Benzonitrile.—A mixture of 12.1 g (0.10 mole) of benzamide, 4.18 g (0.11 mole) of sodium borohydride (Metal Hydrides, Inc.), and 80 ml of diglyme (dried on an alumina column) was stirred and refluxed for 1 hr. Evolution of hydrogen caused considerable foaming for about 45 min as the mixture became light yellow. The cooled mixture was poured into 500 ml of ice water, acidified with 100 ml of 20% acetic acid, and saturated with salt prior to extraction with ether. After drying and evaporation of the ether, the residue was analyzed by gas chromatography and contained 6.1 g (59% yield) of benzonitrile, in addition to diglyme and acetic acid. Distillation gave 4.90 g of the nitrile which was identified by its infrared spectrum and by hydrolysis to benzoic acid. From the distillation residue a trace of 2,4,5-triphenylimidazole, mp 275–276°[9] from aqueous ethanol, was isolated and identified by comparison of its infrared spectrum with that published.[10] Under similar conditions benzonitrile was recovered to the extent of 71% after treatment with excess hydride.

In a similar manner slow addition of phenylacetamide to a refluxing slurry of sodium borohydride in diglyme gave a 58% yield (by gas chromatography) of phenylacetonitrile. The latter compound was recovered (75%) unchanged upon treatment with excess sodium borohydride.

Upon reaction of acetamide and sodium borohydride in a 1:1 molar ratio, acetonitrile (98% pure) was obtained in 66% yield by distillation from the crude reaction mixture. Reaction with hydrochloric acid of the gases evolved during the reaction gave a small amount of ammonium chloride and ethylamine hydrochloride which were separated and identified by their infrared spectra. Acetonitrile was nearly quantitatively recovered under the same conditions.

3-Cyano-1,4,5,6-tetrahydropyridine (I) and 3-Cyanopiperidine (II).—To a well-stirred slurry of 3.78 g (0.1 mole) of sodium borohydride in 50 ml of diglyme maintained at 90–100° was added over 10 min 12.21 g (0.1 mole) of solid nicotinamide. Upon heating to 140° a vigorous reaction began and an orange semisolid separated and slowly solidified as the mixture was cooled to about 100° with a water bath. The yellow suspension was then refluxed for 1 hr and cooled, and 200 ml of ether was added, whereupon the solid which separated was filtered.

Upon addition of 200 ml of ether to the filtrate more solid precipitated and was removed. The filtered solid was washed with ether and from the combined filtrates ether was distilled at atmospheric pressure and diglyme at 75 mm. The sticky residue was distilled at 83–100° (3–3.5 mm) to give 1.71 g of a mixture of 3-cyanopiperidine (II) (91% pure by chromatography, 14% yield) and diglyme, in addition to a tarry residue. The distilled product from several runs was combined in aqueous HCl and the diglyme was removed by careful ether extraction. Compound II was then obtained by ether extraction after rendering the solution alkaline. The dried product was distilled at 77° (2.5 mm), $n^{25}\text{D}$ 1.4776.

Anal. Calcd for $C_6H_{10}N_2$: C, 65.40; H, 9.17; N, 25.43; equiv wt, 110.2. Found: C, 65.26; H, 9.35; N, 25.24; equiv wt, 111.

The tarry residue after removal of the above product was chromatographed in benzene solution on alumina (Alcoa F-20) and eluted with ether. The product was recrystallized from a mixture of ether–petroleum ether (bp 30–60°) containing Norit, yielding 1.82 g (17%) of 3-cyano-1,4,5,6-tetrahydropyridine (I), mp 38–39°. Further recrystallization gave an analytical sample, mp 39–40°.

Anal. Calcd for $C_6H_8N_2$: C, 66.62; H, 7.47; N, 25.91. Found: C, 66.41; H, 7.50; N, 25.69.

Registry No.—I, 7492-87-7; II, 7492-88-8; benzonitrile, 100-47-0; 2,4,5-triphenylimidazole, 484-47-9; phenylacetonitrile, 140-29-4.

Acknowledgment.—The authors are grateful to Mrs. Sylvia Miles for some of the infrared spectra and to Gordon Boudreaux and Dr. Robert Barker for the nmr spectra.

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[9] B. Radziszewski. *Ber.*, **10**, 70 (1877).

[10] Sadtler Spectrum No. 14151.

Migration of the Benzyl Group in the Base-Catalyzed Rearrangement of 4'-Chloro-α-benzylbenzoin[1]

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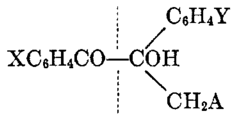
During the course of an investigation of base-catalyzed ether rearrangements,[3] we examined the behavior toward base of 4'-chloro-α-benzylbenzoin (I) and have found evidence for an unusually facile, base-catalyzed ketol rearrangement with migration of a benzyl group. Since work in this area has been temporarily discontinued we publish these results in their present state of completion.

Starting material I was prepared from α-oximinobenzyl 4-chlorophenyl ketone and benzylmagnesium chloride followed by hydrolysis of the oxime group (Scheme I). The isomer, 4-chloro-α-benzylbenzoin (II), was not prepared in a pure state. Addition of benzylmagnesium bromide to 4-chlorobenzil gave a mixture of I and II as shown by its infrared spectrum, nmr spectrum, and carbon–hydrogen analysis. It could not be separated into its constituents by the methods attempted. It was further characterized by mass spectrometry and by cleavage with periodic acid which showed that it consisted of I and II in a ratio of about 1.9.

The utility of mass spectrometry in the analysis of mixtures of α-alkylbenzoins stems from the fact that the major peaks are those with *m/e* corresponding to



$$XC_6H_4CO{-}C(OH)(C_6H_4Y)(CH_2A)$$

cleavage of the type shown below, as has been found previously with other α-hydroxy ketones.[4]

The α-benzylbenzoin (I) was treated with methanolic potassium hydroxide at 56°. Analyses of the product mixtures were carried out by cleavage with periodic acid and submission of the resulting ketone mixture to gas phase chromatography. The results were confirmed qualitatively by mass spectrometry of the original mixture. It was found that the initial ketol I after even 0.5 hr had rearranged significantly to the isomer II with benzyl migration and after 2 hr the ratio of I/II was nearly the same with a value of 1.9 as it was after 23 hr when it was 1.7. There was evidence that the product III was also produced but much more slowly. Phenyl migration was the reaction observed in a previous study of the reaction of the closely

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[1] Taken from the Ph.D. Thesis of A. C. Henry, University of Illinois, 1966.

[2] Roger Adams Fellow, 1962–1963. Grateful acknowledgment is made to the U. S. Army Research Office (Durham) for partial support of this work.

[3] For reviews of previous work, see H. E. Zimmerman, "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 372 ff; D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 230 ff.

[4] See K. Biemann, "Mass Spectrometry," McGraw Hill Book Co., Inc., New York, N. Y., 1962, p 90.

SCHEME I

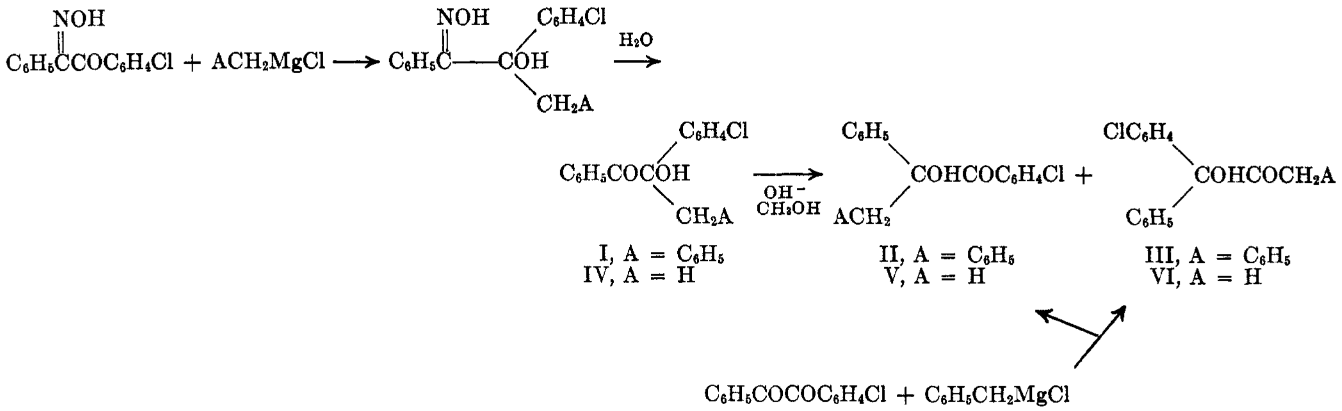


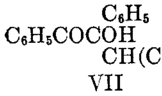
TABLE I

ANALYSES OF REACTION MIXTURES FORMED FROM THE REACTION OF I WITH METHANOLIC POTASSIUM HYDROXIDE AT 56°

Reacn time, hr	Yield of solid[a] product mixture (% of I used)	Product anal., % I[b]	II[b]	III[c]
0.5	55	90	10	..
1.0	59	75	25	..
2.0	51	65	35	..
23.0	36	50	30	20

[a] In addition 4–7% of cleavage to acid plus carbinol (or ketone) occurred. [b] Determined by cleavage with periodic acid followed by gas phase chromatographic analysis of ketone products. [c] Value from nmr determination.

related α-benzhydrylbenzoin VII with base.[5] Results of the studies of the reaction of I with methanolic potassium hydroxide are summarized in Table I.



$$C_6H_5COC(OH)(C_6H_5)CH(C_6H_5)_2$$

VII

Under conditions employed for chloro ketol I the unsubstituted compound, α-benzylbenzoin, gave indications of about 10% of phenyl migration after 23 hr (benzyl migration is, of course, not capable of being observed in this case).

Although the migration of aryl groups in related base-catalyzed ketol rearrangements has frequently been described,[6] there appears to be no precedent for a benzyl migration in such a reaction and it is of particular interest that the benzyl group competes successfully with phenyl migration. For comparison 4'-chloro-α-methylbenzoin (IV) was prepared from α-oximinobenzyl 4-chlorophenyl ketone and methylmagnesium iodide by a method similar to that employed for the benzyl compound I. When the α-methyl ketol (IV) was heated with methanolic potassium hydroxide for 23 hr under the conditions employed for the benzyl compound I it rearranged to the isomer V (with methyl migration) to an extent of less than 4% and to VI (with p-chlorophenyl migration) to not more than 10%.

The order of migration tendencies as deduced from these limited data thus appears to be benzyl > aryl > methyl. However, specific steric and other effects in a particular rearrangement probably play such an important part in governing the relative migrating tendencies that it is unwise to try to assign intrinsic "migratory aptitudes" of migrating groups without further study.

Experimental Section

Melting points are corrected. Nmr spectra were measured by Mr. Dick Johnson and his associates with deuteriochloroform solutions containing 1% tetramethylsilane unless otherwise indicated. Infrared spectra were measured by Mr. Dick Johnson and his associates with a Perkin-Elmer Model 521 spectrophotometer with solutions in chloroform unless otherwise specified. Microanalyses were carried out by Mr. J. Nemeth and his associates. Mass spectra were measured by Mr. J. Wrona with an Atlas CH4 spectrometer.

α-Benzylbenzoin, mp 120.5–121.5° (lit.[7] 120–121°), prepared by the method of Banus and Vila[7] had infrared absorption at 1679, 3450, 3580 cm^{-1} and nmr absorption at τ 2.1–3.2 (complex multiplet), 5.98 (singlet area 1), and an AB quartet (areas 1/4, J = 13.5 cps) centered at 6.37. The singlet at τ 5.98 is attributed to the OH since it was reduced in size when the sample was shaken with D_2O. The mass spectrum showed a very weak parent peak (intensity ~0) at m/e 302 at 15, 40, and 70 ev. At 15 ev there were peaks (and intensities) at 197 (100), 198 (18.2), and 105 (9.1), corresponding to the M and M + 1 peaks of the fragment $C_6H_5COHCH_2C_6H_5$ and to the fragment C_6H_5CO.

4'-Chloro-α-benzylbenzoin Oxime (I Oxime).—α-Oximino-4-chlorodesoxybenzoin, mp 113–115° (lit.[8] mp 113–114°), was prepared from the reaction of 4-chlorodesoxybenzoin with isoamyl nitrite by an adaptation of the method of Cava, Litle, and Napier.[9] Addition of the keto oxime (4.5 g, 0.017 mole) in 40 ml of diethyl ether to benzylmagnesium chloride (from 2.0 g, 0.082 g-atom, of magnesium and 9.1 ml of benzyl chloride in 50 ml of diethyl ether) at 0° followed after 20 min by neutralization and removal of the solvent gave 9.0 g of yellow oil containing solid. Addition of 15 ml of chloroform and filtration gave 3.9 g of white powder, mp 139–141.5°. Recrystallization from diethyl ether–hexane gave 2.2 g of benzyl oxime, mp 146.5–147.5° and further recrystallization brought the melting point to 149.5–150°. The nmr spectrum in acetone-d_6 showed a complex aromatic region at τ 2.4–3.3 (relative area 14), a singlet at 5.6 (area 0.8), and two doublets centered at 5.9 and 6.8 (J = 13 cps, area 2). In addition there was a broad singlet at τ −0.9 (area 1.3). The infrared spectrum (Nujol) showed no carbonyl absorption but there were three relatively weak absorptions at 1603, 1580, and 1533 cm^{-1} with hydroxyl absorption at 3520 and 3150 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}ClNO_2$: C, 71.7; H, 5.2. Found: C, 72.0; H, 5.4.

4'-Chloro-α-benzylbenzoin (I).—The oxime of I (2.4 g, 0.0068 mole) was hydrolyzed by heating for 10 min on a steam bath with 8 ml of concentrated sulfuric acid, 8 ml of water, and 45 ml of ethanol. The solution was cooled in an ice–salt bath and after the addition of 25 ml of water extracted with 25-ml portions of chloroform, the extracts were dried over magnesium sulfate, and the solvent was removed to leave a yellow oily residue. After treatment with 70 ml of boiling hexane and decanting the hexane

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(5) D. Y. Curtin and S. Leskowitz, *J. Am. Chem. Soc.*, **73**, 2633 (1951).

(6) See S. Selman and J. F. Eastham, *Quart. Rev.* (London), **14**, 221 (1960).

(7) A. G. Banus and J. P. Vila, *Anales. Soc. Españ. Fís. y Quím.*, **19**, 326 (1921).

(8) D. Y. Curtin and P. I. Pollak, *J. Am. Chem. Soc.*, **73**, 992 (1951).

(9) M. P. Cava, R. L. Litle, and D. R. Napier, *ibid.*, **80**, 2257 (1958).

from a small amount of insoluble oil, there resulted a solution which when chilled to 6° gave 1.23 g of I as white, fluffy needles, mp 110.5–113°. Recrystallization from hexane gave I, mp 121.5–122.5°, with 70% recovery. The infrared spectrum showed absorption at 3545, 3420, 1674, 1597 (medium intensity), and 1580 (weak) cm^{-1}. The nmr spectrum showed complex aromatic absorption at τ 2.13–3.17 and complex absorption at 6.1–6.8 which was simplified to an AB quartet centered at 6.39 (J = 13 cps) by shaking the solution with deuterium oxide to remove the absorption due to the OH. The mass spectrum at 15 ev showed peaks corresponding to M, $M + 1$, and $M + 2$ of the group $C_6H_5CH_2COHC_6H_4Cl$ at m/e 231 (100), 232 (20), 233 (35). At 40 and 70 ev the ratios of the peaks at 231 ($C_6H_5CH_2COHC_6H_4Cl$) and 197 ($C_6H_5CH_2COHC_6H_5$) were 61/1 and 117/1. Only a trace peak for the parent ion could be seen.

Anal. Calcd for $C_{21}H_{17}ClO_2$: C, 74.9; H, 5.1. Found: C, 74.7; H, 5.1.

Reaction of 4-Chlorobenzil with Benzylmagnesium Chloride. Mixture of 4- and 4′-Chloro-α-benzylbenzoin.—To 4-chlorobenzil,[10] mp 76–76.5°, in 75 ml of diethyl ether cooled in an ice–water bath was added 27 ml of 0.1 M benzylmagnesium chloride[11] over a period of 45 min in an adaptation of the procedure for the unsubstituted compound employed by Banus and Vila.[7] After neutralization and evaporation of the solvent there was obtained 8.9 g of a yellow-white, oily solid. Recrystallization from hexane gave a 46% yield of a mixture of I and II, mp 101–105°, as shown by the near identity of the infrared spectrum with that of I prepared above; the nmr showed a complex multiplet at τ 2.1–3.2 and complex absorption at 6.0–6.8 resembling two AB quartets not resolved from each other and with the further complication of the OH absorption. The mass spectrum at 15 ev showed a parent mass peak at 336 m/e of less than 1%. Peaks at m/e 231 (97), 233 (33.4), and 197 (100) corresponded to the cleavage products of the two isomers with the ratio of the sum of intensities of peaks at 231 and 233 to that at 197 = 1.3 at both 40 and 70 ev. Cleavage with periodic acid and gas phase chromatographic analysis of the neutral fraction as described below gave an average value of 1.9 for I/II.

Anal. Calcd for $C_{21}H_{17}ClO_2$: C, 74.9; H, 5.1. Found: C, 75.1; H, 5.2.

4′-Chloro-α-methylbenzoin (IV) was prepared by the method employed for I by addition of methylmagnesium iodide to α-oximino-4-chlorodesoxybenzoin and hydrolysis of the oxime group. Removal of the solvent gave a yellow oil which crystallized, and recrystallization from hexane gave 50% of the theoretical amount of IV, mp 97.5–98.5°. The infrared spectrum showed absorption at 1673, 3445, and 3605 cm^{-1}. The nmr spectrum showed a complex aromatic absorption at τ 2.1–2.9 (area 9) and singlets at 5.48 (area 1) and 8.15 (area 3). A mass spectrum at 15 ev showed peaks (m/e) (and relative intensities) at 260 (11) (parent mass), 155 (100), 156 (10), 157 (37) ($ClC_6H_4COHCH_3$). At 15, 40, or 70 ev the ratio of peaks at m/e 217 or 121 to 155 was less than 0.01.

Anal. Calcd for $C_{15}H_{13}ClO_2$: C, 69.1; H, 5.0. Found: C, 69.2; H, 4.9.

Reactions of Benzoins I and IV with Methanolic Potassium Hydroxide.—In a typical reaction 4.55 mmoles (0.1 m solution) of benzylbenzoin I was heated with titrated 0.88 M methanolic potassium hydroxide for 23 hr at 56° in a tightly stoppered tube. Addition of water, extraction of the neutral portion into ether, and evaporation of the ether after drying gave 0.145 g of solid with an infrared spectrum superimposable on that of the mixture of I and II prepared from p-chlorobenzil and benzylmagnesium-chloride except for a shoulder in the region 1710–20 cm^{-1} attributed to the presence of unconjugated ketone III. In a typical cleavage experiment 0.0098 g of product mixture was treated with 0.77 ml of 0.195 M solution of periodic acid dihydrate in absolute ethanol. The tube was shaken until solution was complete and allowed to stand at room temperature for 13 hr. Water was added and the mixture was extracted with 0.25 ml of chloroform.

Gas phase analysis was carried out at 240° with a 15-ft column packed with Apiezon-L, 20% on acid-washed silanized Chromasorb-W and with a flow rate of about 100 ml/min. Examination of known materials showed the retention times under these conditions to be for the product ketones as follows: benzophenone, 20.2 min; desoxybenzoin, 27.7 min; p-chlorobenzophenone, 38.1 min; and 4-chlorodesoxybenzoin, 52.4 min. Analysis of known mixtures (employing the products of peak height x width at half-height as measures of peak areas) showed that known mixtures of these substances could be analyzed to give relative amounts with an error of not more than ±5%. In one run the gas phase chromatography fractions were separated and their infrared spectra were shown to be identical with those of known samples.

Qualitative confirmation was provided by the mass spectrum of the neutral fraction at 15 ev which was used to determine the relative intensities of peaks at m/e 231 and 233 ($C_6H_5CH_2COHC_6H_4Cl$ from I) and 197 ($C_6H_5CH_2COHC_6H_5$ from II). Additional evidence for the presence of the benzyl ketone III in the reactions carried out for 23 hr was obtained by the observation of the nmr spectrum of the reaction mixture which showed a singlet at τ 6.15 instead of the $C_6H_5CH_2$ quartet characteristic of I and II by virtue of the fact that the benzyl group is attached directly to an asymmetric carbon atom. The relative areas of the quartet (I + II) and the singlet (III) were 4.5 ± 0.4 in the products of a reaction carrier out for 23 hr. The results are summarized in Table I.

Rearrangement of the α-methyl ketol (IV), mp 97.5–98.5°, for 23 hr under the same conditions used for the benzyl compound I gave 68% of a neutral fraction, mp 97.5–99°, with an infrared spectrum superimposable on the spectrum of IV. The mass spectrum showed, in addition to peaks at m/e 260 (16) and 263 (6) owing to the parent ion of IV, peaks at m/e 155 (100) and 157 (36) owing to the fragment $CH_3COHC_6H_4Cl$ from IV and finally a low peak at m/e 217 (1.4) attributable to the unit $ClC_6H_4COHC_6H_5$ formed from VI, the product of p-chlorophenyl migration. Nmr examination of the crude reaction mixture showed in addition to the CCH_3 singlet at τ 8.16 a new singlet at 7.74 attributed to the rearranged product VI. The ratio of the areas at 8.16 and 7.74 was 13.5 ± 1. Periodic oxidation and gas phase chromatography of the neutral fraction showed no p-chlorobenzophenone. The mass spectrum of the reaction mixture at 15, 40, and 70 ev showed peaks at m/e 121 (corresponding to the unit $C_6H_5COHCH_3$ of the product of methyl migration V) with intensities relative to the peak at 155 of less than 1/69, 1/54, and 1/60, respectively.

Registry No.—I, 7540-92-3; α-benzylbenzoin, 7540-93-4; I oxime, 7540-94-5; IV, 7540-95-6; II, 7548-10-9; III, 7540-96-7.

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[10] H. H. Hatt, A. Pilgrim, and W. J. Hurran, *J. Chem. Soc.*, 93 (1936).

[11] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p 471.

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cis-α-Methyl-β-acetylacrylic Acid

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Several publications have appeared in recent years concerning the ring–chain tautomerism of *cis*-α-methyl-β-acetylacrylic acid. Although the cyclic structure (1) has been advanced,[1] less than definitive evidence has been cited in its support. Structural interpretations based on the chemistry of this substance are also partially in error.

We prepared *cis*-α-methyl-β-acetylacrylic acid according to the method of Buchta and Satzinger[2] *via* the condensation of acetone with pyruvic acid. This substance exhibited a strong band in the infrared at 5.68 μ diagnostic of the five-membered hydroxy lactone structure (1). In the ultraviolet 1 exhibited only end absorption down to 210 mμ, whereas in aqueous alkali,

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[1] Compare (a) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, **48** (1951); (b) N. Hellstrom, *Nature*, **187**, 146 (1960); (c) E. Buchta and G. Satzinger, *Chem. Ber.*, **92**, 468 (1959).

[2] E. Buchta and G. Satzinger, *ibid.*, **92**, 449 (1959).