suspended in 150 ml. of glycerol containing 23 g. of potassium hydroxide in a flask equipped with stirrer. The flask was immersed in an oil-bath kept at 150–170° for 9 hours. The cooled solution was diluted with an equal volume of water, boiled with a little Darco and then filtered. Acidification of the solution with 30 ml. of glacial acetic acid liberated the free acid as colorless thin needles which melted above 300°. The yield was 13.5 g. (88%).

The acid was insoluble in chloroform, benzene and dioxane, slightly soluble in dilute alcohol, and very soluble in dilute sodium hydroxide or ammonia. The acid was first purified by reprecipitation with acetic acid from a dilute ammonia solution and then by dilution of an alcohol solution with water; $\lambda\lambda_{\max}^{\mathrm{EtOH}}$: 330.5 mμ (log ε 4.07), 318 (4.05), 248–251 (4.40), 244 (4.42), 228–233 (4.47), 223 (4.48); $\lambda\lambda_{\min}^{\mathrm{EtOH}}$: 324 (3.99), 270 (3.26), 239 (4.40).

Anal. Calcd. for $C_{11}H_9NO_3$: neut. equiv., 203; methoxyl, 0. Calcd. for $C_{12}H_{11}NO_3$: neut. equiv., 217; methoxyl, 14.28. Found: neut. equiv., 204; methoxyl, 0.35.

Ethyl 4-Hydroxy-6-quinaldinecarboxylate.—Ten grams of the above purified, oven-dried acid was refluxed with 50 ml. of purified thionyl chloride and 50 ml. of dry thiophene-free benzene for 2 hours. Excess thionyl chloride and benzene were removed under reduced pressure at 60° and the residue was refluxed for 2 hours with 60 ml. of absolute alcohol. The excess ethanol was removed by distillation and the residue treated with ice-water and ammonia. The crude ester was recrystallized from dilute alcohol to yield 9 g. (79%) of a light tan crystalline product, m.p. 240–245° (uncor.). The compound recrystallized from dioxane as colorless thin plates, m.p. 267-268°; $\lambda\lambda_{\max}^{\mathrm{EtOH}}$: 331 mμ (log ε 4.08), 320 (4.04), 257.5 (4.38), 250 (4.38), 225 (4.54); $\lambda\lambda_{\min}^{\mathrm{EtOH}}$: 325 (4.04), 271 (3.37), 254 (4.36), 245 (4.34).

Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.51; H, 5.67. Found: C, 67.40; H, 5.88.

4-Hydroxy-6-quinaldine Carbohydrazide.—Seven grams of the ester was added to a mixture of 5 ml. of 85% hydrazine hydrate, 3 ml. of ethanol and 3 ml. of water and the mixture refluxed in an oil-bath at 110° for 6 hours. After chilling the solution, 6.5 g. of the hydrazide was obtained by filtration. An aqueous solution of the crude product was decolorized with Norite and filtered. On cooling, the acid hydrazide separated from the solution as colorless plates with a m.p. above 300°. Further crystallization from water in the absence of decolorizing charcoal caused slight discoloration of the compound. The acid hydrazide was slightly soluble in alcohol but insoluble in dioxane or benzene.

Anal. Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.11. Found: C, 60.76; H, 5.20.

Acknowledgment.—The authors wish to express their thanks to Professor L. S. Strait for helpful discussions regarding the absorption spectrum.

SCHOOL OF PHARMACY
UNIVERSITY OF CALIFORNIA MEDICAL CENTER
SAN FRANCISCO, CALIFORNIA

Rearrangement of 3-Chloro-3-ethylpentane During Acid-catalyzed Alkylation

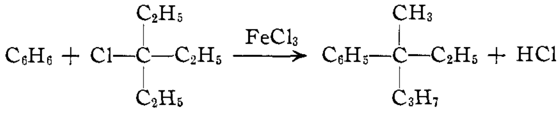
BY PAUL N. RYLANDER AND SEYMOUR MEYERSON

RECEIVED AUGUST 12, 1955

The extent of rearrangement during acid-catalyzed alkylation depends upon the activity of the catalyst and the structure of the alkylating agent.[1] An example of a large variation in the extent of rearrangement brought about by small changes in the structure of the alkylating agent has been observed in our laboratory. Benzene was alkylated with two tertiary chlorides; one rearranged but very slightly and the other completely.

Benzene was first alkylated under mild conditions by 2-chloro-2-methylpentane with ferric chloride catalyst; this catalyst has been recommended for cases where rearrangement is to be avoided.[2] The product was largely the expected, unrearranged isomer, 2-methyl-2-phenylpentane, contaminated with 1–2% of 3-methyl-3-phenylpentane and, unexpectedly, with 1–2% of the secondary isomer, 2-phenylhexane.

Benzene was also alkylated under the same conditions by 3-chloro-3-ethylpentane with ferric chloride catalyst. In sharp contrast to the above results the product was completely rearranged.



$$C_6H_6 + Cl-\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{C}}-C_2H_5 \xrightarrow{FeCl_3} C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle C_3H_7}{C}}-C_2H_5 + HCl$$

The yield was 90–95% 3-methyl-3-phenylhexane contaminated with an isomeric phenylheptane, tentatively identified as 2,3-dimethyl-2-phenylpentane. Because the expected product 3-ethyl-3-phenylpentane was not isomerized to 3-methyl-3-phenylhexane by ferric chloride in benzene, rearrangement must have occurred before or during alkylation.

Conceivably, rearrangement could have taken place during the preparation of the chloride from 3-ethyl-3-pentanol.[3] The chloride has been prepared previously, but no proof of structure has been attempted.[4-8] Hydrolysis of the chloride gave good first-order rate constants, which indicated that the material was not a mixture[8] but did not preclude total rearrangement to 3-chloro-3-methylhexane. To settle this point the chloride was examined by mass spectrometer. The spectrum was consistent with the 3-chloro-3-ethylpentane structure and clearly inconsistent with that of 3-chloro-3-methylhexane. Hence no rearrangement had occurred during the preparation of the chloride.

TABLE I

PARTIAL MASS SPECTRA OF ISOMERIC ALCOHOLS AND CHLORIDES

Spectra corrected for normally occurring C^{13}, Cl^{37} and H

	3-Ethyl-3-pentanol	3-Methyl-3-hexanol	3-Chloro-3-ethylpentane	3-Chloro-3-methylhexane
		Relative intensities[a]		
Parent	0.0	0.0	0.3	0.0
Parent less methyl	0.0	14.6	0.0	2.2
Parent less ethyl	100.0	100.0	100.0	100.0
Parent less propyl	1.1	150.1	6.5	154.3

[a] Values of 100.0 assigned to relative intensity at parent mass less ethyl.

Isomerization must have taken place during the alkylation. An analogous skeletal rearrangement of 3-ethylpentane to, among other things, 3-

---

(1) C. C. Price, "Organic Reactions," Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1946, p. 4.

(2) M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **74**, 292 (1952).

(3) For examples of rearrangements, see H. C. Brown and R. B. Kornblum, *ibid.*, **76**, 4511 (1954).

(4) E. Schriner, *J. prakt. Chem.*, [2] **82**, 294 (1910).

(5) F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55**, 1559 (1933).

(6) O. R. Quayle, K. Owen and E. M. Beavers, *ibid.*, **61**, 3107 (1939).

(7) J. Shorter and C. Hinshelwood, *J. Chem. Soc.*, 2412 (1949).

(8) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

methylhexane occurs in sulfuric acid.[9] Evidently the triethylmethyl structure has a strong tendency to rearrange.

Experimental

Ethylmagnesium bromide was allowed to react with ethyl carbonate[10] to give 3-ethyl-3-pentanol and with methyl propyl ketone[5] to give 3-methyl-3-hexanol. The corresponding chlorides were prepared by stirring the alcohols with two volumes of concentrated hydrochloric acid for one hour at 25°.[8] The layers were separated, the chloride was washed with water, dried over calcium chloride and distilled through a glass-packed column at 100 mm. Both chlorides were contaminated with olefin, which did not, however, interfere with analysis of the spectra.

Partial spectra of the alcohols and chlorides are given in Table I. The symmetrical compounds have small peaks corresponding to the loss of a propyl group. The unsymmetrical compounds have sizable peaks at these masses and the ratio of the relative intensities corresponding to the loss of ethyl and propyl groups is 2:3. The spectra are consistent with the assigned structures. This same correlation is observed with 3-methyl-3-phenylhexane and other secondary and tertiary alkylbenzenes.[11]

In both alkylations, 0.1 mole of the chloride was dissolved in 1.0 mole of benzene and the solution was cooled to 5°. To this was added 0.06 mole of anhydrous ferric chloride. The solution was allowed to warm slowly and, when evolution of hydrogen chloride ceased, water was added. The hydrocarbon layer was washed successively with 10% hydrochloric acid, 5% sodium bicarbonate and water, and was dried over calcium chloride. Both alkylates were purified by fractionation in a spinning-band column 90 cm. long × 5 mm. in diameter.[12] Selected cuts from the principal plateaus were analyzed with a Consolidated model 21-102 mass spectrometer. The 2-methyl-2-phenylpentane, 98% pure, boiled at 89.5° (20 mm.), n^{20}_{D} 1.4930. The 3-methyl-3-phenylhexane boiled at 110° (20 mm.), n^{20}_{D} 1.4950.

Reference samples of 2-methyl-2-phenylpentane and 2-phenylhexane were kindly supplied by Professor Herman Pines of Northwestern University. Reference samples of 3-methyl-3-phenylpentane and 3-ethyl-3-phenylpentane were prepared by sodium-catalyzed ethylation of ethylbenzene and toluene.[13]

---

[9] D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, THIS JOURNAL, **74**, 3269 (1952).

[10] "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1946, p. 602.

[11] S. Meyerson, *Applied Spectroscopy*, in press.

[12] J. C. Winters and R. A. Dinnerstein, *Anal. Chem.*, **27**, 546 (1955).

[13] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955).

RESEARCH DEPARTMENT
STANDARD OIL COMPANY (INDIANA)
WHITING, INDIANA

Ketones Contained in a Gilsonite Distillate

BY JAMES M. SUGIHARA AND THOMAS F. MCCULLOUGH

RECEIVED AUGUST 1, 1955

During the investigation of a Gilsonite coker-distillate,[1] the presence of carbonyl compounds was detected in a low-boiling fraction, by the formation of 2,4-dinitrophenylhydrazones. Acetone,[2,3] 2-butanone[2] and 3-pentanone,[2] have been found in shale oil.

The portion of the Gilsonite distillate boiling at 27–125°[1] was fractionated. The fractions collected at 29–52°, 59–64° and 67–81° were found to react with a 2,4-dinitrophenylhydrazine reagent[4] to form crystalline hydrazones. Intervening, lower and higher fractions gave extremely faint or no visible evidence of reaction.

The 2,4-dinitrophenylhydrazones isolated were identified as those of 2-butanone, 3-methyl-2-butanone and 2-pentanone. In addition the *p*-nitrophenylhydrazone of 2-butanone was obtained.

The presence of carbonyl compounds in the three separate fractions suggested an efficient separation, possibly as azeotropes. Ketones are known to form azeotropes with hydrocarbons such as cyclohexane and hexane.[5]

Chromatography of mixtures of 2,4-dinitrophenylhydrazones of carbonyl compounds has been described as a satisfactory method of separation of these compounds.[6] Derivatives of monocarbonyls, containing not more than four carbon atoms, have been separated. Paper chromatography is reported[7] to enable separation of some of the higher homologs. In our hands the chromatography of the mixture of the 2,4-dinitrophenylhydrazones of 2-butanone, 3-methyl-2-butanone and 2-pentanone on silicic acid failed to effect a satisfactory separation.

Experimental[8]

Separation of Ketones.—The portion of the Gilsonite coker-distillate[1] boiling between 27 and 125° (300 ml.) was fractionated in a Todd precise fractionation assembly using a column (850 × 12 mm.) packed with glass helices. At periodic intervals a few drops of distillate were collected and tested with the carbonyl reagent.[4] Formation of colored hydrazones was observed for fractions of boiling ranges 29–52° (24 ml.) (A), 59–64° (26 ml.) (B), and 67–81° (14 ml.) (C). The fraction, b.p. 64–67° (11 ml.), gave a faint test. The fractions, b.p. 27–29° (4 ml.), 52–59° (25 ml.), and 81–125°, gave negative tests.

2,4-Dinitrophenylhydrazones.—Each of the fractions A, B and C was shaken with 5 ml. of the hydrazine reagent. The resulting precipitates were collected, washed with 50 ml. of water and dissolved in 25 ml. of ether. The ether solutions were washed in succession with equal volumes of water, 5% aqueous sodium bicarbonate, water, and concentrated. The hydrazones were recrystallized from ethanol and water to constant m.p. From A, a 2,4-dinitrophenylhydrazone of m.p. 111–112° (reported[9] for 2-butanone 2,4-dinitrophenylhydrazone, 115°) was obtained. From B, a 2,4-dinitrophenylhydrazone of m.p. 123–124° (reported[10] for 3-methyl-2-butanone 2,4-dinitrophenylhydrazone, 122–122.5°) was obtained. The purified compound isolated from C had a m.p. of 140–141° (reported[9] for 2-pentanone 2,4-dinitrophenylhydrazone, 141°). Melting points of mixtures of these compounds with authentic samples of like melting points were not depressed. Yields were 80 mg. from A, 30 mg. from B and 40 mg. from C (crude).

The infrared spectra of the three 2,4-dinitrophenylhydrazones, determined with a Perkin–Elmer recording spectrophotometer, model 21, with pressed potassium iodide discs, were indistinguishable from those of authentic samples.

Other Derivatives.—The *p*-nitrophenylhydrazone of 2-butanone, m.p. 125–126.5° (reported[9] 128–129° (124°)),

---

[1] J. M. Sugihara and D. P. Sorensen, THIS JOURNAL, **77**, 963 (1955).

[2] G. Gejrot, *Varmlandska Bergsmanna Foreningens Ann.*, 87 (1945).

[3] G. Gellsing, *Arkiv. Kemi, Mineral. Geol.*, **7**, No. 29 (1921); *C. A.*, **15**, 3552 (1921).

[4] G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951).

[5] L. H. Horsley and co-workers, "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, pp. 82, 112 and 141.

[6] B. E. Gordon, F. Wopat, Jr., H. D. Burnham and L. C. Jones, *Anal. Chem.*, **23**, 1754 (1951), and earlier references, which are therein cited.

[7] D. F. Meigh, *Nature*, **170**, 579 (1952).

[8] All melting points are corrected. Boiling points are uncorrected and recorded at prevailing atmospheric pressure, about 640 mm.

[9] L. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, pp. 387 and 494.

[10] S. Winstein and L. L. Ingraham, THIS JOURNAL, **74**, 1160 (1952).