30% hydrogen peroxide. The solution was allowed to stand at room temperature for one hour, after which it was heated on the water-bath for two hours. The solution was made alkaline with sodium carbonate and extracted with ether. The ether extract was dried and the ether removed. The residual oil distilled over at 86° under 11 mm. pressure; this was proved to be phenylbutadiene, and must have been formed from the decomposition of some of the chloride which was not ozonized. One and one-half grams of phenylbutadiene was recovered. The combined alkaline extracts were acidified with dilute sulfuric acid. Benzoic acid (1.5 g.) was precipitated. This was proved by its melting point and a melting point of a mixture with known benzoic acid. The yield of benzoic acid was 65%.

In another experiment a considerable quantity of the chloride was ozonized in chloroform solution. Alkali was not used in working up the ozonide, since it was shown that alkali readily removes hydrogen chloride from the compound. The ozonide was therefore decomposed by warming its aqueous solution on the water-bath, and then extracted with ether. The ether solution was dried, the ether removed by vaporization, and the residual oil was distilled. The largest portion distilled over between 79–86°. This was proved to be α-chloropropionic aldehyde by analysis and oxidation to acetic acid with alkaline permanganate. This differentiates it from the β-isomer which boils at 125–130° and easily polymerizes.

*Cis*-1-phenyl-3-chloro-$\Delta^1$-butene was shaken for ten minutes with 10% sodium hydroxide at room temperature. The reaction mixture was extracted with ether, the ethereal solution dried, the solvent removed by vaporization and the residual oil distilled under reduced pressure. The major portion of the oil distilled over at 86° under 11 mm. pressure, which is the boiling point of *cis*-phenylbutadiene.

*Cis*-1-phenyl-3-chloro-$\Delta^1$-butene was refluxed with an excess of silver oxide suspended in water until no further reaction occurred. The reaction mixture was extracted with ether, the ethereal solution dried, the solvent removed by vaporization and the residual oil distilled under reduced pressure. The oil distilled at 144° under 21 mm. pressure, which is the boiling point of *cis*-1-phenyl-3-hydroxy-$\Delta^1$-butene. The identity of this carbinol was further proved by its reactions.[6]

## Summary

The mono-hydrogen chloride addition products of the two geometric isomers of 1-phenylbutadiene were prepared and their structures proved. In each case addition occurred in the 3,4-double bond to give 3-chloro derivatives. This is in complete accord with the electronic theories of Muskat and his collaborators on the addition reactions of conjugated systems.

NEW YORK, N. Y. RECEIVED FEBRUARY 20, 1934

---

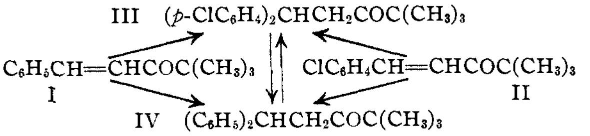
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# The Reversibility of the Friedel–Crafts Reaction. The Interconversion of α-(Benzohydryl)-pinacolones

BY HARRY H. WEINSTOCK, JR., AND REYNOLD C. FUSON

The theory that the addition of aromatic compounds to α,β-unsaturated carbonyl compounds in the presence of aluminum chloride and hydrogen chloride[1] is reversible leads to the prediction that β,β-diaryl carbonyl compounds of the type $(Ar)_2CHCH_2CO—$ should be interconvertible according to the equation $(Ar)_2CHCH_2CO— + 2Ar'H = (Ar')_2CHCH_2CO— + 2ArH$. An interconversion of this type has now been realized.

For this work the α-(benzohydryl)-pinacolones have been selected; this was partly because of their ready accessibility and partly on account of the fact that the tertiary butyl group, unlike aryl groups, cannot lead to the formation of indanones.



Preliminary exploration in this field showed that the benzalpinacolones behaved in a manner very similar to that previously outlined for the benzalacetophenones.[1b] Benzalpinacolone (I), and *o*- and *p*-chlorobenzalpinacolones (II) were found to yield α-(benzohydryl)-pinacolone (IV) when treated with benzene, and α-(*p*,*p*'-dichlorobenzohydryl)-pinacolone (III) when chlorobenzene was used. The conversion of benzalpinacolone to III was remarkable because it was the first instance in which a phenyl group had been replaced. Moreover, it foreshadowed the interconversion of III and IV—a result which depended on such a replacement.

The conversion of III into IV, as already intimated, was accomplished by treatment of the dichloro compound with benzene, aluminum chloride and hydrogen chloride. This process could be *reversed* by subjecting IV to the action of chlorobenzene, aluminum chloride and hydrogen

---

(1) (a) Fuson, Kozacik and Eaton, THIS JOURNAL, **55**, 3799 (1933); (b) Eaton, Black and Fuson, *ibid.*, **56**, 687 (1934).

chloride. These two processes represent an interconversion of the two α-(benzohydryl)-pinacolones—a result which accords with the theory of reversibility previously suggested.

## Experimental

***p*-Chlorobenzalpinacolone.**—To 20 g. of pinacolone in a 500-cc. bottle were added 31.3 g. of *p*-chlorobenzaldehyde, 76 cc. of 95% ethyl alcohol, 26 cc. of water and 20 cc. of 10% sodium hydroxide solution. The bottle was stoppered tightly and shaken for seventeen hours. The product, after recrystallization from 95% ethyl alcohol, melted at 85.0–85.5°. The yield was 70% of the theoretical amount.

*Anal.* Calcd. for $C_{13}H_{15}OCl$: C, 70.1; H, 6.8; Cl, 15.9. Found: C, 70.3; H, 6.6; Cl, 16.0.

***o*-Chlorobenzalpinacolone.**—The procedure was similar to that used for the para compound. The product, after recrystallization from 95% alcohol, melted at 53.5–54.5°. The yield was 46% of the theoretical amount.

*Anal.* Calcd. for $C_{13}H_{15}OCl$: C, 70.1; H, 6.8; Cl, 15.9. Found: C, 70.2; H, 6.7; Cl, 15.8.

**Condensations.**—The general procedure used has been described earlier.[1] In the condensation of benzene with *p*-chlorobenzalpinacolone the reaction mixture contained 200 cc. of benzene, 17.5 g. of anhydrous aluminum chloride and 10 g. of the pinacolone. A stream of dry hydrogen chloride was passed into this mixture during a period of five minutes and the whole was allowed to stand for twenty hours. The product was α-(benzohydryl)-pinacolone, which after recrystallization from alcohol melted at 83.5–84.5°. When benzalpinacolone or *o*-chlorobenzalpinacolone was used this same product was obtained. It was always very difficult to purify. Its identity was established by a comparison with a specimen made by the method of Kohler.[2]

When the foregoing condensations were repeated using chlorobenzene in place of benzene, the product in each case was α-(*p*,*p'*-dichlorobenzohydryl)-pinacolone (III). In these experiments the excess chlorobenzene was driven off by steam distillation and the residue allowed to crystallize. Again repeated recrystallization from alcohol was required to purify the product. The latter melted at 153.0–153.5°.

*Anal.* Calcd. for $C_{19}H_{20}OCl_2$: C, 68.0; H, 6.0; Cl, 21.2. Found: C, 68.2; H, 5.8; Cl, 20.9.

**Oxidation.**—The structure of III was confirmed by oxidation. Treatment with alkaline permanganate converted it into *p*,*p'*-dichlorobenzophenone, melting at 142–143°. A mixed melting point of the latter with an authentic specimen showed no depression.

**Conversion of α-(Benzohydryl)-pinacolone (IV) into α-(*p*,*p'*-Dichlorobenzohydryl)-pinacolone (III).**—To a mixture of 2.9 g. of IV, 75 cc. of chlorobenzene and 7 g. of anhydrous aluminum chloride, dry hydrogen chloride was added. The reaction mixture was then shaken for twenty hours. A yield of 1.7 g. of crude III was obtained. After five recrystallizations from alcohol the product melted at 151–152.5°. Its identity was established by the method of mixed melting points.

**Conversion of α-(*p*,*p'*-Dichlorobenzohydryl)-pinacolone (III) into α-Benzohydrylpinacolone (IV).**—A mixture of 2.9 g. of III, 75 cc. of benzene and 7 g. of anhydrous aluminum chloride was treated with hydrogen chloride in the usual manner and shaken for nine hours. A yield of 1.2 g. of crude IV was obtained. After six recrystallizations from alcohol the product melted at 82–83°. A mixed melting point with an authentic specimen of IV showed no depression.

## Summary

In the presence of hydrogen chloride and aluminum chloride, benzene reacts with benzal-, *p*-chlorobenzal- or *o*-chlorobenzalpinacolone to yield α-(benzohydryl)-pinacolone; when chlorobenzene is used the product in each case is α-(*p*,*p'*-dichlorobenzohydryl)-pinacolone.

Under the same conditions the action of chlorobenzene converts α-(benzohydryl)-pinacolone into α-(*p*,*p'*-dichlorobenzohydryl)-pinacolone. The latter is reconverted to the former when benzene replaces chlorobenzene in the reaction mixture.

These results show that the Friedel–Crafts reaction is reversible in the case of the addition of aromatic compounds to an olefinic linkage which is conjugated with a carbonyl group.

URBANA, ILLINOIS RECEIVED FEBRUARY 23, 1934

---

(2) Kohler, *Am. Chem. J.*, **38**, 511 (1907).