such small amounts would have had a negligible effect on the dielectric constant. The distillate was deiodized with copper and fractionally distilled with absolute alcohol to separate the isomers. Runs 25 and 26 were made with the *trans* isomer so obtained. The apparent slightly higher percentage of *cis* in the final equilibrium mixture in run 26 may be due to some impurity. The runs from the *cis* side are probably more reliable, and the others agree sufficiently to indicate that the state reached in these reactions was indeed an equilibrium between the two isomers as was assumed.

The changes in free energy, entropy, and heat content on isomerization are all zero within experimental error. As good an estimation as can be made is to say that the equilibrium constant, K, for the reaction *trans*-$C_2H_2Br_2 \rightleftarrows$ *cis*-$C_2H_2Br_2$ is 0.984 at 145° and 0.975 at 170°. The changes in thermodynamic quantities on isomerization at 158° become $\Delta F^0 = 17 \pm 40$ cal./mole. $\Delta H^0 = -130 \pm 300$ cal./mole. $\Delta S^0 = -0.34 \pm 0.8$ cal./mole degree.

So little is known about the vibration frequencies of the isomers that it is impossible to make a statitstical mechanical treatment of the equilibrium as was done by Wood and Stevenson.[2]

Summary

The gaseous equilibrium of *cis* and *trans* dibromoethylenes catalyzed by iodine has been studied in the range from 144 to 178° and has been found to correspond to equal amounts of the two isomers over the entire interval within the experimental error in analysis. Hence the standard free energy, entropy and heat content changes are all zero for the isomerization.

PASADENA, CALIFORNIA RECEIVED APRIL 27, 1943

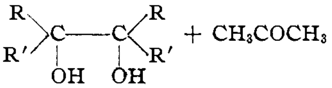
NOTES

Photochemical Pinacolization

BY FELIX BERGMANN AND YEHUDA HIRSHBERG

In a previous paper from this Laboratory,[1] pinacolization of ketones under the influence of ultraviolet light was studied with the aim of elucidating the elementary process in the mutual oxidation and reduction of ketones and secondary alcohols, according to the scheme

$2RCOR' + CH_3CHOHCH_3 \longrightarrow$



$$RR'C(OH)\text{—}C(OH)RR' + CH_3COCH_3$$

We have now extended this investigation and found very narrow structural limits for the applicability of this type of reaction.

1. The fact that benzophenone and acetophenone are pinacolized quantitatively according to the above scheme would indicate that at least one aryl group is necessary to activate the carbonyl group. However, neither α- nor β-acetyl-naphthalene gave any reaction, and, likewise, α-naphthyl phenyl ketone and di-α-naphthyl ketone remained unchanged. Also, phenyl *p*-biphenylyl ketone, like its *o*-isomer, was not attacked, although the *m*-compound has been reported to yield the pinacol.[2] It is apparent that a change in the type of the aromatic substituent both in benzophenone and acetophenone nearly always impairs the photochemical reactivity.

2. Systematic changes were now applied to the non-aromatic part of acetophenone. Desoxybenzoin yielded the (higher-melting) α-pinacol in about 80% yield; no trace of the β-form was detected. The next higher homolog, benzyl-acetophenone, was inactive, but 1,4-diphenylbutanone-1 yielded a small amount of a liquid pinacol, which perhaps represents a mixture of both stereoisomers. It is very significant that the same behavior was encountered in the cyclic analogs of the last two ketones: α-indanone (I), comparable to $C_6H_5COCH_2CH_2C_6H_5$, was not pinacolized, but yielded, instead, the condensation product II: α-tetralone corresponding to $C_6H_5COCH_2CH_2CH_2C_6H_5$ yielded the pinacol in yields up to 75%.

3. On the principle of vinylogy, the styryl group was presumed to behave like the phenyl

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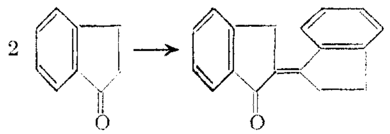
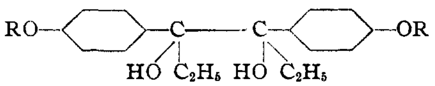
[1] Weizmann, E. Bergmann and Hirshberg, THIS JOURNAL, 60, 1530 (1938).

[2] Hatt, Pilgrim and Stephenson, *J. Chem. Soc.*, 478 (1941).



I II



III

nucleus. However, benzalacetophenone and benzalacetone, the vinylogs of benzophenone and acetophenone, respectively, were not affected.

4. In a further set of experiments the influence of aromatic substitution on the pinacolization of acetophenone was studied with the view of synthesizing the pinacol III, which could serve as a suitable starting material for stilboestrol.[3] *p*-Methoxypropiophenone did not react at all, and the *p*-acetoxy-, propoxy- and butyroxyacetophenone only suffered partial deacylation to *p*-hydroxypropiophenone; the acetoxy compound yielded also traces of pinacol III (R = CH_3CO–).

Finally, it was found that under our experimental conditions benzoin undergoes a reverse Cannizzaro reaction, giving benzaldehyde as the only reaction product.

Experimental Part

Under the conditions used, benzophenone in 6.7% solution gave 100% of pinacol after fifteen hours of irradiation, acetophenone 70%.

(1) **α-Indanone.**—The ketone (20 g.) in isopropanol (150 cc.) was irradiated for ten hours and the mixture fractionated. The residue was triturated with toluene. From isopropanol it gave prisms of II, m. p. 142–143°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 87.0; H, 5.7.

When the same reaction was carried out in sunlight (30 days), a small amount of another product was obtained, which crystallized from nitrobenzene or pyridine in beautiful brown rods, m. p. 352–353°. With concd. sulfuric acid a violet color appears which turns slowly to red-brown; no reaction with bromine. No method was found for determining the molecular weight.[4]

Anal. Calcd. for $C_{36}H_{26}O(2 \times C_{18}H_{14}O - H_2O)$: C, 91.1; H, 5.5. Found: C, 92.8, 93.1; H, 5.65, 5.5.

(2) **α-Tetralone.**—After evaporation of the solvent, the pinacol crystallized only partially, most of it was obtained in solid form only after distillation, b. p. 220° (4 mm.); from butyl acetate as beautiful prisms, m. p. 192°.[5] Ten grams of tetralone yielded 7.5 to 8 g. of pinacol. For identification the product was converted into the diene by dehydration in acetic acid–acetic anhydride mixture. From high-boiling petroleum ether the diene gave prismatic blocks, m. p. 141–142°.

Pinacolization of the tetralone was favored by dilution, mainly because the formation of a brown film around the quartz lamp was thereby avoided. Thus, using 50 g. of tetralone in 100 cc. of either isopropanol or isopropanol and benzene, there was obtained a 3% yield of pinacol in ten hours; using 20 g. and 5 g. in 150 cc. of isopropanol, there were obtained in ten and twenty hours, 10 and 80% yields of pinacol, respectively. Ten grams of tetralone in 10 cc. of isopropanol after thirty days in sunlight gave a 40% yield of pinacol.

(3) **Desoxybenzoin.**—The residue from the distillation of unreacted ketone was recrystallized from butanol, m. p. 214°, and identified with an authentic sample of the pinacol.

(4) **1,4-Diphenylbutanone-1.**—This ketone was prepared by a Grignard reaction between benzonitrile (18 g.) and γ-phenylpropylmagnesium bromide (one-sixth mole). On working up the mixture with dilute sulfuric acid, the ketimine was hydrolyzed in the cold and the ketone obtained directly, b. p. 180° (6 mm.),[6] 155° (0.2 mm.), yield 50%. The irradiation yielded a small amount of a high-boiling sirup, b. p. 190° (0.25 mm.), which could not be induced to crystallize.

Anal. Calcd. for $C_{32}H_{34}O_2$: C, 85.3; H, 7.6; mol. wt., 450. Found: C, 85.8; H, 7.45; mol. wt., 395.

(5) ***p*-Acetoxypropiophenone.**—The sirup which was left after distillation of the starting material was distilled in a high vacuum. Crystallization from butyl acetate gave beautiful prisms, m. p. 214° (III, R = $COCH_3$).[7]

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.4; H, 6.7. Found: C, 68.5; H, 6.6.

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[3] Dodds, Golberg, Lawson and Robinson, *Proc. Roy. Soc.* (London), **B127**, 140 (1939).

[4] It is very probable, that this substance is impure bouxene, $C_{27}H_{18}$, the m. p. of which is given as 369–370° by Stobbe, *Ber.*, **60**, 457 (1927). We thank Dr. Ernst Bergmann for this suggestion.

[5] Barnett and Lawrence, *J. Chem. Soc.*, 1104 (1935).

[6] Stoermer and Schenck, *Ber.*, **61**, 2320 (1928).

[7] Dodds and co-workers (ref. 3) report a m. p. of 200°. Their pinacol may represent the other stereoisomer, although it was converted into the high-melting form of hexoestrol.

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RECEIVED NOVEMBER 6, 1942

The Iodination of Tyrosine by Iodine Monochloride

BY PAUL BLOCK, JR., AND GARFIELD POWELL

Tyrosine was first iodinated to diiodotyrosine by Wheeler and Jamieson[1] who added solid iodine to a solution of tyrosine in sodium hydroxide. Oswald[2] improved the yield by performing the reaction at 0°. More recently Harington[3] and also Savitskii[4] have described the iodination of tyrosine in ammonia using iodine dissolved in potassium iodide. Bauer and Strauss[5] used iodine

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[1] Wheeler and Jamieson, *Am. Chem. J.*, **33**, 365 (1905).

[2] Oswald, *Z. physiol. Chem.*, **59**, 320 (1909).

[3] Harington, *Biochem. J.*, **22**, 1434 (1928).

[4] Savitskii, *Chem. Abs.*, **34**, 741 (1940).

[5] Bauer and Strauss, *Ber.*, **69**, 245 (1936).