assigned structure.



Oxidation of an ethereal solution of IV with aqueous alkaline ferricyanide followed by concentration under nitrogen gave bisgalvinoxyl (I) as a dark crystalline solid with a metallic luster. Iodometric titration of various samples of oxidized IV indicated that 1.8–1.9 equiv. of hydrogen had been removed from IV. The sole product of this reduction, isolated in 86% yield, was IV. The infrared spectrum of I has a strong band at 6.35 μ as does galvinoxyl itself.¹⁰ Its ultraviolet spectrum is quite complex and the absorption of a 10⁻³ *M* solution extends out to 1.2 μ .¹¹ The biradical is fairly stable as a solid but dilute solutions (10⁻³–10⁻⁴ *M*) in inert solvents are bleached by air in a few hours. The stability of I seems comparable to that of galvinoxyl. It is possible to write a singlet structure for I which requires the formation of a biscyclopropylidene group in the center of the molecule. However, the steric strain inherent in this structure would probably preclude its formation. The infrared spectrum of I rules out the presence of any appreciable amount of this tautomer.

The e.p.r. spectrum of I in several glasses at 77°K. (originally 10⁻² *M* solutions) clearly indicates that it is a triplet species. In 2-methyltetrahydrofuran, the medium which gave the best results, we were able to resolve lines of comparable intensity at ± 56 and ± 72 gauss, with respect to the strong $g = 2$ line (at 3280 gauss) of the remaining monoradical. There is also a weaker pair of lines at ± 110 gauss. The splitting of these $\Delta m = 1$ transitions, using a model of two point dipoles,¹² indicates that the average interelectronic distance in I is ca. 6 Å. The presence of several lines is a consequence of the asymmetry of the molecule.¹³ The spectrum also has a weak $\Delta m = 2$ line at 1635 gauss. Its low intensity is in accord with the weak interelectronic interaction deduced from the $\Delta m = 1$ region of the spectrum.

We followed the e.p.r. spectrum of a CH₂Cl₂ solution of IV as it was oxidized by PbO₂ in a sealed, degassed system. The five-line, cleanly resolved ($a = 1.23$ gauss) spectrum of the monoradical appeared immediately. As oxidation proceeded the line width increased and the hyperfine of the monoradical was superposed on a broad (ca. 40 gauss) absorption. This spectrum

(1) In choosing a name for this somewhat elaborate structure we have put aside the official (*Chemical Abstracts*) rules and followed the principle expressed by Professor Bartlett [P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962)].

(2) S. I. Weissman, *Ann. Rev. Phys. Chem.*, **12**, 151 (1961); E. A. Chandross and R. Kreilick, *J. Am. Chem. Soc.*, **85**, 2530 (1963); **86**, 117 (1964).

(3) G. M. Coppinger, *Tetrahedron*, **18**, 61 (1962).

(4) N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960).

(5) D. Kearns and S. Ehrenson, *ibid.*, **84**, 739 (1962).

(6) Melting with decomposition in an evacuated capillary, uncorrected.

(7) *Anal.* Calcd. for C₂₈H₃₆O₄: C, 82.15; H, 10.23. Found: C, 82.46, 82.44; H, 10.27, 10.33.

(8) Extinction coefficient recorded as log ϵ .

(9) *Anal.* Calcd. for C₂₈H₃₂O₄: C, 82.60; H, 9.80; mol. wt., 843. Found C, 82.23, 82.02; H, 10.30, 10.47; mol. wt., 830.

(10) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

(11) The spectrum shows λ C₆H₁₂ 265 sh μ (log ϵ 4.0), 302 (4.2), 335 sh (4.1), 387 (4.5), 410 sh (4.5), 435 (4.7), 565 (4.0), and 800–900 (3.0). The bands at 410 and 435 μ may be due to monoradical; for the spectrum of galvinoxyl see the paper quoted in ref. 1.

(12) For the analogous case in n.m.r. see G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

(13) The interpretation of the spectrum is based on the lines at ± 56 and ± 110 gauss. For the related spectrum of triplet naphthalene in a randomly oriented sample see W. A. Yager, E. Wasserman, and R. M. R. Cramer, *ibid.*, **37**, 1148 (1962). The lines at ± 72 gauss may be due to another conformation of the molecule which has been trapped in the glass.