

vapor phase chromatography. The tetrahydrocannabinol as obtained in the initial chromatography is not isomerized in the subsequent reactions. This was shown by the infrared and n.m.r. spectra, which remained unchanged during all purification steps, except for the disappearance of bands due to small impurities consisting mainly of cannabinol. Sulfur dehydrogenation of I gave cannabinol (II) in practically quantitative yield. This reaction defines the carbon skeleton of I.

The n.m.r. spectrum of I (see Table I) shows the presence of only one aliphatic methyl group and of

TABLE I^a

N.M.R. SPECTRUM OF TETRAHYDROCANNABINOL (I)	
Group	Chemical shift, p.p.m.
-CH ₃	0.88 (t) (3)
-CH ₃ (olefinic and α to O)	1.08 (s) 1.38 (s) 1.65 (s)
	(9)
C-3H	3.14 (br,d; $J = 10$ c.p.s.)
C-2H	6.35 (br,s) (1)
H (aromatic)	6.00 (d; $J = 2$ c.p.s.) (1)
	6.18 (d; $J = 2$ c.p.s.) (1)
-OH ^b	(1) ^b

^a Determined on a Varian A-60 spectrometer in CCl₄; values are given in p.p.m. relative to (CH₃)₄Si as internal standard; letters in parentheses denote singlet (s), doublet (d), triplet (t), broad (br), coupling constant (J); numbers in parentheses denote number of protons determined by integration of areas. ^b Peak disappears on addition of D₂O.

three methyl groups which are either α to an oxygen or are olefinic. This observation places the double bond in the Δ^1 or $\Delta^{1(6)}$ position. It is of interest to compare the chemical shifts of the C-2 and C-3 protons in tetrahydrocannabinol (I) and in cannabidiol⁶ (III). The olefinic proton in I (δ 6.35) is unshielded as compared to that in III (δ 5.59), while the reverse relationship exists as regards the C-3 protons (I, δ 3.14; III, δ 3.85). This can be readily understood by examination of molecular models of these two compounds. In cannabidiol, the aromatic ring, which can rotate freely, is most probably in the same plane as the C-3 hydrogen, which is therefore unshielded.⁷ In tetrahydrocannabinol the additional ring tilts the aromatic ring, so that the latter is now in (or nearly in) the same plane as the olefinic proton, which is therefore unshielded. Such an effect is possible only if the double bond occupies the Δ^1 position and the protons on the two asymmetric carbons are *trans*, *i.e.*, if tetrahydrocannabinol possesses structure I.

This structural determination is supported by a partial synthesis. A solution of cannabidiol (III) in absolute ethanol containing 0.05% hydrochloric acid on boiling for 2 hr. gives a mixture of the starting material and I. It can be assumed that these rather mild conditions cause no isomerization of the asymmetric centers or of the double bond.

Tetrahydrocannabinol (I) shows strong activity in the ataxia test⁸ in dogs. A full report will be submitted elsewhere by Dr. H. Ederly.

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THE DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

Y. GAONI
R. MECHOULAM

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An Improved Method of Calculating Spin Properties from Spin-Polarized Wave Functions

Sir:

Amos and Hall¹ have given formulas for π -electron spin properties computed by the application of an annihilation operator to a single determinant wave function. They assumed that the annihilator could be taken as idempotent and that it commuted with the spin density operator. We would like to report π -electron spin properties, the spin density ρ , and the expectation value $\langle S^2 \rangle$, computed with new formulas which remove these assumptions and which correspond to integrations in which the annihilator operates upon the single determinant everywhere it appears in an integrand.

The single determinant we use is a spin-polarized open-shell (LCAO-MO-SCF)² function, *i.e.*, one having different molecular orbitals for electrons with different spins. Let p electrons have α -spin and q β -spin (with $p > q$). The major spin component of the determinant will have multiplicity $2s + 1$ where $s = 1/2(p - q)$ but there will also be spin states of higher multiplicities included in the wave function. Because of their presence, spin properties deduced from the single determinant will only approximate those of its major components. Considerable improvement might be expected if the most important cause of this, the spin state with multiplicity $2s + 3$, were removed from the wave function by applying the annihilator $[S^2 - (s + 1)(s + 2)]$ since the remainder of the spin components usually have negligible effect.¹

Spin densities and $\langle S^2 \rangle$ for a number of π -electron radicals when this is done accurately are shown in Tables I and II and subscripted (aa). The same properties computed using the approximate formulas of Amos and Hall are also given and subscripted (asa). For comparison we include the results deduced from the original determinant (sd) and from Hückel orbitals (h). The calculations were carried out on an I.B.M. 7090 computer with the Parr-Pariser³ integral approximations; all C-C bond lengths were assumed equal. Full details of the calculations and the lengthy new formulas will be given later as will a large number of applications.

As can be seen from the tables, the errors involved in the approximate formulas are small but so are some of the quantities to be calculated. In particular we note that $\langle S^2 \rangle_{asa}$ can sometimes fall below $s(s + 1)$, which is certainly wrong, whereas $\langle S^2 \rangle_{aa} > s(s + 1)$ as must be true. The annihilated single determinant must be very nearly the pure major spin component since $\langle S^2 \rangle_{aa}$ is very close to $s(s + 1)$ for the radicals considered here. For the single determinant we find $\langle S^2 \rangle_{sd}$ much larger than $s(s + 1)$. From Table I we see that negative spin densities occur in ρ_{aa} , ρ_{asa} , and ρ_{sd} at carbon atoms for which $\rho_h = 0$. At these atoms $\rho_{aa} \approx$

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(2) J. Pople and R. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

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(6) R. Mechoulam and Y. Shvo, *Tetrahedron*, **19**, 2073 (1963).

(7) L. M. Jackman, "N.M.R. Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 125.

(8) S. Loewe, *Arch. Exptl. Pathol. Pharmacol.*, **211**, 175 (1950).

TABLE I
 π -ELECTRON SPIN DENSITIES

		ρ_{exp}	ρ_{aa}	ρ_{aaa}	ρ_{sd}	ρ_h
Allyl	C ₁	+0.58 ^a	+0.547	+0.604	+0.651	+0.5
	C ₂	-0.16	-0.093	-0.208	-0.302	0
Pentadienyl	C ₁	+0.349 ^b	+0.383	+0.471	+0.545	+0.333
	C ₂	-1.03	-0.094	-0.211	-0.307	0
	C ₃	+0.506	+0.422	+0.479	+0.524	+0.333
Naphthalene ⁻	C ₁	+0.218 ^c	+0.214	+0.239	+0.262	+0.181
	C ₂	+0.081	+0.048	+0.037	+0.026	+0.069
	C ₉		-0.024	-0.051	-0.076	0
Naphthalene*	C ₁	+0.418 ^d	+0.443 ^e	+0.463	+0.480	+0.362
	C ₂		+0.095	+0.098	+0.101	+0.138
	C ₉		-0.077	-0.122	-0.162	0

^a Reference 4, C₁ is end carbon. ^b Reference 5, data is for cyclohexadienyl radical. ^c Reference 6, assumes $Q = 22.5$ as for benzene⁻. ^d Reference 7, spin density in phosphorescent triplet state. ^e Computed for lowest π -electron triplet state.

TABLE II
 EXPECTATION VALUE OF S^2

	$s(s+1)$	$(S^2)_{aa}$	$(S^2)_{aaa}$	$(S^2)_{sd}$
Allyl	0.75000	0.75000	0.75000	0.84133
Pentadienyl	0.75000	0.76762	0.73938	0.95625
Naphthalene ⁻	0.75000	0.75147	0.74913	0.79619
Naphthalene* ^a	2.00000	2.00169	1.99886	2.06671

^a Lowest π -electron triplet state.

$\frac{1}{3}\rho_{sd}$. This is a consequence of the symmetrical way in which the underlying almost closed shell molecular orbitals split, as will be elaborated in a subsequent paper. Finally, we find that ρ_{exp} generally falls closer to ρ_{aa} than to ρ_h or ρ_{sd} . It is encouraging that with the Parr-Pariser approximations, which give a qualitatively correct prediction of spectra for closed shell aromatics, the method described here can give a good account of the spin density distribution in π -electron radicals.

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BELL TELEPHONE LABORATORIES
 INCORPORATED
 MURRAY HILL, NEW JERSEY
 MATHEMATICS DEPARTMENT
 NOTTINGHAM UNIVERSITY
 ENGLAND

LAWRENCE C. SNYDER
 TERRY AMOS

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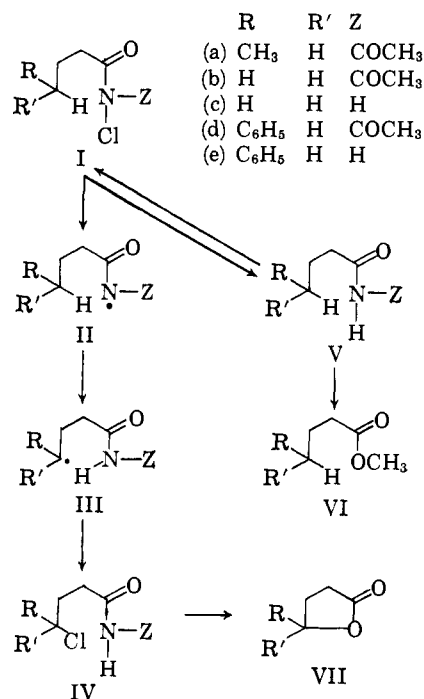
Photochemical Rearrangement of N-Chloroimides to 4-Chloroimides. A New Synthesis of γ -Lactones

Sir:

The hydrogen-abstracting, chain-carrying species in aliphatic¹ as well as in allylic and benzylic² halogenations by N-halosuccinimides seems normally to be the halogen atom, rather than the succinimidyl radical. However, since intramolecular rearrangements are often more rapid than the corresponding intermolecular reactions, it seemed possible that acyclic imidyl radicals such as II (Z = COCH₃) might rearrange (to III, Z = COCH₃) at rates fast enough to permit selective introduction of functional groups at the γ -position of imides. Such a rearrangement would be analogous to the Hofmann-Löffler reaction³ and to a number of recently discovered rearrangements of oxy radicals.⁴

(1) P. S. Skell, D. L. Tuleen, and P. D. Read, *J. Am. Chem. Soc.*, **85**, 2850 (1963).

(2) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963), and references cited.



In confirmation of this hypothesis we now present evidence that N-chloroimides I (Z = COCH₃), having primary, secondary, and benzylic γ -hydrogen, do indeed afford their γ -chloro isomers when irradiated under mild conditions. Under these conditions N-chloroamides (I, Z = H) do not appear to rearrange. This interim report is prompted by the recent communication by Barton and Beckwith⁵ of a new synthesis of γ -lactones from primary and secondary amides by irradiation in the presence of excess iodine and lead tetraacetate and subsequent alkaline hydrolysis. A rearrangement of N-iodoamides similar to that proposed here, but involving amidyl radicals (RCONH \cdot), was suggested as the key step.

N-Chloro-N-acetyl amides do not seem to have been made before. After some disappointing attempts to N-chlorinate N-acetyl amides⁶ with hypochlorous acid, which gave products with too much active chlorine, it was found that pure N-chloro-N-acetyl amides I are readily available in excellent yields from the N-acetyl amides by treatment with excess *t*-butyl hypochlorite in methanol.⁷

N-Chloroimides were irradiated, neat or in solution in Freon-11^{8a} or -113,^{8b} at about 2° until the active chlorine content was negligible. The yields of the major products were determined by gas chromatography after conversion of 4-chloroimides to γ -lactones and other imides to methyl esters by successive treatments with boiling 10% sulfuric acid and diazomethane.⁹ The esters VI, the major by-products, which arose by dechlorination of the starting material, and the γ -lactones VII were collected and identified by comparing their

(3) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

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(5) D. H. R. Barton and A. J. L. Beckwith, *Proc. Chem. Soc.*, 335 (1963).

(6) P. Dunn, E. A. Parkes, and J. B. Polya, *Rec. Trav. Chim.*, **71**, 676 (1952).

(7) This reagent was used by S. S. Israelstam, *J. S. African Chem. Inst.*, **9**, 30 (1956), for a preparation of N-chloro-*p*-toluenesulfonamide.

(8) (a) Fluorotrichloromethane; (b) 1,1,2-trichlorotrifluoroethane.

(9) The yields reported are minimal, being based on the assumption that these conversions are quantitative.