

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.

(4) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(5) R. W. Fessenden and R. H. Schuler, *ibid.*, **38**, 773 (1963).

(6) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(7) C. A. Hutchison and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).

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

LAWRENCE C. SNYDER
TERRY AMOS

RECEIVED FEBRUARY 20, 1964

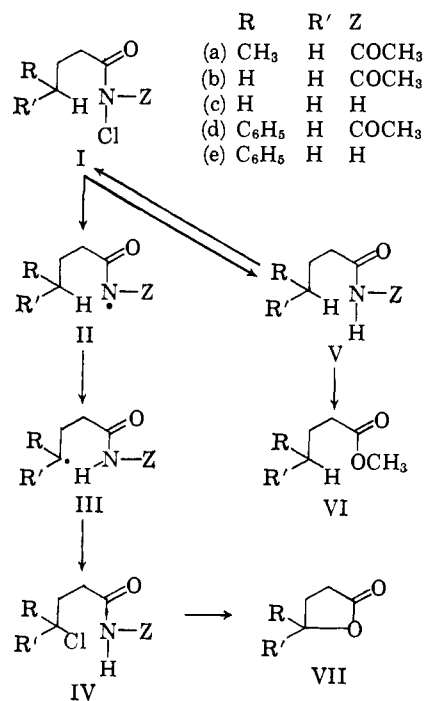
Photochemical Rearrangement of N-Chloroimides to 4-Chloroimides. A New Synthesis of γ-Lactones

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·), 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).

(4) See D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962), for a recent review.

(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.

infrared spectra and retention volumes with those of authentic samples.

N-Chloro-N-acetylvaleramide¹⁰ (Ia), a pale yellow oil, ν (neat) 1730 cm^{-1} , was prepared in 91% yield from N-acetylvaleramide (Va), m.p. 68°, ν (CHCl_3)¹¹ 3400, 3270, 3210, 3150, 1745, and 1710 cm^{-1} . Irradiation of pure Ia under helium in a Rayonet chamber reactor (3500 Å. lamps)^{12a} augmented by a Victor 500-watt mercury vapor lamp^{12b} for 1.5 hr. gave a solid containing 4-chloro-N-acetylvaleramide (IVa) in 67% yield, N-acetylvaleramide (Va) (17%), and several minor by-products. The yield of IVa was lower when only one light source was employed (Rayonet, 57%; Victor, 48%), or, using just the Victor lamp, when Ia was in solution in Freon-11 or -113 (30–60%, variable) or toluene (13%). Raising the temperature also lowered the yield, while neither air nor addition of cyclohexene had a marked effect.

In the following irradiation experiments the yields of 4-chloroimides can undoubtedly be improved, since they were done under conditions (dilute Freon-11 solution, Victor lamp) which gave only 35% of IVa from Ia.

N-Chloro-N-acetylbutyramide (Ib), ν (neat) 1725 cm^{-1} , was obtained in 93% yield from N-acetylbutyramide (Vb), m.p. 64° (lit.⁶ m.p. 119°),¹⁰ ν (CHCl_3) 3400, 3270, 3210, 3160, 1740, and 1700 cm^{-1} . Irradiation gave 27% 4-chloroimide IVb and 40% dechlorination to Vb. The beneficial effect of the N-acetyl group on rearrangement of a primary hydrogen is clear from the results of irradiating N-chlorobutyramide¹³ under identical conditions. Only 30% of the active chlorine disappeared in 18 hr. and a mere 3% of this went to the 4-position, very likely by intermolecular chlorination.

N-Acetyl-4-phenylbutyramide (Vd), m.p. 96.5°, ν (CHCl_3) 3400, 3260, 3200, 1735, 1710, 1675, and 1595 cm^{-1} , gave N-chloroimide Id, m.p. 30–33°, ν (neat) 1725 cm^{-1} , in 91% yield. Irradiation of Id gave 37% of the 4-chloro isomer and 38% Vd. In contrast crude N-chloro-4-phenylbutyramide (Ie), ν (Nujol) 3100 and 1660 cm^{-1} (*Anal.* Found: active Cl, 16.4), was resistant to light, requiring 8 hr. to decompose at 25°, and yielded only half as much 4-chloroamide IVe (19%). The by-products included Ve (32%) and serious amounts of products not formed from the N-chloro-N-acetyl- amide Id; these are thought to be the result of intermolecular chlorination. Clearly the N-acetyl group aided rearrangement involving benzylic γ -hydrogen; it is quite probable that the benzylic chlorination which took place when Ie was irradiated was by the normal chlorine atom mechanism.

The reason why a second carbonyl group on N-Cl promotes rearrangement is not yet known. It puts a stronger partial positive charge on the nitrogen atom, giving the presumed intermediate II a closer resemblance to the fully charged aminium radical intermediate³ of the Hofmann-Löffler reaction. It is hoped that more insight into these phenomena will be gained in the

(10) Satisfactory analytical data have been obtained for N-acetylbutyramide and for all new compounds described.

(11) The infrared spectra of Nujol mulls of all N-acetyl amides studied to date are so different from those of solutions as to be unrecognizable. ν (Va) (Nujol) 3265, 3175, 1737 cm^{-1} .

(12) (a) Southern N. E. Ultraviolet Co., Middletown, Conn. We thank Professor G. W. Griffin (Tulane University) for lending us this equipment. (b) Victor X-Ray Corp., Chicago, Ill.

(13) E. Roberts, *J. Chem. Soc.*, **123**, 2779 (1923).

course of attempts now in progress to further define the scope, limitations, and mechanisms of the rearrangement.

Acknowledgments.—We thank Mr. Clifford Parent for excellent technical assistance. A. W. is grateful to the Cancer Association of Greater New Orleans, Inc., for a summer fellowship.

(14) National Science Foundation Undergraduate Research Participant 1963–1964.

HEALTH RESEARCH CENTER
DEPARTMENT OF CHEMISTRY
LOYOLA UNIVERSITY, NEW ORLEANS
NEW ORLEANS, LOUISIANA 70118

ROBERT C. PETTERSON
ANTHONY WAMBSGANS¹⁴

RECEIVED FEBRUARY 1, 1964

The Formation of 2,4-Dimethoxy-6-methylphenylacetone from 3,5-Dimethoxybenzyl Isopropenyl Ether. A New Variant of the Claisen Rearrangement

Sir:

The thermal conversion of allyl vinyl ethers to 5-pentenals, of importance especially when the vinylic double bond is part of an aromatic nucleus, has not been observed when the allylic double bond is part of an aromatic system.¹ Thus, benzyl α -styryl ether upon heating is converted to β -phenylpropiophenone rather than to *o*-tolylacetophenone,² and benzyl vinyl ether itself gives β -phenylpropionaldehyde rather than *o*-tolylacetaldehyde.³ We wish to report that 3,5-dimethoxybenzyl isopropenyl ether, upon heating to 240° in an evacuated sealed tube for 1 hr., forms about 80% of 2,4-dimethoxy-6-methylphenylacetone, which can be purified by high temperature gas chromatography and recognized by its n.m.r. spectrum (peaks at τ 6.26, 3.75, 3.71, 3.53, 2.17, and 1.96 with relative intensities of 2.1, 3.0, 3.0, 1.9, 3.1, and 2.9, respectively). About 10% of 3,5-dimethoxybenzylacetone was also isolated. *m*-Methoxybenzyl isopropenyl ether gave a 50–50 mixture of the two corresponding ketones, again recognized by the n.m.r. spectrum; in this case only the benzylacetone could be isolated in pure form. A further number of benzyl isopropenyl

TABLE I
PROPERTIES OF SOME BENZYL VINYL ETHERS, THEIR PRECURSORS, AND PRODUCTS

R ₁	R ₂	M.p. of acid, °C.	n_D^{25}			M.p. of semicarbazone, °C.
			1	11	111	
H	H	121–123	a	a
CH ₃	H	122–123 ^b	1.5126	1.5112 ^c	...	144–145 ^d
CH ₃	<i>p</i> -CH ₃	153–155	1.5077	1.5145	...	155–156
CH ₃	<i>p</i> -Cl	146–147	1.5245	1.5315	...	155–158
CH ₃	<i>p</i> -OCH ₃	151–152 ^e	<i>f</i>	M.p. 10 ^o ^e	...	167–168 ^e
CH ₃	<i>m</i> -OCH ₃	115–116	1.5181	1.5220	<i>f</i>	125–127
CH ₃	3,5-Di-OCH ₃	172–173	M.p. 37 ^o	^h	1.5273 ^g	139–140

^a Recognized by comparison of its infrared spectrum with that of the known compounds. ^b Lit. 121–122° [W. Autenrieth, *Ber.*, **29**, 1639 (1896)]. ^c Lit. n_D^{25} 1.511 [A. Klages, *Ber.*, **37**, 2301 (1904)]. ^d Lit. 142° (ref. c); oxime m.p. 85–87°, lit. 85–88° [P. W. Neber and E. Uber, *Ann.*, **467**, 52 (1928)]. ^e See ref. 5. ^f Not isolated in pure form. ^g M.p. of semicarbazone, 178–179°. ^h Not measured.

(1) A closely related case was observed by S. M. McElvain, H. I. Anthes, and S. H. Shapiro [*J. Am. Chem. Soc.*, **64**, 2525 (1942)], who found benzyl *o*-tolylacetate to be the product upon treatment of dibenzyl bromoacetate with potassium *t*-butoxide.

(2) K. B. Wiberg, R. R. Kintner, and E. L. Motell, *ibid.*, **85**, 450 (1963).
(3) A. W. Burgstahler, L. K. Gibbons, and I. C. Nordin, *J. Chem. Soc.*, 4986 (1963).