

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.

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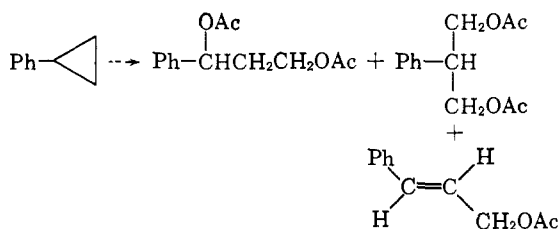
RECEIVED NOVEMBER 22, 1963

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.

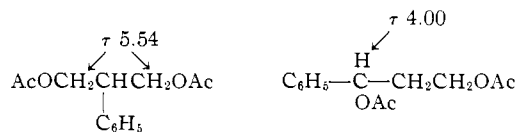
Phenylcyclopropane is cleaved by lead tetraacetate in acetic acid at 75° . A quantitative yield (greater than 98% by vapor phase chromatography) based on phenylcyclopropane is obtained. 1-Phenyl-1,3-diacetoxypropane, 2-phenyl-1,3-diacetoxypropane, and cinnamyl acetate are obtained in 63, 5, and 32% yields,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



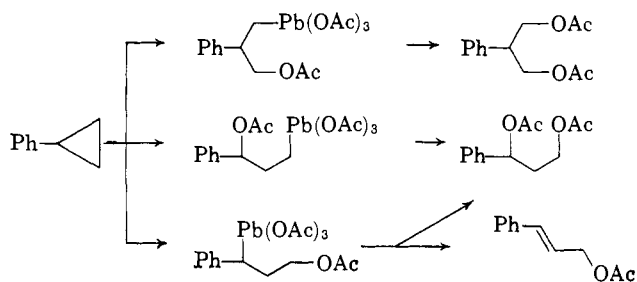
In a typical experiment, 0.50 g. (0.0042 mole) of phenylcyclopropane was dissolved in 10 ml. of anhydrous acetic acid and 1.00 g. (0.0032 mole) of recrystallized lead tetraacetate was added. The lead tetraacetate was not soluble at 75° under the reaction conditions, but gradually disappeared as the reaction 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

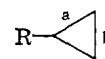
The reaction products were examined on columns of varying polarity. Only two peaks were found. The peak with the shortest retention time on a 6 ft. column of 20% SF-96 on chromosorb W was shown to be identical with that of *trans*-cinnamyl acetate. The n.m.r. and infrared spectra of the collected "peak" 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.



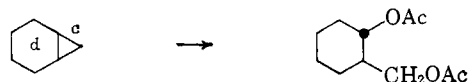
R = phenyl, *p*-bromophenyl, and ethyl

(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.

p-Bromophenylcyclopropane yields a higher amount of symmetrical cleavage relative to unsymmetrical cleavage than does phenylcyclopropane. An exact number is not available at this time due to decomposition of the products on the v.p.c. column at the high temperatures necessary for analysis and collection. However, analysis of the n.m.r. spectrum of the crude reaction product indicates that the ratio of cleavage at bond a to bond b is 4. Furthermore *p*-bromophenylcyclopropane reacts slower than phenylcyclopropane by a factor of approximately 2. The kinetics of this system have not been investigated and the order of the reaction is not known. The observations with regard to rates have been made on heterogeneous parallel reactions in which the product composition was determined.

Alkyl-substituted cyclopropanes react slower than phenylcyclopropane. The ratio of unsymmetrical to symmetrical cleavage in ethylcyclopropane is approximately 6. Thus alkyl groups, which are less capable than phenyl of stabilizing an incipient positive charge, allow increased cleavage at bond b. The reactivity of aryl- and alkyl-substituted cyclopropanes and the product composition as a function of substitution will be published in a full paper.

The stereochemistry of the reaction with bicyclic systems is currently under investigation. Criegee² reported that the strained bicyclo[2.1.0]pentane is cleaved by lead tetraacetate. Two fractions were separated by distillation. Saponification of the higher boiling fraction gave *cis*-1,3-cyclopentandiol. We have found that norcarane is cleaved at bonds c and d to yield unsaturated monoacetates and saturated diacetates containing 6- and 7-membered rings. The major product is *trans*-2-acetoxymethylcyclohexyl acetate. The *cis* isomer has not been detected although



the v.p.c. and n.m.r. methods employed do not allow the detection of this substance below 3% of the reaction mixture. The stereochemistry of 1,3-diacetoxycycloheptane which is also obtained has not been established.³

Further experiments to reconcile the differences between the work of Criegee and our observations is underway.

Acknowledgment.—The authors wish to thank Dr. Lloyd Dolby for authentic samples of *cis*- and *trans*-2-acetoxymethylcyclohexyl acetate.

(2) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 417 (1957).

(3) The n.m.r. spectrum of this compound indicates that two equivalent acetate methyl groups of equal intensity are contained in the molecule. This suggests that this product is the *trans* isomer.

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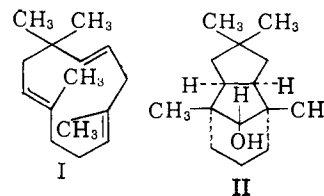
RECEIVED FEBRUARY 8, 1964

Total Synthesis of α -Caryophyllene Alcohol

Sir:

Acid-catalyzed hydration of humulene (I) or commercial "caryophyllene" (which generally contains humulene) under various conditions leads to an interesting and long-known saturated tricyclic alcohol which has been designated as α -caryophyllene alcohol

in the terpene literature.¹ This substance has recently been assigned structure II on the basis of an X-ray diffraction study.² We report here a total synthesis of α -caryophyllene alcohol by a short process consisting of three steps from known compounds.



Slow addition by syringe of a solution of 3-methyl-2-cyclohexenone³ in pentane to a solution of 4,4-dimethylcyclopentene⁴ (*ca.* -10°) under ultraviolet irradiation, using the apparatus previously described,⁵ led to the formation of three isomeric 1:1 adducts of structure III, A, B, and C, in the ratio 74:12:14, respectively, as the only volatile products.⁶ Passage of this mixture in ether through a column of neutral alumina (Woelm, activity I) caused isomerization of C to B and, hence, these ketones differ only in configuration at the methine carbon α to the carbonyl group; isomer C possesses a *trans* 4-6 fusion and B a *cis* 4-6 fusion (see ref. 5). Isomer A was not changed by this treatment and is assigned a *cis* 4-6 fusion. Since isomer A predominates threefold over B plus C, this was taken to be the *cis-anti-cis* adduct and was used for the synthesis of II. The ketone IIIA [b.p. *ca.* 75° (0.08 mm.), infrared maximum 5.88μ (CCl_4), found: C, 81.15; H, 10.69, n.m.r. peaks due to three unsplit methyl groups at 0.80, 1.00, and 1.11 p.p.m. (all shifts are downfield from tetramethylsilane for solutions in CCl_4 at 60 Mc.)], was purified by vapor phase chromatography.⁷

Reaction of the pure ketone IIIA with methyl lithium produced a crystalline tertiary alcohol, m.p. $97-98^{\circ}$; hydroxyl absorption at 2.67 and 2.84μ in the infrared (CHCl_3), but no carbonyl absorption; n.m.r. peaks due to four methyl groups (all singlets) at 0.81 p.p.m. (one CH_3), 0.90 p.p.m. (one CH_3), and 1.09 p.p.m. (two CH_3); found: C, 81.01; H, 11.85. The same compound was obtained more conveniently from the mixture of isomers IIIA and IIIB by methylation and subsequent recrystallization from pentane. Treatment of the tertiary alcohol in tetrahydrofuran with

(1) See Y. Asahina and T. Tsukamoto, *J. Pharm. Soc. Japan*, **484**, 463 (1922); J. Bell and G. G. Henderson, *J. Chem. Soc.*, 1971 (1930); S. Dev, *Current Sci.* (India), **20**, 296 (1951); A. Nickon, J. R. Mahajan, and F. J. McGuire, *J. Org. Chem.*, **26**, 3617 (1961).

(2) Personal communication from Dr. G. A. Sim, The University, Glasgow; K. W. Gemmill, W. Parker, J. S. Roberts, and G. A. Sim, *J. Am. Chem. Soc.*, **86**, 1438 (1964). Chemical studies leading to II have also been reported by A. Nickon, F. J. McGuire, J. R. Mahajan, B. Umezawa, and S. A. Narang, *ibid.*, **86**, 1437 (1964).

(3) See G. F. Woods, P. H. Griswald, Jr., B. H. Armbrrecht, D. I. Blumenthal, and R. Plapinger, *ibid.*, **71**, 2028 (1949). Methyl lithium was used in the preparation, however.

(4) See H. Kwart and J. A. Ford, Jr., *J. Org. Chem.*, **24**, 2060 (1959).

(5) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964).

(6) Vapor phase chromatography of this mixture at 185° , using a column of 10% fluorosilicone on Diatoport with a helium flow rate of 50 ml./min., separated A, B, and C; their retention times were 23, 20.3, and 25.5 min., respectively.

(7) The photocondensation of olefins with conjugated ketones has been investigated independently by P. E. Eaton [*J. Am. Chem. Soc.*, **84**, 2554 (1962); Abstracts, American Chemical Society, 145th National Meeting, Sept., 1963, p. 4Q] and in these laboratories by R. B. Mitra, K. Sestanj, and J. D. Bass (to be published). For a previous application to the synthesis of the caryophyllenes see ref. 5 and earlier paper.