amounts of solvent from the once-distilled product by washing with water. The product which came over before hydrolysis gave 5.8 g. of crude 3-methyl-1-butyne (positive ammoniacal silver nitrate test), and the product after hydrolysis gave 12.7 g., b.p. 20.5–24.0°, $n^{17}\mathrm{D}$ 1.3659–1.3657, and 8.5 g., b.p. 26.0–28.4°, $n^{17}\mathrm{D}$ 1.3575–1.3550 (Trubore column).

A single run was made with 15 g. (0.39 mole) of lithium aluminum hydride and 44 g. (0.38 mole) of 1-chloro-1,2-hexadiene in 200 ml. of Diethylcarbitol following the directions given above. The product that came over before hydrolysis, 1.5 g., $n^{25}\mathrm{D}$ 1.4065, gave a positive test with ammoniacal silver nitrate. The material obtained after hydrolysis was fractionally distilled through the Trubore column to yield 22.8 g. (50% yield) of hydrocarbons distributed as follows: 2.1 g., b.p. 50–65°, $n^{25}\mathrm{D}$ 1.3748; 3.2 g., b.p. 65–66.1°, $n^{25}\mathrm{D}$ 1.3798; 4.1 g., b.p. 66.1–66.7°, $n^{25}\mathrm{D}$ 1.3798; 5.9 g., b.p. 66.7–68°, $n^{25}\mathrm{D}$ 1.3789; 3.1 g., b.p. 68–68.5°, $n^{25}\mathrm{D}$ 1.3765, and 2.9 g., b.p. 68.5–69.0°, $n^{25}\mathrm{D}$ 1.3755; reported[18] for 1-hexene, b.p. 63.485°, $n^{25}\mathrm{D}$ 1.38502; *cis*-2-hexene, b.p. 68.84°, $n^{25}\mathrm{D}$ 1.3948; *trans*-2-hexene, b.p. 67.87°, $n^{25}\mathrm{D}$ 1.3907; hexane, b.p. 68.740°, $n^{25}\mathrm{D}$ 1.37226. Thus the final fraction appears to be relatively pure hexane, and earlier fractions are mixtures probably containing more than one hexene.

Bromopropadiene was dehalogenated exactly as described for propargyl bromide. The evolution of gas during the addition was somewhat slower; this gas was pure propyne within the limits of accuracy of the infrared spectrophotometer. A yield of 1.37 g. (68.5%) was obtained before hydrolysis and 0.42 g. (21.0%) after hydrolysis.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Benzoin Condensations with Pivalaldehyde[1]

BY T. GLENN ROBERTS AND PEYTON C. TEAGUE

RECEIVED APRIL 25, 1955

The aliphatic aldehyde, pivalaldehyde, fails to form pivaloin by the benzoin condensation. Crossed condensation with benzaldehyde gives a mixture of isomeric acyloins, phenylpivalylcarbinol and benzoyl-*t*-butylcarbinol.

The benzoin condensation is a common reaction of aromatic aldehydes such as benzaldehyde, 4-phenylbenzaldehyde, 3,4-methylenedioxybenzaldehyde, 2- and 4-methoxybenzaldehyde, furfural and the pyridine and quinoline aldehydes. Certain substituted benzaldehydes fail to undergo the reaction. These include 4-dimethylaminobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 4-nitrobenzaldehyde.[2] Even though 4-dimethylaminobenzaldehyde will not undergo self-condensation, it will condense with benzaldehyde to produce an unsymmetrical benzoin.[3] The carbonyl group of the product is adjacent to the ring having the electron-releasing substituent.[4] In practically all crossed condensations this result has been reported.[5]

The only benzoin condensations of aldehydes in which the carbonyl group is not attached directly to an aromatic ring have been achieved in the glyoxal series. Benzoylformoin ($C_6H_5COCOCH$-$OHCOC_6H_5$) was prepared from phenylglyoxal[6] and acetylformoin from methylglyoxal.[7]

An aliphatic aldehyde which has an α-hydrogen atom undergoes aldol condensation in alkaline solution. Thus the major product of the treatment of isobutyraldehyde with sodium cyanide was found to be the cyanohydrin of isobutyraldol.[8]

Pivalaldehyde is the simplest aliphatic aldehyde, other than formaldehyde, with no α-hydrogen atom. The only report of an attempt to cause the benzoin condensation of pivalaldehyde is that of Franke and Hinterberger.[9] They isolated a small amount of an acidic substance. This material was apparently not extensively investigated, but solely on the basis of its equivalent weight it was assumed to be the aliphatic analog of benzilic acid, di-*t*-butylglycolic acid [$(t\text{-Bu})_2COHCOOH$]. The authors explained its formation by supposing that pivaloin was formed initially and was oxidized by air to pivalil which in turn underwent the benzilic acid rearrangement. We have made numerous attempts to obtain a benzoin condensation with pivalaldehyde and to duplicate the results of Franke and Hinterberger. Pivalaldehyde was heated with various proportions of sodium or potassium cyanide for periods ranging from forty-five minutes to one week. The majority of the reactions were carried out in an atmosphere of nitrogen. With the exception of small amounts of pivalic acid, probably produced after the reaction mixtures were exposed to the air, the only product which could be detected was pivalaldehyde cyanohydrin. In an attempt to obtain the acidic substance described by Franke and Hinterberger, the reaction was run while a slow stream of air was passed through the reaction mixture. Pivalaldehyde cyanohydrin was again produced along with a considerable amount of pivalic acid. The infrared absorption spectrum of the acid matched that of pure pivalic acid so closely that it did not seem possible that another acid could be present.

Pivaloin was prepared from ethyl pivalate by the acyloin condensation and was oxidized to pivalil. The pivalil was very resistant to the action of hot sodium hydroxide solution and no evidence of a benzilic acid rearrangement was found.

The failure of pivalaldehyde to undergo the benzoin condensation may be due to the inductive effect of the *t*-butyl group which would reduce to some

---

[1] This work was supported by the Office of Ordnance Research, Contract No. DA-36-034-ORD-1518RD.

[2] For a general review and bibliography of the reaction see W. S. Ide and J. S. Buck, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 272–286.

[3] H. Staudinger, *Ber.*, **46**, 3530, 3535 (1913); S. S. Jenkins, J. S. Buck and L. A. Bigelow, THIS JOURNAL, **52**, 4495 (1930).

[4] S. S. Jenkins, L. A. Bigelow and J. S. Buck, *ibid.*, **52**, 5198 (1930).

[5] For an extensive bibliography of these reactions see ref. 2.

[6] H. G. Soderbaum and P. W. Abenius, *Ber.*, **24**, 3034 (1891).

[7] R. Nozu and S. Kunitika, *Bull. Chem. Soc. Japan*, **15**, 211 (1940), from *C. A.*, **34**, 6931 (1940).

[8] L. Claisen, *Ann.*, **306**, 322 (1899).

[9] A. Franke and H. Hinterberger, *Monatsh.*, **43**, 655 (1923).

extent the density of charge on the carbonyl carbon atom. The steric effect of the *t*-butyl group may be a more important factor in preventing the reaction.

The pivalaldehyde used in this research was prepared by a modification of the method of Campbell[10] by the addition of *t*-butylmagnesium chloride to methyl formate. By maintaining a lower temperature during the addition the yield was improved over that previously reported. The preparation by the addition of dimethylformamide to *t*-butylmagnesium chloride at room temperature was also found to be satisfactory.

Since pivalaldehyde would not undergo self-condensation, the crossed condensation reaction with benzaldehyde was investigated. Equimolar mixtures of the two aldehydes in the presence of cyanide ion reacted to give a product which was found to contain benzoin together with a mixture of approximately 30 to 40% phenylpivalylcarbinol $[C_6H_5CHOHCOC(CH_3)_3]$ and 60 to 70% benzoyl-*t*-butylcarbinol $[C_6H_5COCHOHC(CH_3)_3]$. The reaction of pivalaldehyde cyanohydrin with benzaldehyde in the presence of a small amount of sodium hydroxide gave a mixture of the isomers in the same ratio. This indicated that the product actually isolated was not necessarily the initial condensation product. To test this, a sample of pure phenylpivalylcarbinol was treated with an alcoholic solution of potassium cyanide. It isomerized to give a mixture of the same composition as that produced in the condensation reaction. Benzoyl-*t*-butylcarbinol was found to isomerize under the same conditions, and it was demonstrated by the use of sodium hydroxide that the isomerization is subject to general base catalysis. A sample of phenylpivalylcarbinol was recovered unchanged after treatment with dilute hydrochloric acid. This fact suggested that dinitrophenylhydrazone formation in an acidic medium would not be accompanied by isomerization and would thus provide a method for the determination of the composition of the crossed condensation product.

A number of experiments were performed to identify the products and determine their ratio. Oxidation of the mixture by the method used on phenylpivalylcarbinol by Fuson, Gray and Gouza[11] gave the diketone, phenyl pivalyl ketone, which was characterized by conversion to 2-*t*-butyl-3-phenylquinoxaline and preparation of the dinitrophenylhydrazone. Treatment of the mixture with benzoyl chloride produced the benzoate of phenylpivalylcarbinol but none of the isomeric benzoate. Treatment with 2,4-dinitrophenylhydrazine gave the yellow derivative of benzoyl-*t*-butylcarbinol after 3.5 hours at room temperature. The filtrate on standing for several days gave a nearly quantitative yield of the orange derivative of phenylpivalylcarbinol. The quantities indicated a composition of the mixture of 60% benzoyl-*t*-butylcarbinol and 35% phenylpivalylcarbinol.

Benzoyl-*t*-butylcarbinol, a new compound, was prepared from phenylmagnesium bromide and pivalaldehyde cyanohydrin.

The infrared spectrum of the mixture of isomers shows absorption at the carbonyl stretching frequencies, 5.87 and 5.94 μ, the former peak exhibited by phenylpivalylcarbinol and the latter by benzoyl-*t*-butylcarbinol. The ultraviolet absorption of the mixture shows a maximum at 246.5 mμ corresponding to the wave length of maximum absorption shown by benzoyl-*t*-butylcarbinol.[12] Phenylpivalylcarbinol shows no absorption in this region. The extinction coefficient (ε) for benzoyl-*t*-butylcarbinol, 10,100, is comparable to that for benzoin, 12,600. On the basis of their extinction coefficient maxima, various samples of the mixture of isomers were found to contain benzoyl-*t*-butylcarbinol in percentages ranging from 70 to 82%. The infrared spectrum of a synthetic mixture consisting of 61% benzoyl-*t*-butylcarbinol and 39% phenylpivalylcarbinol exhibited peaks with the same relative heights as those in the spectrum of the crossed condensation product. The discrepancy in the values found by the two methods of analysis was attributed to traces of benzoin which we were unable to remove by the purification procedure employed.

In a few instances it has been reported that the product of crossed benzoin condensations consisted of a mixture of two isomeric benzoins,[13] but none of these results have been conclusively demonstrated.[14] A single isomer has been reported as the product in all other crossed condensations, and in the cases in which both isomers are known, one is unstable and under the influence of cyanide ion or dilute alkali rearranges to the other. There is at least one instance of the existence of an equilibrium between the members of a pair of isomers in alkaline solution[15]; these were not prepared by the crossed benzoin condensation. Insofar as we have been able to determine, the identification of phenylpivalylcarbinol and benzoyl-*t*-butylcarbinol as products of the crossed condensation of pivalaldehyde and benzaldehyde represents the first clearly established case of the formation of both isomers in the crossed benzoin condensation.

It seems likely that steric effects play the most important role in preventing the self-condensation of pivalaldehyde. Compounds containing the *t*-butyl group adjacent to the reactive center are known to undergo reactions at abnormally slow rates. In the present case, it is to be expected that there will be considerable steric hindrance to the approach of one neopentyl system to another. Further work is in progress on the synthesis of other aldehydes which will have approximately the same electrical effect found in pivalaldehyde but will be less sterically hindered.

Experimental[16]

Pivalaldehyde.—The procedure of Campbell[10] was modified by keeping the temperature between −45 and −50°.

---

[10] K. N. Campbell, THIS JOURNAL, **59**, 1981 (1937).

[11] R. C. Fuson, H. Gray and J. J. Gouza, *ibid.*, **61**, 1937 (1939).

[12] The authors wish to thank Dr. R. E. Lutz for helpful suggestions on the ultraviolet analysis.

[13] J. S. Buck and W. S. Ide, THIS JOURNAL, **52**, 220 (1930); M. Tiffeneau and J. Levy, *Bull. soc. chim.*, [4] **49**, 725 (1931).

[14] J. S. Buck and W. S. Ide, THIS JOURNAL, **54**, 3302 (1932).

[15] H. H. Weinstock, Jr., and R. C. Fuson, *ibid.*, **58**, 1986 (1936).

[16] All melting points are corrected; boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer double-beam recording spectrophotometer, using a sodium chloride prism and sodium chloride cells; samples used were 1% solutions in carbon tetrachloride. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

This resulted in an improved yield of 30.9% based on the *t*-butyl chloride used, b.p. 71–74°, $n^{20}D$ 1.3790–1.3791. The preparation from dimethylformamide and *t*-butylmagnesium chloride gave almost as good a yield (26.8%) without the necessity of cooling and allowed addition of the amide to the Grignard reagent instead of *vice versa*.

Pivalaldehyde Cyanohydrin.—The sodium bisulfite addition compound prepared from 17.2 g. (0.2 mole) of pivalaldehyde was shaken with 15 g. of sodium cyanide in 50 ml. of water for 15 minutes with cooling. The layers were separated and the aqueous layer extracted with several portions of ether. The combined organic portions were stabilized with a few crystals of hydroquinone, dried over calcium sulfate and distilled to yield 13.3 g. (58.8%) of the colorless cyanohydrin, b.p. 76.5–78° (6 mm.). The product solidified, and after drying overnight in a vacuum desiccator, a sample melted at 42.5–44°. This material has been reported as a liquid,[17] b.p. 100° (100 mm.). The compound is very hygroscopic and liquefies rapidly on exposure to moist air.

Anal. Calcd. for $C_6H_{11}NO$: N, 12.31. Found: N, 12.15.

Identification was confirmed by hydrolysis to trimethyllactic acid.

Pivalic acid[18a] **and pivaloin**[18b] were prepared by standard methods for purposes of obtaining reference infrared spectra. **Pivalil** was obtained by refluxing pivaloin with an excess of nitric acid for 21 hours, b.p. 165–170°; reported[19] 170–172°, 168–169°.

Reaction of Pivalaldehyde in the Presence of Cyanide Ion.—A series of reactions were carried out in an atmosphere of nitrogen to prevent the air oxidation of any pivaloin which might be produced. The following experiments are typical. I. A mixture of 8.6 g. (0.1 mole) of pivalaldehyde, 6.5 g. (0.1 mole) of potassium cyanide and 20 ml. of 50% aqueous ethanol was refluxed for 2 hours while a slow stream of nitrogen was passed into the flask. The mixture was seeded with a crystal of pivaloin and cooled in an ice-bath for several hours without effect. The solution was extracted with several portions of ether and the combined extracts dried over sodium sulfate. The solvents and unchanged pivalaldehyde were removed by distillation, and the residue yielded 2 g. of pivalaldehyde cyanohydrin, b.p. 75–78° (6 mm.).

II. A mixture of 10 g. of pivalaldehyde, 2 g. of sodium cyanide and 20 ml. of 50% aqueous ethanol was refluxed for 7 hours in an atmosphere of nitrogen. Seeding and overnight cooling in a refrigerator failed to cause any precipitation. The mixture was extracted with ether and the dried extracts evaporated *in vacuo*. The infrared spectrum of the residue matched that of the pure cyanohydrin so closely that only minute traces of any other material could have been present.

III. A mixture of 17.2 g. (0.2 mole) of pivalaldehyde, 1.3 g. (0.02 mole) of potassium cyanide and 50 ml. of the usual solvent was placed in a heavy-walled 250-ml. bottle equipped with an electrical heating jacket. Air was swept out of the vessel with nitrogen, a desulfurized rubber stopper inserted and the bottle mounted in a mechanical shaker. A temperature of 80–90° was maintained for a period of one week. The mixture was seeded and placed in a refrigerator for 2 days without effect. Ether extraction and distillation yielded 2 g. of residue whose infrared spectrum could be adequately accounted for by comparison with the spectra of pivalic acid and pivalaldehyde cyanohydrin.

An attempt was made to obtain the aliphatic analog of benzilic acid referred to previously.[9] A mixture of 10 g. of pivalaldehyde, 2 g. of potassium cyanide and 20 ml. of the common solvent was refluxed for 84 hours as a slow stream of air was passed into the flask. Ether extraction and distillation produced 2.6 g. of residue identified as a mixture of pivalic acid and pivalaldehyde cyanohydrin by comparison of its infrared spectrum with the reference spectra.

The aqueous portion of the reaction mixture was acidified with concentrated hydrochloric acid, and the organic layer which separated was combined with ether extracts of the aqueous layer. The solvent was removed by distillation. The infrared spectrum of the residue (4.9 g.) matched that of pure pivalic acid so closely that it did not seem possible any other acidic substance could be present.

Crossed Condensation of Pivalaldehyde and Benzaldehyde.—Pivalaldehyde (34.4 g., 0.4 mole), benzaldehyde (42.4 g., 0.4 mole), potassium cyanide (10 g.) and 150 ml. of 50% aqueous ethanol were placed in the electrically heated reaction vessel described above, and the mixture was heated for one week at 90–100°. (In earlier experiments, it was found that shorter heating periods resulted in correspondingly lower yields.) The mixture was extracted with several portions of methylene chloride and the combined dried (sodium sulfate) extracts were distilled to remove the more volatile components. The residue was distilled at 0.5 mm. and yielded a fraction, b.p. 71–83° (11.7 g.), consisting of a mixture of phenylpivalylcarbinol and benzoyl-*t*-butylcarbinol contaminated with traces of benzoin. (In some instances the last portion of this distillate solidified in the side-arm; this solid was identified as benzoin.) The infrared spectrum of the product possessed all of the peaks associated with the hydroxyl, *t*-butyl, non-conjugated carbonyl, conjugated carbonyl and phenyl groups.

In an effort to remove the traces of benzoin, the material was steam distilled. Extraction of the distillate with methylene chloride and redistillation gave 9.1 g., b.p. 110–112° (2.5 mm.), which, as will be shown below, consisted of 60–70% of benzoyl-*t*-butylcarbinol and 30–40% of phenylpivalylcarbinol.

Reaction of Pivalaldehyde Cyanohydrin with Benzaldehyde.—A mixture of 5.7 g. (0.05 mole) of the cyanohydrin, 5.3 g. (0.05 mole) of benzaldehyde, 0.5 g. of sodium hydroxide and 20 ml. of the usual solvent was refluxed for 12 hours. Extraction with ether and distillation yielded a residue which partially solidified. The solid, identified as benzoin, was removed by filtration and the filtrate gave 0.4 g., b.p. 130–145° (9 mm.), of the mixture of isomeric acyloins.

Characterization of the Product.—The material was shown to be the crossed-benzoin condensation product of pivalaldehyde and benzaldehyde by oxidation to the corresponding mixed benzil, phenyl pivalyl ketone, and conversion to 2-*t*-butyl-3-phenylquinoxaline. These two compounds have been reported by Fuson, *et al.*[11] **The 2,4-dinitrophenylhydrazone of the diketone** was prepared, m.p. 173–174°.

Anal. Calcd. for $C_{18}H_{18}N_4O_5$: C, 58.37; H, 4.90; N, 15.13. Found: C, 58.27; H, 4.93; N, 15.10.

Determination of the relative amounts of the isomeric benzoins was made by conversion to the corresponding 2,4-dinitrophenylhydrazones. A solution of 1.0 g. of the mixture of isomers in dinitrophenylhydrazine reagent was allowed to stand at room temperature for 8 hours. The yellow precipitate (1.5 g.) was dissolved in benzene and adsorbed on a column of anhydrous alumina. The first band was eluted with benzene and afforded a few milligrams of the dinitrophenylhydrazone of benzoin. The second, broad yellow band was eluted with a 1:1 ether–benzene mixture and afforded 1.2 g. (60%) of the **dinitrophenylhydrazone of benzoyl-*t*-butylcarbinol**, m.p. 139–141°. It was recrystallized from aqueous ethanol as small yellow crystals, m.p. 141.5–142°.

Anal. Calcd. for $C_{18}H_{20}N_4O_5$: C, 58.05; H, 5.41; N, 15.05. Found: C, 58.36; H, 5.41; N, 15.11.

The filtrate from the preceding experiment gave 0.7 g. (35%) of the previously reported[11] 2,4-dinitrophenylhydrazone of phenylpivalylcarbinol after standing for 6 days at room temperature, m.p. 156–167°. A sample was recrystallized from ethanol; m.p. 173.5–174.5°.

Benzoyl-*t*-butylcarbinol.—To the Grignard reagent prepared from 107.4 g. (0.684 mole) of bromobenzene and 16.5 g. of magnesium turnings in 550 ml. of absolute ether was added dropwise with stirring a solution of 9.6 g. (0.085 mole) of pivalaldehyde cyanohydrin in 50 ml. of ether. The resulting solution was refluxed for 52 hours and hydrolyzed with 200 ml. of cold 20% sulfuric acid. The layers were separated, and the aqueous layer, after several extractions with methylene chloride, was boiled under reflux for 2 hours. Extraction with methylene chloride and distilla-

---

[17] A. Richard, *Ann. chim. phys.*, [8] **21**, 371 (1910); *C. A.*, **5**, 472 (1911). Attempts to distil samples of the crude cyanohydrin at 100 mm. resulted in decomposition.

[18] (a) S. V. Puntambeker and E. A. Zoellner, *Org. Syntheses*, **8**, 106 (1928); (b) J. M. Snell and S. M. McElvain, *ibid.*, **13**, 26 (1933).

[19] (a) V. I. Jegorova, *J. Russ. Phys. Chem. Soc.*, **46**, 1319 (1914); *C. A.*, **9**, 1904 (1915); (b) G. F. Hennion and T. F. Banigan, THIS JOURNAL, **68**, 1202 (1946).

tion to remove the solvent gave 3.5 g. of residue which partially solidified at room temperature. The crude product was distilled and the major fraction collected at 109–112° (2.5 mm.). The distillate solidified, m.p. 29.5–31°. Recrystallization from pentane yielded an analytical sample as fluffy, colorless needles, m.p. 30–31°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.08; H, 8.35.

The acyloin absorbs strongly at 5.94 μ in the infrared and at 246.5 mμ in the ultraviolet (ϵ 10,100), absorption maxima characteristic of phenyl ketones.

Isomerization of Phenylpivalylcarbinol and Benzoyl-*t*-butylcarbinol.—A mixture of the acyloin (in one case 2.0 g. of phenylpivalylcarbinol; in the other case 0.2 g. of benzoyl-*t*-butylcarbinol) and 10% of its weight of potassium cyanide in 6–10 ml. of 50% aqueous ethanol was refluxed for 3 hours. The mixture was extracted with several portions of pentane, and the dried extracts (sodium sulfate) were allowed to evaporate *in vacuo*. The infrared spectra of the two residues matched each other and the spectrum of the crossed condensation product except for very slight differences in the relative heights of the carbonyl absorption bands at 5.87 and 5.94 μ.

A second sample of phenylpivalylcarbinol (2.0 g.) and 1 ml. of 10% sodium hydroxide in 10 ml. of 50% aqueous ethanol was refluxed for 2 hours. The mixture was extracted as before to yield a residue whose infrared spectrum possessed all of the features of those referred to above.

A sample of phenylpivalylcarbinol was recovered unchanged after refluxing for 2 hours in the presence of dilute hydrochloric acid.

Spectral Analysis of the Crossed Condensation Product.—A series of synthetic mixtures of phenylpivalylcarbinol and benzoyl-*t*-butylcarbinol ranging in composition from 60 to 77% benzoyl-*t*-butylcarbinol were prepared and their infrared spectra determined. Comparison of the relative heights of the carbonyl peaks in the spectrum of the condensation product with the heights of the corresponding peaks in the reference spectra led to the assignment of the composition, 61% benzoyl-*t*-butylcarbinol and 39% phenylpivalylcarbinol to the condensation product and 60 to 70% benzoyl-*t*-butylcarbinol in the mixtures of isomers produced by the isomerization of both pure isomers. The absorption of the condensation product at 246.5 mμ indicated the presence of 77% benzoyl-*t*-butylcarbinol, and the mixtures produced by alkaline isomerization of the pure isomers were found to contain from 74 to 82% benzoyl-*t*-butylcarbinol. It was demonstrated by means of a synthetic mixture of the pure isomers that the ultraviolet absorption method provides a very reliable measure of the amount of benzoyl-*t*-butylcarbinol present if impurities other than phenylpivalylcarbinol are known to be absent. It was therefore concluded that some impurity, most likely benzoin, which is absent in the synthetic mixtures, is responsible for the discrepancy in the composition determination by the two methods.

COLUMBIA, SOUTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Stereochemistry of the Reaction of Alkyl Halides with Silver Nitrite[1,2]

BY NATHAN KORNBLUM, LEON FISHBEIN AND ROBERT A. SMILEY

RECEIVED OCTOBER 11, 1954

When optically active 2-bromoöctane is treated with silver nitrite the 2-nitroöctane and 2-octyl nitrite produced both have the inverted configuration and both are optically pure or very nearly so. The same result is obtained with active 2-iodoöctane. In contrast, the reaction of optically active α-phenylethyl chloride with silver nitrite yields α-phenylethyl nitrite of the same configuration as the chloride and α-phenylnitroethane of the opposite configuration from the halide; furthermore, the α-phenylethyl nitrite and α-phenylnitroethane are far from optically pure. The stereochemical relationships between alcohols and nitrite esters in the α-phenylethyl and in the 2-octyl systems have been established.

The present study is part of a program designed to gain an insight into the mechanism of the reaction of silver nitrite with alkyl halides. The literature on the stereochemistry of this reaction consists of a statement alleging that when 2-bromoöctane reacts with silver nitrite the 2-nitroöctane and 2-octyl nitrite produced have the same configuration as the 2-octyl bromide.[3] The present investigation demonstrates that the reverse is actually true.

Fortunately, configurational relationships in the 2-octyl and in the α-phenylethyl systems are well established. In each system the chloride, bromide, iodide, alcohol, nitrite ester and amine possessing the same sign of rotation belong to the same configurational series (see Chart I). Furthermore, the rotations of the optically pure alcohols, nitrites and amines are known. However, with the exception of α-phenylethyl chloride, the rotations of the optically pure halides have not been established. The rotations of the optically pure alcohols, nitrites and amines are given in Table I; also included are the highest recorded rotations of the halides.

CHART I

	Y					
	–Cl	–Br	–I	–OH	–ONO	–NH$_2$
n-$C_6H_{13}CHYCH_3$	(+)[a, b, c]	(+)[b, c]	(+)[b, c]	(+)[a, b, c]	(+)[d]	(+)[c, e]
$C_6H_5CHYCH_3$	(+)[b, c, f]	(+)[b, c]		(+)[b, c, f]	(+)[g]	(+)[c, h]

[a] A. J. H. Houssa, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1700 (1929). [b] E. D. Hughes, C. K. Ingold and S. Masterman, *ibid.*, 1196–1270 (1937). [c] E. D. Hughes, C. K. Ingold, P. Brewster and P. Rao, *Nature*, 166, 178 (1950). [d] N. Kornblum and E. P. Oliveto, THIS JOURNAL, 71, 226 (1949); S. J. Cristol, A. Shadan and B. Franzus, Abstract of Kansas City Meeting, March 24–April 1, 1954; p. 20N. [e] P. A. Levene and A. Rothen, *J. Biol. Chem.*, 115, 423 (1936). [f] J. Kenyon and H. Phillips, *J. Chem. Soc.*, 173 (1933). [g] N. Kornblum and S. A. Herbert, Abstract 121st National Meeting, American Chemical Society, March 30–April 3, 1952, Milwaukee, Wisc., p. 61K. [h] P. A. Levene, A. Rothen and M. Kuna, *J. Biol. Chem.*, 120, 777 (1937).

The 2-Octyl System.—A total of six runs were made using optically active 2-bromoöctane; these are summarized in Table II. The rotations of Table II all were obtained using very carefully purified products.

---

(1) Paper VII in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(2) This research was supported by the United States Air Force under Contract No. AF 18 (600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

(3) B. Eistert, "Chemismus und Konstitution," Ferdinand Enke, Stuttgart, Germany, p. 301, 1948. This statement apparently is based on a paper by R. H. Eastman and S. D. Ross, THIS JOURNAL, 68, 2398 (1946). Actually, Eastman and Ross briefly investigated the reaction of (+)α-phenylethyl chloride with silver nitrite, but aside from the fact that the α-phenylethyl nitrite produced had undergone considerable racemization, no stereochemical conclusions can be drawn from their paper.