

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.

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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

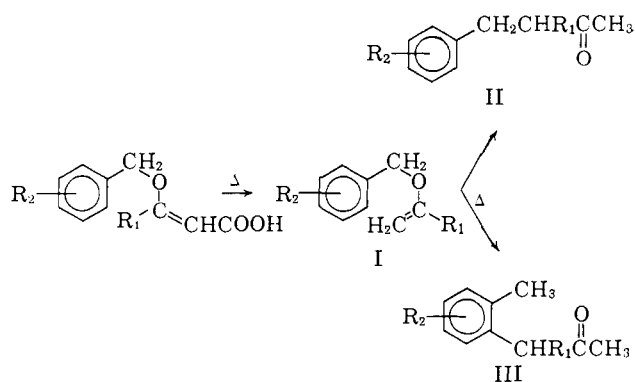
R ₁	R ₂	M.p. of acid, °C.	n_D^{25}			M.p. of semicarbazone, °C.
			I	II	III	
H	H	121–123	^a	^a
CH ₃	H	122–123 ^b	1.5126	1.5112 ^c	...	144–145 ^d
CH ₃	<i>p</i> -CH ₃	153–155	1.5077	1.5145	...	155–156
CH ₃	<i>p</i> -Cl	146–147	1.5245	1.5315	...	155–158
CH ₃	<i>p</i> -OCH ₃	151–152 ^e	^f	M.p. 10 ^g	...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

ethers yielded benzylacetones only; the n.m.r. spectra of these products closely corresponded to that published for the parent compound.⁴ The ethers were prepared by the decarboxylation of the corresponding crotonic acids as described earlier⁵; the properties of the principal compounds studied are shown in Table I.⁶



We are studying the mechanisms of these two competing rearrangements with a view to the possibility that either might be promoted as desired, and, furthermore, to consider the question whether the formation of *o*-methylbenzyl ketones involves the 2,4-cyclohexadiene *exo*-methylenes as intermediates.

Acknowledgment.—We thank Dr. S. Seltzer and Professor P. Lauterbur for help with the n.m.r. spectra, and the Research Corporation for financial support.

(4) S. S. Danyluk, *Can. J. Chem.*, **41**, 387 (1963).

(5) W. J. le Noble and P. J. Crean, *J. Org. Chem.*, **27**, 3875 (1962).

(6) Satisfactory elemental analyses were obtained for all new compounds described in this paper (Schwarzkopf Microanalytical Laboratory, New York, N. Y.); the neutralization equivalents of the acids were also measured and found to agree with predicted values.

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A New Method of Aromatic Substitution Yielding Unusual Orientation. Amination with N-Haloamines Catalyzed by Aluminum Chloride

Sir:

We wish to report a novel method of aromatic substitution which results in unusual orientation. The reaction involves amination of aromatic compounds with N-haloamines in the presence of aluminum chloride catalyst. Under these conditions, "*ortho-para*" directive groups produced *meta* derivatives. Apparently, this is the first example of essentially complete *meta* orientation by the familiar *ortho-para* directors.

Aminations were carried out with an excess of the aromatic component, a 1.7–2 molar ratio of catalyst to N-chloramine reactant, and an aryl halide additive. Treatment of toluene with di-^{1,2} or trichloramine^{1,2} and aluminum chloride gave *m*-toluidine in 25% yield at temperatures selected from the range –35 to 15°. Similarly, at reaction temperatures in the vicinity of 110°, N-chloromethylamine³ yielded N-methyl-*m*-toluidine, although in somewhat lower yield. The unusual

orientation was also obtained with dichloramine and other aromatic compounds which are classified as *ortho-para* orienters: *m*-chloroaniline from chlorobenzene and 3,5-xylidine from *m*-xylene.⁴ In general, the *meta* derivative comprised at least 75% of the basic product, with less than 2% of isomeric amines. Distillation residue and, in some cases, high boiling material made up the remainder. The reaction may be illustrated by the equation



In control experiments in which aluminum chloride was omitted from the toluene and *m*-xylene reaction mixtures, no aromatic amine was formed. The presence of haloaromatic compounds was found to exert a profound influence on the yield of basic product. Best results were obtained with *o*-dichlorobenzene and 1,2,4-trichlorobenzene. For example, a 20% yield of *m*-toluidine was obtained at 10° from dichloramine and toluene in the presence of *o*-dichlorobenzene, in contrast to a 12% yield in the absence of the haloaromatic diluent. Failure to observe this general mode of substitution previously may be due to the various, strictly defined properties requisite of the reagents, catalyst, and solvent.

In order to ascertain whether or not the isolated amines were formed by rearrangement, the *ortho* and *para* isomers were subjected to simulated reaction conditions. There was no evidence of isomerization in any of these cases.^{5,6}

The major product of the toluene reactions consisted of chlorotoluenes, identified by comparison with authentic materials. The isomer distribution (*o*:*m*:*p* = 68:1:31 with dichloramine) indicates an electrophilic mechanism for the halogenation pathway.

Direct amination has also been effected with other attacking species, such as hydroxylamine derivatives^{6–8} and hydrazoic acid,^{5,9} under Friedel–Crafts conditions. In contrast, these techniques afford orientations characteristic of electrophilic substitution.

The principal significance of our contribution relates to the theory of aromatic substitution and to the synthesis of aromatic isomers difficult to obtain by classical routes. Extension of this novel method to other aromatic types and other substituting entities comes to mind. The reaction scope, as well as the theoretical aspects, will be treated more fully in forthcoming publications.

Amination of Toluene with Dichloramine.—Solutions of dichloramine in toluene were prepared from calcium hypochlorite¹⁰ and ammonium acetate by a modification of the procedure of Coleman.³ The concentration of dichloramine was determined by Volhard analysis. Appropriate precautions should be taken in handling N-haloamines.

A cold toluene solution (150 ml.) of dichloramine (0.141 mole) was added, with stirring during 45 min.,

(4) All of the products were characterized by comparison with authentic materials. Yields are based on the haloamines.

(5) P. Kovacic, R. L. Russell, and R. P. Bennett, *J. Am. Chem. Soc.*, **86**, 1588 (1964).

(6) P. Kovacic, R. P. Bennett, and J. L. Foote, *ibid.*, **84**, 759 (1962); P. Kovacic and J. L. Foote, *ibid.*, **83**, 743 (1961).

(7) P. Kovacic and R. P. Bennett, *ibid.*, **83**, 221 (1961); P. Kovacic, R. P. Bennett, and J. L. Foote, *J. Org. Chem.*, **26**, 3013 (1961).

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(9) G. M. Hoop and J. M. Tedder, *J. Chem. Soc.*, 4685 (1961).

(10) M. J. Teherniak, *Bull. Soc. Chim.*, [2] **25**, 160 (1876).

(1) R. M. Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929).

(2) Adapted from the method of W. A. Noyes, *Inorg. Syn.*, **1**, 65 (1939).

(3) Adapted from the procedure of G. H. Coleman, *J. Am. Chem. Soc.*, **55**, 3001 (1933).