TABLE I

CONDENSATION REACTIONS USING HYDROGEN FLUORIDE INVOLVING OXYGEN CONTAINING COMPOUNDS

Alkyl compounds	Aromatic compound	Product	Yield, %	B. p., °C.
t-Butyl alcohol	Benzene	Mono-*t*-butylbenzene	3	165
		Di-*t*-butylbenzene	8	78–78.5[a]
t-Butyl chloride	Phenol	*p*-*t*-Butylphenol	85	234–238[b]
t-Butyl chloride	Ethyl furoate	Ethyl 5-*t*-butylfuroate	54	116–117 (16 mm.)[c]

[a] Melting point. A mixed melting point with known *p*-di-*t*-butylbenzene was 77–78°. [b] The *p*-*t*-butylphenol melted at 97–98°, *p*-toluenesulfonate of it melted at 108–109°. [c] n^{20} 1.4749, the ester on saponification gave 5-*t*-butylfuroic acid which melted at 105–105.5°.

are formed, and this reaction requires further study. The constant boiling fraction represents about 18% yield.

Tertiary Butyl Chloride and Cyclohexene.—Distillation of the reaction products gave a fraction boiling 40–42° under a pressure of 18 mm. and at 141.5–142° at 739 mm. The refractive index of this fraction was 1.4578. It decolorized bromine water and gave only a very weak chloride ion test. Since neither boiling point nor refractive index checks whatsoever with di- or triisobutylene, and since it appears to be an olefin, it is very probable that polymerization has occurred between the tertiary butyl chloride and the cyclohexene to give either a tertiary butyl cyclohexene or a substituted cyclohexyl ethylene.

The yield of this fraction was 31% of the theoretical. A triisobutylene fraction of less than 10% was also obtained.

Conclusions.—The general usefulness of hydrogen fluoride as a reagent in organic reactions has now been well established. The technique of its use is somewhat different than that of other similar reagents but its utility seems to be much greater than any of them. There are reactions such as that between an olefin and a tertiary chloride which it promotes that have not been previously reported.

Summary

Hydrogen fluoride has been found useful to catalyze reactions between tertiary butyl chloride and both trimethylethylene and cyclohexene. It also has been found to catalyze reactions involving oxygen containing compounds. Tertiary butyl alcohol has been caused to react with benzene, tertiary butyl chloride formed tertiary butylphenol upon reaction with phenol, and ethyl 5-*t*-butylfuroate was formed from tertiary butyl chloride and ethyl furoate.

An explanation for the general utility of hydrogen fluoride in organic reactions is sought in its chemical and physical properties.

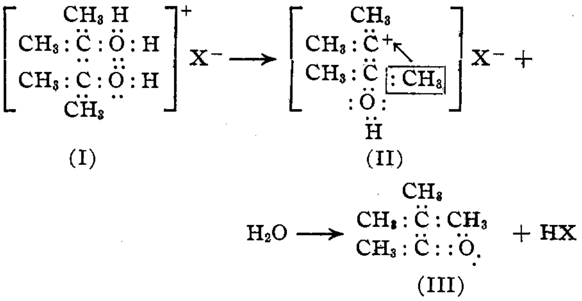
STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 1, 1938

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Pinacol–Pinacolone Rearrangement: the Preparation and Rearrangement of Tetramethylethylene Bromohydrin

BY GEORGE W. AYERS, JR.[1]

The Stieglitz mechanism[2] of the pinacol–pinacolone rearrangement assumes that an intermediate oxonium salt (I) loses water to leave a nucleus[3] (II) in which one of the carbon atoms possesses only three pairs of electrons. This "fault" in the molecule is then repaired by the migration of a negative methyl group, with its full complement of electrons, from the adjacent carbon atom to the electron deficient carbon atom



This rearrangement, in which one carbon atom is completely reduced and another completely oxi-

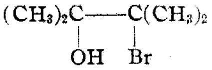
---

(1) Under the superv sion of the late Dr. Julius Stieglitz. This paper is a portion of the thesis presented by the author to the Graduate School of the University of Chicago for the degree of Doctor of Philosophy in December, 1931.

(2) (a) Stieglitz, *Am. Chem. J.*, **39**, 29, 166 (1908); (b) Derby, *ibid.*, **39**, 437 (1908); (c) McCracken, *ibid.*, **39**, 437, 586 (1908); (d) Migita, *Bull. Chem. Soc. Japan*, **3**, 308 (1928); (e) R. B. Cooper, Doctor's Dissertation, University of Chicago, 1930; (f) K. H. Adams, Doctor's Dissertation, University of Chicago, 1932; (g) Stieglitz, Cooper and Ayers, *Trans. Ill. State Acad. Sci.*, **25**, 173 (1933); for a review of previous work see Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, 1938, p. 720, and Porter, "Molecular Rearrangements," 1928, p. 85.

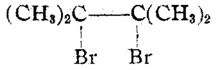
(3) See Whitmore, THIS JOURNAL, **54**, 3274 (1932).

dized, is a manifestation of the tendency of compounds in an intermediate stage of oxidation or reduction to revert, through migrations of electrons, to a state of complete oxidation or reduction. As a corollary of this mechanism it should be possible to bring about the rearrangement of halohydrins by elimination of halide ion, to the corresponding ketone. Adams observed that tetramethylethylene chlorohydrin did not decompose at 150°, and that only at 175°, in benzene solution, did any noticeable decomposition take place. Since halide ion can be separated more easily from an alkyl bromide than from the corresponding chloride, it was of interest to ascertain whether rearrangement of tetramethylethylene bromohydrin (IV) can be induced by heating. This hitherto unknown compound was found to lose hydrogen bromide, even at 100°, to yield pinacolone. The corresponding iodohydrin[1] was stable only in solution; the solid, which resisted purification, decomposed spontaneously to pinacolone and other products.



$(CH_3)_2\underset{OH}{\underset{|}{C}}-\underset{Br}{\underset{|}{C}}(CH_3)_2$

(IV)



$(CH_3)_2\underset{Br}{\underset{|}{C}}-\underset{Br}{\underset{|}{C}}(CH_3)_2$

(V)

The preparation of tetramethylethylene bromohydrin (IV) from anhydrous pinacol and gaseous hydrogen bromide provided several interesting observations. Dependent on dilution, nature of the solvent and rate of addition of hydrogen bromide, a variety of products could be isolated. In the absence of solvent a mixture of bromohydrin (IV) and dibromide (V) was obtained. In anhydrous ether, primarily, a mixture of pinacol hydrobromides was formed, which, upon continued passage of hydrogen bromide, was converted to bromohydrin (IV). Further reaction with hydrogen bromide brought about formation of dibromide (V). In chloroform, the same reagents caused precipitation of a white crystalline compound, the composition of which corresponded to (I), in which X^- is bromide. This hydrobromide was unstable, losing water from the solid state within a few hours, and passed over into the bromohydrin (IV). The corresponding hydrochloride was made in a similar manner by Harries,[4] who observed that it decomposed at 55° but failed to identify the products. Finally, in ligroin or carbon tetrachloride there was formed a crystalline compound, stable for several weeks at room temperature, which had a composition corresponding to dipinacol hydrobromide, $[(C_6H_{14}O_2)_2H]Br$. Formation of a dimolecular product indicated that pinacol itself might be dimolecular in certain solvents, and this was found to be the case in benzene. This dipinacol hydrobromide can also be separated from the mixture of hydrobromides formed in anhydrous ether, since pinacol hydrobromide (I) is converted to bromohydrin (IV) which volatilizes, leaving the pure dimolecular compound.

The pure bromohydrin (IV) is quite unstable, decomposing slightly even on standing overnight in the refrigerator. In an open tube at 110° it rearranges to pinacolone. When mixed with dry sodium bicarbonate, to remove any trace of catalyzing acid formed by decomposition, the bromohydrin (IV) showed evidence of decomposition even at 100°. After extremely thorough drying of a benzene solution of the bromohydrin, the latter rearranged to pinacolone when the solution was heated at 100° for six hours. Rearrangement to pinacolone also took place when an ether solution of the bromohydrin was shaken with aqueous solutions of silver nitrate or sodium thiosulfate, or with silver oxide.

The properties of pinacol hydrobromide (I) ($X = Br$) lend support to the Stieglitz mechanism of the pinacol rearrangement. Under the ordinary conditions of the acid catalyzed rearrangement in aqueous solution the small amount of pinacol hydrohalide must be in the form of the highly ionized oxonium salt (I). In water the oxonium and halide ions are separated by so many intervening water molecules that the "fault" occurring in the molecule (II) when water is split off can be adjusted only by rearrangement to pinacolone. On the other hand, in the crystalline hydrobromide, the bromide ions are within atomic distances of the oxonium ions, and can, when water is lost by the latter, slip to the positively charged carbon atom, with formation of the bromohydrin (IV).

Experimental

Anhydrous Pinacol.—Pinacol hydrate was prepared according to "Organic Syntheses."[5] The best yields were obtained when most of the acetone was added before the reaction started. Dehydration[6,2f] was effected

---

(4) Harries, *Ann.*, **383**, 183 (1911).

(5) "Org. Syntheses," Vol. V, 1926, p. 87; Coll. Vol. I, 1932, p. 448.

(6) Städeler, *Ann.*, **111**, 281 (1859); Linnemann, *Ann. Suppl.*, **3**, 377 (1865); Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921); King and Stewart, *Proc. Trans. Nova Scot. Inst. Sci.*, **17**, 262 (1930).

as follows. The hydrate, in a large round-bottomed flask, was heated with an oil-bath to 110°; suction was then applied with a water-pump until evaporation of water stopped. The flask was returned to atmospheric pressure, the bath temperature raised by 10° and the previous operation was repeated. The same series of operations was repeated until a high-boiling liquid started to condense on the walls of the flask. The pinacol was then distilled at atmospheric pressure and the fraction boiling at 170–175° collected as anhydrous pinacol, yield, *ca.* 30%. About 50% of the charge was recovered from the condensate formed in dehydration or as partially hydrated pinacol in the fore-run of the distillation.

The water-white product solidified upon standing, and could be used for most purposes without further treatment. Absolutely anhydrous pinacol, m. p. 38°, b. p. 172°,[7] was obtained by redistillation at atmospheric pressure.

Tetramethylethylene Bromohydrin.—A rapid stream of hydrogen bromide was passed continuously through a solution of 25 g. of anhydrous pinacol in 375 cc. of anhydrous ether. The white precipitate which started to form in one minute settled as a faintly yellow, viscous liquid. After twenty-five minutes the whole mixture became homogeneous and was washed immediately with four portions of distilled water and dried over sodium sulfate. The filtered solution was concentrated, either under reduced pressure or by evaporation in a gentle stream of air, to a pasty crystalline mass. This was dried in a desiccator on porous plate, over calcium chloride and paraffin; yield, 21–27% (8–10.4 g.). The melting point of the impure bromohydrin varied with different preparations from 66 to 71°. The purest samples were obtained in small preparations with low yields. The crude bromohydrin was recrystallized from ligroin in the same manner that it was originally isolated from ether solution. It was thus obtained as a fluffy white crystalline powder, which, after drying over calcium chloride and paraffin, melted at 70.5°. Large pure crystals of the same melting point were obtained as a sublimate from impure samples of the bromohydrin, which had been stored in the refrigerator.

Anal. Calcd. for $C_6H_{13}OBr$: Br, 44.13. Found: Br, 44.22, 44.24.

The solid bromohydrin is extremely volatile, with a camphoraceous odor and lachrymatory properties. If it contains traces of water it develops brown specks, on standing overnight, with lowering of the melting point. However, perfectly dry samples can be preserved for some time.

Pinacol Hydrobromide, $C_6H_{14}O_2 \cdot HBr$.—Gaseous hydrogen bromide was passed into an ice-cold solution of 5 g. of anhydrous pinacol in eight volumes of chloroform. The solution remained clear for some time, when it suddenly solidified. Hydrogen bromide was passed through for an additional minute; the mixture was filtered with suction, washed once with chloroform and sucked dry. The crystals were pressed on porous plate and dried over calcium chloride and paraffin.

Anal. Titration with 0.09632 *N* KOH. Calcd. for $C_6H_{14}O_2 \cdot HBr$: HBr, 40.65. Found: HBr, 40.88.

Pinacol hydrobromide is a colorless, crystalline solid, soluble in water and fuming in moist air. A sample, kept in a desiccator on porous plate, over calcium chloride and paraffin, for two days, disappeared to leave only a trace of material which contained only 35.9% of hydrogen bromide. That it had been converted to bromohydrin (IV) was evident from the odor of the latter and the absence of hydrogen bromide.

Dipinacol Hydrobromide, $(C_6H_{14}O_2)_2 \cdot HBr$. (**A**).—A solution of 5 g. of anhydrous pinacol in 125 cc. of ligroin (30–50°) was treated with hydrogen bromide until precipitation was complete. The sticky white product was washed four times with ligroin and dried overnight on a porous plate over sulfuric acid and paraffin.

(**B**).—A solution of 5 g. of anhydrous pinacol in 75 cc. of carbon tetrachloride was treated with hydrogen bromide until the primarily formed oily layer, after becoming extremely viscous, changed to a granular solid. The solid was washed four times with carbon tetrachloride, pressed on porous plate and dried overnight over calcium chloride and paraffin.

Anal. Titration with 0.4363 *N* KOH, phenolphthalein indicator. Calcd. for $(C_6H_{14}O_2)_2 \cdot HBr$: HBr, 25.5. Found: HBr, A, 25.3; B, 25.4.

Freshly precipitated dipinacol hydrobromide is granular, changing, on standing, to well-defined crystals, m. p. 52–54°. Under anhydrous conditions it is stable, showing no change in composition after two weeks. It dissolves instantly in water, and deliquesces in the air to form a solution of the components.

Dipinacol hydrobromide was also isolated from the mixture of hydrobromides formed, as a viscous liquid, in the first stage of the preparation of the bromohydrin (IV). On standing for several days in a desiccator, over calcium chloride and paraffin, the true hydrobromide became converted to bromohydrin (IV), which sublimed to leave pure dipinacol hydrobromide.

Molecular Weight of Anhydrous Pinacol.—The molecular weight was determined cryoscopically in benzene.

				Molecular weight	
Expt.	Weight of pinacol	Weight of benzene	ΔT	Found	Calcd. $(C_6H_{14}O_2)_2$
1	24.138	526.4	0.960°	245	236
2	23.201	554.4	0.927°	231	236

Thermal Rearrangement of Tetramethylethylene Bromohydrin.—Equal volumes (10 cc.) of a solution of 1.12 parts of bromohydrin in 10 parts of benzene, previously dried over sodium sulfate for eighteen days in the refrigerator, were sealed in four Pyrex tubes and heated for six hours, two at 100° and two at 150°. All were then acid to methyl orange and gave copious precipitates with Nessler's solution, indicating pinacolone formation. More voluminous precipitates were obtained from the tubes heated at 150° than from those at 100°, indicating more nearly complete rearrangement at the higher temperature.

An analytical sample (1 g.) of the bromohydrin decomposed when heated in an open glass tube in a bath at 110°. This experiment was repeated with a sample that had been mixed with four parts of sodium bicarbonate, and ketone formation was demonstrated with Nessler's solution.

---

[7] "Int. Crit. Tables," Vol. 1, 1926, p. 204, gives m. p. 38° and b. p. 172.8°.

Rearrangement of Tetramethylethylene Bromohydrin by Chemical Reagents.—Portions of a solution of bromohydrin in absolute ether were treated with aqueous solutions of (1) silver nitrate and (2) sodium thiosulfate and (3) an aqueous suspension of silver oxide. After treatments (1) and (3) gave precipitates of silver bromide, excess sodium chloride solution was added and the precipitates were removed by filtration. In treatment (2) the ether was decanted from the turbid aqueous layer. All three then gave copious precipitates with Nessler's solution. A fourth sample, untreated otherwise, gave no precipitate with this reagent, nor did an aqueous solution of pinacol hydrate, which had been previously treated, as above, with silver nitrate and sodium chloride.

Summary

1. Depending on the reaction conditions, the action of gaseous hydrogen bromide on anhydrous pinacol leads to tetramethylethylene bromohydrin, tetramethylethylene dibromide, pinacol hydrobromide or dipinacol hydrobromide. Pinacol hydrobromide is the intermediate in bromohydrin formation, as well as the postulated intermediate in the hydrobromic acid-catalyzed rearrangement of pinacol to pinacolone.

2. Tetramethylethylene bromohydrin rearranges to pinacolone on heating or on treatment, at room temperature, with halide abstracting reagents. This lends support to the Stieglitz mechanism of the pinacol–pinacolone rearrangement.

CHICAGO, ILLINOIS RECEIVED JULY 13, 1938

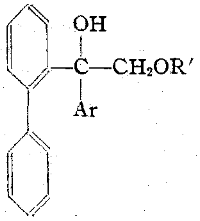
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Synthesis of Phenanthrene Derivatives. I. 9-Phenyl- and 9-*p*-Tolylphenanthrene

BY CHARLES K. BRADSHER AND ALLAN K. SCHNEIDER

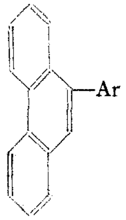
With the exception of the elaborate Pschorr[1] synthesis, all of the methods usually employed for the synthesis of phenanthrene derivatives have a common disadvantage. They involve one step in which hydrophenanthrenes are dehydrogenated at high temperatures by the action of sulfur, selenium or platinum. Frequently a desired phenanthrene derivative is incapable of surviving such a treatment, and it was in the hope of providing a means for the synthesis of such derivatives that this research was undertaken.

A new cyclization reaction has been discovered giving promise of accomplishing this end. When compounds of type I were treated with mineral acids they lost the elements corresponding to one molecule of water and one molecule of methyl alcohol or phenol to form the corresponding 9-arylphenanthrene (II).



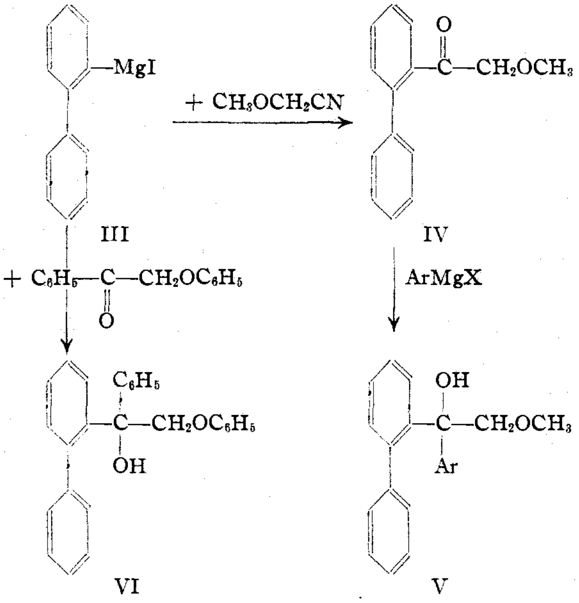
I

(R′ = CH_3 or C_6H_5)



II

The carbinols used were prepared by two methods.



In the first, 2-xenylmagnesium iodide (III) was treated with methoxyacetonitrile. Upon hydrolysis the reaction product gave 2-(ω-methoxyaceto)-biphenyl (IV). This upon treatment with phenyl- or *p*-tolylmagnesium bromide gave the corresponding carbinol (V).

In the second method, ω-phenoxyacetophenone was treated with 2-xenylmagnesium iodide (III) to form 1-phenyl-1-(2-xenyl)-2-phenoxyethanol-1 (VI).

When treated with concentrated sulfuric acid

---

[1] Pschorr, *Ber.*, **29**, 496 (1896).