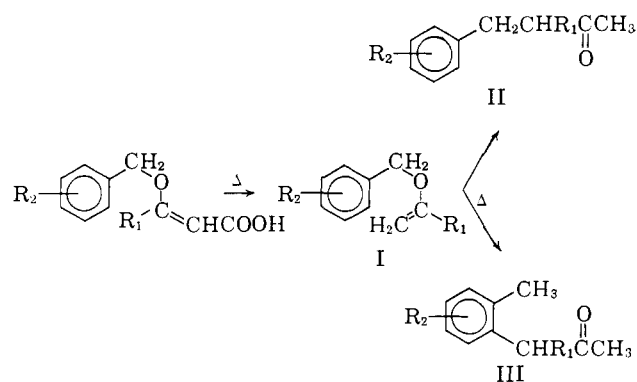


ethers yielded benzylacetones only; the n.m.r. spectra of these products closely corresponded to that published for the parent compound.⁴ The ethers were prepared by the decarboxylation of the corresponding crotonic acids as described earlier⁵; the properties of the principal compounds studied are shown 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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RECEIVED FEBRUARY 24, 1964

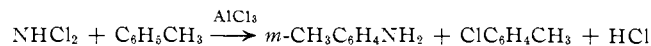
A New Method of Aromatic Substitution Yielding Unusual Orientation. Amination with N-Haloamines Catalyzed by Aluminum Chloride

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).

(8) R. N. Keller and P. A. S. Smith, *J. Am. Chem. Soc.*, **66**, 1122 (1944).

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

(10) M. J. Tcherniak, *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).

to a mixture of toluene (225 ml.), *o*-dichlorobenzene (0.363 mole), and aluminum chloride (0.242 mole) at -35° . After an additional 45 min. at -35° , the reaction mixture was added to dilute hydrochloric acid. The layers were separated, and the organic phase was washed with dilute hydrochloric acid. Following extraction of the combined acid solutions with ether, the aqueous portion was made basic in the cold with caustic. Ether extraction, removal of the solvent, and then distillation provided 3.73 g. of *m*-toluidine (25% yield), b.p. $79-83^\circ$ (9 mm.), lit.¹¹ b.p. $95-97^\circ$ (16 mm.). The infrared spectrum was identical with that of the authentic substance. Additional characterization (n_D^{21} 1.5679, lit.¹² n_D^{20} 1.5686) was carried out with corresponding material obtained from another experiment. The benzoyl derivative melted at $123-124^\circ$, lit.¹³ m.p. 125° . The distillation residue consisted of 0.67 g.

(11) R. L. Russell, M.S. Thesis, Case Institute of Technology, 1964.

(12) I. Heilbron and H. M. Bunbury, Ed., "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 522.

(13) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 289.

(14) (a) National Science Foundation Fellow, 1962-1963; (b) National Science Foundation Fellow, 1958-1960.

(15) National Science Foundation Undergraduate Summer Fellow, 1963.

(16) Support by a grant from the National Science Foundation is acknowledged.

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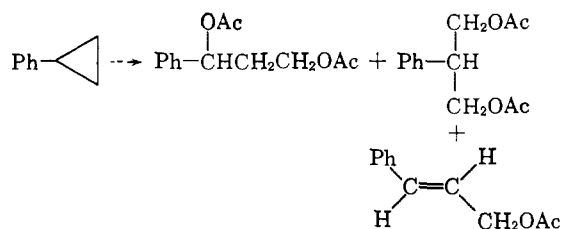
RECEIVED NOVEMBER 22, 1963

The Cleavage of Cyclopropanes by Lead Tetraacetate

Sir:

Lead tetraacetate in acetic acid cleaves cyclopropanes to yield 1,3-diacetates and unsaturated monoacetates. The reaction has been found to be general for alkyl and aryl cyclopropanes.

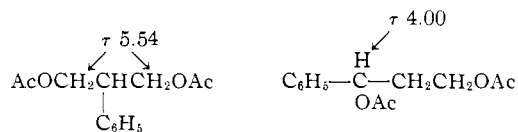
Phenylcyclopropane is cleaved by lead tetraacetate in acetic acid at 75° . A quantitative yield (greater than 98% by vapor phase chromatography) based on phenylcyclopropane is obtained. 1-Phenyl-1,3-diacetoxypropane, 2-phenyl-1,3-diacetoxypropane, and cinnamyl acetate are obtained in 63, 5, and 32% yields, respectively.



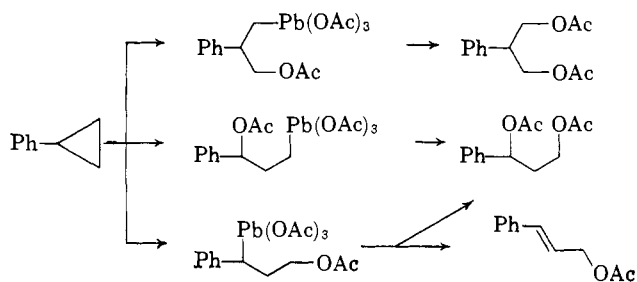
In a typical experiment, 0.50 g. (0.0042 mole) of phenylcyclopropane was dissolved in 10 ml. of anhydrous acetic acid and 1.00 g. (0.0032 mole) of recrystallized lead tetraacetate was added. The lead tetraacetate was not soluble at 75° under the reaction conditions, but gradually disappeared as the reaction proceeded. After 10 hr., water was added to the reaction and the aqueous layer extracted with ether. No lead dioxide was observed when water was added to the reaction, thus indicating complete conversion

of the lead tetraacetate into lead diacetate. Vapor phase chromatography of the ethereal solution showed two peaks in addition to the unreacted phenylcyclopropane.¹

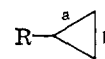
The reaction products were examined on columns of varying polarity. Only two peaks were found. The peak with the shortest retention time on a 6 ft. column of 20% SF-96 on chromosorb W was shown to be identical with that of *trans*-cinnamyl acetate. The n.m.r. and infrared spectra of the collected "peak" are identical with those of an authentic sample of *trans*-cinnamyl acetate. The material with the longer retention time consists of two components which were inseparable on a variety of columns. Although the retention times of 1-phenyl-1,3-diacetoxypropane and 2-phenyl-1,3-diacetoxypropane are slightly different, known mixtures of the two compounds merge to form broad unsymmetrical peaks. Collection of the "merged peak" and examination of the n.m.r. spectrum showed the presence of both suspected products. The entire spectrum was consistent with that of a mixture of only two components. The benzylic proton of 1-phenyl-1,3-diacetoxypropane (triplet at τ 4.00) and the four methylene protons (doublet at τ 5.54) of 2-phenyl-1,3-diacetoxypropane are in mutually exclusive regions from all other protons of both compounds. The composition of the mixture was determined by planimetry of the τ 4.00 and 5.54 regions and a correction factor of four was applied.



A mechanism which is consistent with the product analysis and relative rates of reaction involves electrophilic attack of lead tetraacetate or some derived species such as $\text{Pb}(\text{OAc})_3^+$ on the cyclopropane ring followed by decomposition of the γ -acetoxy organolead intermediates. Some degree of positive charge should



be generated at the carbon adjacent to the point of attack of the lead species, and substituents attached to the aromatic nucleus should thus influence the course of the reaction. The amount of cleavage at bond b relative to bond a should increase as the electron-withdrawing character of the aromatic nucleus increases.



R = phenyl, *p*-bromophenyl, and ethyl

(1) An internal standard in a separate identical reaction showed that the sum of the reaction products and the unreacted phenylcyclopropane was in agreement within 98% with the initial amounts of phenylcyclopropane and lead tetraacetate.