This halogenation procedure has also been used with monocarboxylic acids and has given practically quantitative yields of ethyl α-bromocyclohexyl acetate, ethyl α-bromophenyl acetate and ethyl α-chlorophenyl acetate. Table I represents the data for several α-bromo and α-chloro acids which have been prepared.

Experimental

The preparation of ethyl α-bromoadipate will illustrate the procedure for α-monobromination of dicarboxylic acids: In a 500-cc., round-bottom flask fitted with an adapter carrying a condenser protected by a calcium chloride tube and dropping funnel,[7] there was placed 174 g. (1.0 mole) of ethyl hydrogen adipate and 300 cc. of purified thionyl chloride.[8] The mixture was refluxed for approximately two hours and 168 g. (1.05 moles) of bromine added over a period of two to three hours. Gentle refluxing was maintained during the addition, and the mixture, after standing overnight, was poured cautiously into 500 cc. of commercial absolute ethyl alcohol. The resulting alcoholic solution was kept at room temperature for two to three hours, then poured into water and extracted with three 150-cc. portions of ether. The combined ether extracts were washed with water, dilute sodium bicarbonate solution and finally washed neutral with water. After drying over sodium sulfate, the ether was removed and the residue fractionated *in vacuo* in a 28-cm. Vigreux column.

The reaction mixture may be worked up by removing the excess thionyl chloride *in vacuo* following the bromination. The α-bromoester–acid is then added slowly to 200 cc. of commercial absolute alcohol and the α-bromo diester purified by distillation.

The monocarboxylic acids were brominated in essentially the same manner as described for ethyl α-bromoadipate: A mixture of one mole of the acid in 200 cc. of thionyl chloride was refluxed for two hours and then 168 g. (1.05 moles) of bromine added. After completion of the reaction, the α-bromo acid chloride was converted into the α-bromo ester by either of the two methods outlined.

Ethyl α-chloroadipate and ethyl α-chlorophenyl acetate were prepared by the procedure described for the bromination except that 450 cc. of sulfuryl chloride was used in place of the bromine. It was found advantageous to remove both the thionyl chloride and excess sulfuryl chloride *in vacuo* prior to converting the α-chloro acid chloride to the α-chloro ester.

Acknowledgment.—The authors wish to express their appreciation to Miss Hilda Hankin and Miss Virginia Peterson for their assistance.

Summary

A method for the mono-α-bromination of dicarboxylic acids is described wherein excellent yields are obtained. The method has been applied to aryl and cycloalkyl acetic acids with good results. Under similar conditions, α-chlorination of these acids also can be obtained in good yields with sulfuryl chloride.

BLOOMFIELD, N. J. RECEIVED MARCH 4, 1948

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[7] All glass apparatus was used for the reaction.

[8] Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass., 1941, p. 381.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Condensation of Butanal with 4-Heptanone and 3-Hexanone and Attempted Condensation of 2-Ethyl-2-hexenal with 4-Heptanone

BY S. G. POWELL AND ARNOLD T. NIELSEN[1]

This paper is concerned with three base-catalyzed aldehyde–ketone condensations. The first condensation between butanal and 4-heptanone gave a very low yield (3.6%) of a ketol, 5-ethyl-6-hydroxy-4-nonanone (I), in the presence of *N* alcoholic potassium hydroxide. Much of the 4-heptanone was recovered unreacted and as a result of a side reaction *n*-butyraldol and 2-ethyl-2-hexenal were formed in one run in yields of 26 and 47%, respectively. By heating I with iodine it readily dehydrated to form 5-ethyl-5-nonen-4-one (II), which on hydrogenation gave 5-ethyl-4-nonanone (III). Ketone III was also prepared from 5-ethyl-4-nonanol (IV), which was synthesized from 2-ethyl-1-hexanal and *n*-propylmagnesium bromide. The melting point of a mixture of the hydantoin derivatives formed from each of the two samples of ketone showed no depression.

In a second run, using a slightly different procedure, the unsaturated ketonic material isolated proved to be a mixture of II and 5-ethyl-6-nonen-4-one (V). Treatment of this mixture with an excess of sodium and alcohol reduced II to IV and V to 5-ethyl-6-nonen-4-ol (VI). Ozonolysis of the mixture formed by reduction yielded 2-ethyl-2-hexenal, the latter resulting from the dehydration of *n*-butyraldol, a possible ozonolysis product of VI. The propionaldehyde was not isolated.

$$\text{VI}\quad CH_3CH_2CH_2CHOHCH(CH_2CH_3)CH{=}CHCH_2CH_3 \longrightarrow CH_3CH_2CHO + CH_3CH_2CH_2CHOHCH(CH_2CH_3)CHO$$

$$CH_3CH_2CH_2CHOHCH(CH_2CH_3)CHO \xrightarrow{\text{heat}} CH_3CH_2CH_2CH{=}C(CH_2CH_3)CHO + H_2O$$

The amount of IV recovered and the yield of ozonide obtained indicate that the original mixture contained about one-third II. The formation of V was probably caused by excessive heating during fractional distillation.[2]

The second study pertains to the condensation of butanal with 3-hexanone. A survey of numerous aldehyde–ketone condensations reveals that in alkaline medium aldehydes condense on the α-methylene group of methyl ketones (CH_3-

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[1] From the Ph.D. thesis of Arnold T. Nielsen, June, 1947.

[2] Powell and Hagemann (THIS JOURNAL, **66**, 372 (1944)) report such a mixture of α,β and β,γ unsaturated ketones resulting from the condensation of isobutyraldehyde with 2-heptanone.

$COCH_2R$) unless steric factors prevent it, in which case condensation occurs on the methyl group. Since no unsymmetrical ketones other than methyl ketones have been condensed with aldehydes, the condensation of butanal with 3-hexanone was undertaken in order to determine the course of reaction. The experimental evidence obtained indicates that the only product formed results by condensation on the α-methylene carbon of the ethyl group. Compared to the butanal and 4-heptanone condensation the combined yield of ketol and unsaturated ketone was somewhat higher (10–12%). The structure of the condensation product was proved by ozonolysis of the α,β unsaturated ketone, 5-methyl-5-nonen-4-one (VII), to form 2,3-hexanedione which was identified by its dioxime. Ketone VII was hydrogenated to 5-methyl-4-nonanone (VIII) and further reduced to 5-methyl-4-nonanol (IX) with sodium and alcohol. Careful fractionation in a 28-plate column of VIII and IX separately showed both compounds to boil over a very narrow temperature range (1–1.5°). Apparently the condensation results in the formation of only one product unless the two isomers boil less than four degrees apart. It is not surprising to find that the reaction occurs in this manner in view of the greater reactivity of 3-pentanone with aldehydes in comparison with 4-heptanone. Isobutyraldehyde, for example, gives a 61% yield of a ketol with 3-pentanone.[2]

On standing for approximately one year, a sample of VII was partially oxidized into *n*-butyric acid. This ease of oxidation by air is a common property of several α,β unsaturated ketones and has been noted by other investigators.[3]

The third investigation concerns the attempted condensation of 2-ethyl-2-hexenal with 4-heptanone. It was noted by Freure[4] that α-branched aldehydes give higher yields of condensation products with ketones than do those without branching. However, he found 2-ethyl-1-hexanal to give only 8–10% yield of the unsaturated ketone with 4-heptanone. In the present work no condensation between 4-heptanone and 2-ethyl-2-hexenal was found to occur. Instead, the 2-ethyl-2-hexenal hydrates in the alkaline medium forming *n*-butyraldol which then dealdolizes to form butanal. The butanal reacts to form I and II (in the same yield) which were produced in the butanal and 4-heptanone condensation. No evidence was found for condensation products containing fifteen carbon atoms.

Acknowledgment.—The authors are indebted to Professor H. J. Dauben of this Laboratory for his valuable assistance which aided in completing this work.

Experimental[5]

Condensation of Butanal with 4-Heptanone.—The procedure employed was similar to that of Powell.[6] Butanal (144 g., 2 moles), b. p. 74–79°, was added dropwise with stirring to a solution of 550 g. (4.8 moles) of 4-heptanone and 50 cc. of *N* alcoholic potassium hydroxide solution. The mixture was stirred for two hours after addition of the aldehyde was complete and more alkali was added when necessary to keep the mixture slightly alkaline since the *p*H of the mixture dropped slightly during the reaction.

After working up the mixture in the usual manner there was obtained 51 g. (47%) of 2-ethyl-2-hexenal, b. p. 65–66° (15 mm.). The semicarbazone, m. p. 152–152.5°, when mixed with authentic 2-ethyl-2-hexenal semicarbazone of m. p. 153.4–154.4°[7] showed no depression in melting point. *n*-Butyraldol (38 g., 26%) was also formed, b. p. 105–110° (15 mm.). On redistillation it gave the constants: b. p. 105–106° (12 mm.); d^{24}_4 0.942; n^{24}_D 1.4475; M_D (calcd.) 40.68, M_D (found) 40.8. On dehydration of the *n*-butyraldol by distilling with a few crystals of iodine 2-ethyl-2-hexenal was formed.

5-Ethyl-6-hydroxy-4-nonanone.—Also obtained from the condensation was a fraction containing 27.5 g. (3.6%) of this ketol, b. p. 120–135° (15 mm.). On redistillation it gave the constants: b. p. 117.5° (17 mm.), 141–142° (37 mm.); d^{24}_4 0.910; n^{24}_D 1.4447; M_D (calcd.) 54.53, M_D (found) 54.4.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.60, 70.69; H, 11.65, 11.70.

5-Ethyl-5-nonen-4-one.—Dehydration of 13.6 g. of 5-ethyl-6-hydroxy-4-nonanone by distilling with a few iodine crystals gave 9.8 g. (80%) of 5-ethyl-5-nonen-4-one, b. p. 80–93° (8.5 mm.). The pale yellow ketone had a sharp, pleasant odor and the constants: b. p. 93° (8.5 mm.), 104–106° (15 mm.), 117–118° (30 mm.), 210° (760 mm.); d^{21}_4 0.849; n^{21}_D 1.4505; M_D (calcd.) 52.54, M_D (found) 53.4.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 77.84,[8] 78.13,[9] 77.85[8]; H, 12.07, 12.15, 12.30.

The **semicarbazone** melted at 121.2° after three recrystallizations from dilute alcohol.

Anal.[10] Calcd. for $C_{11}H_{23}N_3O$: C, 63.96; H, 10.29. Found: C, 63.9; H, 10.3.

5-Ethyl-4-nonanol.—This alcohol was prepared in the usual manner from 2-ethyl-1-hexanal and *n*-propylmagnesium bromide. The yield was 46% of material of b. p. 114–115° (17 mm.). Physical constants found are: b. p. 112–113° (15 mm.); d^{16}_4 0.837; n^{16}_D 1.4412; M_D (calcd.) 54.52; M_D (found) 54.4.

Anal. Calcd. for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.68, 76.50; H, 14.09, 13.98.

5-Ethyl-4-nonanone.—Oxidation of 5-ethyl-4-nonanol in the usual manner using sodium dichromate and sulfuric acid gave 5-ethyl-4-nonanone. The yield was 38% of material of b. p. 92–93° (13 mm.). The ketone having a pleasant, sweet, fruity odor had the constants: b. p. 92–93° (13 mm.); d^{24}_4 0.821; n^{24}_D 1.4250; M_D (calcd.) 53.03; M_D (found) 53.0.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.18, 77.34; H, 12.82, 13.13.

Attempts to prepare a semicarbazone, 2,4-dinitrophenylhydrazone and a 2,4-dinitrophenylsemicarbazone were unsuccessful.

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(3) (a) Lieben and Zeisel, *Monatsh.*, **4**, 10 (1883); (b) Franke and Kohn, *ibid.*, **20**, 876 (1899); (c) Dautwitz, *ibid.*, **27**, 773 (1906); (d) Meerwein, *Ann.*, **358**, 71 (1908); (e) Ecott and Linstead, *J. Chem. Soc.*, 905 (1930).

(4) (a) Wickert and Freure, U. S. Patent 2,088,018 (July 27, 1937); (b) Freure, private communication.

(5) Melting points are corrected. Boiling points are uncorrected.

(6) Powell, THIS JOURNAL, **46**, 2514 (1924).

(7) Powell and Ballard *ibid.*, **60**, 1914 (1938)) give the melting point as 152°.

(8) Sample analyzed several hours after being distilled.

(9) Sample distilled thrice and analyzed immediately.

(10) A small bubbler containing C. P. concentrated sulfuric acid was placed between the two absorption tubes to remove oxides of nitrogen as recommended by Burger, *Angew. Chem.*, **55**, 260 (1942).

A **hydantoin** was prepared using the directions of Speer and Henze[11] except that a period of heating of one week was required to obtain reaction. After six recrystallizations from dilute ethanol the derivative melted at 110.5–112.5°. The purification of the hydantoin was difficult due to the presence of a small amount of impurity which after repeated recrystallization from dilute ethanol melted at 140°. Insufficient material was available to purify it further.

Anal. Calcd. for $C_{13}H_{24}N_2O$: C, 64.96; H, 10.07. Found: C, 65.2; H, 10.1.

Hydrogenation of 5-Ethyl-5-nonen-4-one to 5-Ethyl-4-nonanone.—A 0.1035-g. sample of 5-ethyl-5-nonen-4-one, b. p. 90–93° (8.5 mm.), was hydrogenated in 15 cc. of absolute ethanol at 1 atm. and 24° with a platinum black catalyst. One mole-equivalent of hydrogen was absorbed within thirty minutes, after which time absorption ceased (calculated for one mole-equivalent, 15.0 ml.). A larger sample of the unsaturated ketone was hydrogenated to 5-ethyl-4-nonanone of b. p. 89–93.5° (13 mm.).

A hydantoin was prepared; m. p. 113.5–114.5° after four recrystallizations from dilute ethanol. When mixed with authentic 5-ethyl-4-nonanone hydantoin of m. p. 110.5–112.5° it melted at 109.5–113.5°.

Preparation and Ozonolysis of 5-Ethyl-4-nonanol and 5-Ethyl-6-nonen-4-ol Mixture.—In a second run in which twenty-five moles of butanal were used in six separate condensations the ratio of aldehyde to ketone was one to two. The condensation products were subjected to fractionation and heating with iodine in order to dehydrate the ketol and purify the unsaturated ketone. The purified unsaturated ketonic material obtained had the physical properties: b. p. 111° (15.5 mm.); $n^{25}D$ 1.4473; $d^{25}{}_4$ 0.862. Reduction of a 30-g. sample of this material with a large excess of sodium and moist ether gave material having the properties: b. p. 110–111° (16 mm.); $d^{25}{}_4$ 0.848; $n^{25}D$ 1.4415. (*Anal.* Found: C, 76.22, 76.24; H, 13.01, 12.96.) The reduction product decolorized bromine in a carbon tetrachloride solution without evolution of hydrogen bromide. 2-Ethyl-2-hexenal (837 g., 53%) was formed in the second run.

A 15.2-g. sample of the above reduction product was ozonized without use of a solvent until absorption of ozone was complete. After decomposing the ozonide (18 g.) there was obtained 5.2 g. of 5-ethyl-4-nonanol, b. p. 215–218° (760 mm.), 1.0 g. of 2-ethyl-2-hexenal, b. p. 170–180° (760 mm.), and 1.5 g. of residue, b. p. above 226° (760 mm.). The crude 5-ethyl-4-nonanol was purified by hydrogenation to remove traces of unsaturated impurities and treatment with sodium and alcohol to remove traces of ketonic material. The purified sample, b. p. 106–110° (14 mm.), $n^{23}D$ 1.4385, showed 0.92 mole-equivalent of active hydrogen and no additional methylmagnesium iodide reacted in a Zerewitinoff determination. The only ozonolysis product isolated was 2-ethyl-2-hexenal which formed a semicarbazone, m. p. 147.5–148.5°. This derivative showed no depression in melting point when mixed with an authentic sample of 2-ethyl-2-hexenal semicarbazone.

Condensation of Butanal with 3-Hexanone.—3-Hexanone was prepared by oxidation of 3-hexanol which was synthesized from ethylmagnesium bromide and butanal.[12] The condensation was accomplished by using the same procedure as in the butanal and 4-heptanone condensation. From 16.3 moles of butanal in ten separate condensations the following three fractions were obtained: (1) b. p. 61–73° (15.5 mm.), 585 g. (53%) of 2-ethyl-2-hexenal; (2) b. p. 90–104° (14 mm.), 226 g. (9%) of 5-methyl-5-nonen-4-one; (3) b. p. 96–101° (6.5 mm.), 27 g. (1%) of 6-hydroxy-5-methyl-4-nonanone. A second run gave 12.3% of the unsaturated ketone.

5-Methyl-5-nonen-4-one.—This ketone had the physical properties: b. p. 93–94° (12.3 mm.), 88–89° (9 mm.); $d^{26}{}_4$ 0.861; $n^{26}D$ 1.4505; $n^{23}D$ 1.4480; *M*D (calcd.) 47.92; *M*D (found) 48.2. A quantitative hydrogenation of a 0.1101 g. sample using a platinum catalyst at 1 atm. showed 17 ml. of hydrogen absorbed in thirty minutes after which time absorption ceased (calculated hydrogen absorbed for one mole-equivalent, 17.6 ml.).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 73.6, 74.7[13]; H, 11.3, 11.4.[13]

The **semicarbazone** melted at 121.5° after five recrystallizations from dilute alcohol.

Anal. Calcd. for $C_{11}H_{21}N_3O$: C, 62.52; H, 10.02. Found: C, 62.6; H, 10.2.

6-Hydroxy-5-methyl-4-nonanone.—The ketol had the constants: b. p. 103° (5.5 mm.); $n^{24.5}D$ 1.4458; $d^{24.5}{}_4$ 0.912; *M*D (calcd.) 49.92; *M*D (found) 50.0.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.3; H, 11.7.

Ozonolysis of 5-Methyl-5-nonen-4-one.—A 15.4-g. sample of the unsaturated ketone dissolved in 45 cc. of ethyl acetate was used. After ozonization was complete the solution of the ozonide was poured directly into an ice-cold solution containing an excess of hydroxylamine hydrochloride and sodium acetate.[14] After working up the mixture there was obtained 0.61 g. of 2,3-hexanedione dioxime, m. p. 161.5–165.5° (4% yield). Recrystallization twice from dilute ethanol gave a melting point of 168–169°. When mixed with an authentic sample of m. p. 172.5–173.5° the melting point of the mixture was 170.5–172.5°.[15]

Oxidation of 5-Methyl-5-nonen-4-one by Air.—A sample of the unsaturated ketone, b. p. 102–105° (19 mm.), *ca.* 110 cc., was left standing in a glass-stoppered bottle for nearly one year. The liquid became more viscous and had a sharp odor. On distillation at 10 mm. pressure the following fractions were obtained: (1) b. p. 50–72°, 24 cc. containing mainly *n*-butyric acid; (2) b. p. 82–88°, 50 cc. of 5-methyl-5-nonen-4-one; (3) b. p. 88–129°, 11 cc. of unidentified material; (4) 20 cc. of undistillable residue at a bath temperature of 205°. Fraction 1 was identified as butyric acid by the anilide, m. p. 96°; a mixed melting point determination with authentic *n*-butyranilide showed no depression. Fraction 2 was shown to be recovered 5-methyl-5-nonen-4-one by its semicarbazone, m. p. 121–121.5°.

5-Methyl-4-nonanone.—A large sample of 5-methyl-5-nonen-4-one was hydrogenated at three atmospheres pressure, using a platinum catalyst, to 5-methyl-4-nonanone. Fractional distillation of this reduced material was carried out in a 28-plate helix-packed column and all of the ketone distilled within a 1.5° temperature range; no evidence was found of a break in the distillation curve (milliliters distilled *versus* temperature). The colorless ketone, having a sweet, fruity odor, had the constants: b. p. 68–69° (6.0 mm.); $d^{26}{}_4$ 0.818; $n^{26}D$ 1.4195; *M*D (calcd.) 48.3; *M*D (found) 48.4.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.2; H, 12.8.

2,4-Dinitrophenylsemicarbazone.—The method of McVeigh and Rose[16] was used to give the crude derivative, m. p. 106–110°. After ten recrystallizations from dilute ethanol the pale yellow derivative, which resembles sulfur in appearance, melted at 128–129°.

Anal. Calcd. for $C_{12}H_{25}N_5O_5$: C, 53.81; H, 6.64. Found: C, 53.8; H, 7.8.[17]

5-Methyl-4-nonanol.—5-Methyl-4-nonanone was reduced to 5-methyl-4-nonanol with a large excess of sodium and alcohol. The pure alcohol when carefully fractionated in a 28-plate helix packed column distilled within a one degree temperature range. A small holdup of 7 cc. was dis-

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[11] Speer and Henze, THIS JOURNAL, **64**, 522 (1942).

[12] Procedure of Petrov and Kaplan, *J. Gen. Chem. U. S. S. R.*, **12**, 99–103 (1942); *cf. C. A.*, **37**, 1983 (1943).

[13] Second value obtained after redistilling thrice. Low values are probably due to rapid oxidation of the sample by air.

[14] Procedure first used by Broadbooks, Ph.D. thesis, University of Washington, 1939.

[15] Ponzio (*Gazz. chim. ital.*, **51**, II, 221 (1921)) gives the melting point as 175°.

[16] McVeigh and Rose, *J. Chem. Soc.*, 713–714 (1945).

[17] Although many precautions were taken, hydrogen values were always high.

tilled separately in a small Claisen flask and boiled at the same temperature. The sweet smelling alcohol had the constants: b. p. 80–81° (6.0 mm.); d^{27}_{4} 0.826; $n^{24.3}_{D}$ 1.4340; M_D (calcd.) 49.9; M_D (found) 49.7.

Anal. Calcd. for $C_{10}H_{24}O$: C, 75.88; H, 14.01. Found: C, 75.9; H, 13.9.

Attempted Condensation of 2-Ethyl-2-hexenal with 4-Heptanone.—The procedure was the same as that used in the butanal and 4-heptanone condensation except that stirring was continued for three days after all of the 2-ethyl-2-hexenal had been added. Two and one-half moles (315 g.) of 2-ethyl-2-hexenal and 8 moles (892 g.) of 4-heptanone were used. After removal of the unreacted aldehyde and ketone the following fractions were obtained: (1) b. p. 87–88° (9.5 mm.), 25 cc. (2.5%) of 5-ethyl-5-nonen-4-one; (2) b. p. 124–126° (14 mm.), 20 cc. (1.6% of 5-ethyl-6-hydroxy-4-nonanone; (3) b. p. above 170° (20 mm.), tarry residue.

Fraction 1 appears to be the same unsaturated ketone obtained in the butanal and 4-heptanone condensation. The following properties may be compared with those given above for 5-ethyl-5-nonen-4-one: b. p. 87–88° (9.5 mm.); n^{23}_{D} 1.4496; m. p. of semicarbazone 118–119° (melting point of mixed semicarbazones 112–114°); anal. semicarbazone: C, 63.1; H, 10.5. The melting point of the mixed semicarbazones was always lowered 5–6° despite repeated recrystallizations. No explanation for this fact can be given except that a small amount of impurity may be present in one or both of the derivatives. On quantitative hydrogenation a sample of the 5-ethyl-5-nonen-4-one from this condensation absorbed 1.27 mole-equivalent of hydrogen.

Fraction 2 appears to be identical with the ketol obtained in the butanal and 4-heptanone condensation. Its physical properties may be compared with those given above for 5-ethyl-6-hydroxy-4-nonanone; b. p. 118–119° (18 mm.); d^{21}_{4} 0.927. Dehydration of the ketol by heating with iodine at atmospheric pressure gave 5-ethyl-5-nonen-4-one, b. p. 90–93° (11 mm.), and water.

Summary

Butanal has been condensed with 4-heptanone and 3-hexanone in the presence of alkali and the mono-condensation products were isolated in small yields and identified in each case. With 4-heptanone, condensation occurs on the methylene group; with 3-hexanone, condensation occurs on the α-carbon of the ethyl group.

An attempt was made to condense 2-ethyl-2-hexenal with 4-heptanone, but the unsaturated aldehyde hydrates in the alkaline medium forming *n*-butyraldol, which dealdolizes to form butanal. The butanal formed then reacts with the 4-heptanone giving the same unsaturated ketone and ketol isolated in the 4-heptanone and butanal condensation.

SEATTLE, WASHINGTON RECEIVED MARCH 6, 1948

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY OF WESLEYAN UNIVERSITY]

The Use of Fluorescent Silica Gel Mixtures in the Chromatography of Colorless Compounds[1]

BY JOHN W. SEASE

Brockmann and Volpers[2] and Sease[3] have shown that the development of chromatograms of certain colorless, non-fluorescing compounds may be observed visually, provided that specially prepared fluorescent adsorbents are employed and the chromatographic column is illuminated with ultraviolet light. Brockman and Volpers prepared their adsorbents by adsorbing fluorescent organic materials on the adsorbent, while Sease obtained fluorescent silica gel by mixing 2.5% of a fluorescent zinc sulfide with silica. The use of this latter adsorbent was limited by the characteristics of the zinc sulfide to those compounds which exhibited appreciable absorption in the region 330–390 mμ. The present work, undertaken to determine the feasibility of extending the range by employing a fluorescent material sensitive to wave lengths below 330 mμ, shows that this may be achieved by admixture of a zinc silicate whose practical excitation range is approximately 230–290 mμ. By practical excitation range is meant the usable range when the adsorbent–fluorescent material mixture is packed in a chromatographic tube and wet with petroleum ether. Inclusion of both this zinc silicate and the zinc sulfide used in earlier work[3] gives a mixture whose excitation range is continuous from 390–230 mμ.

On such an adsorbent, containing 2.5% of each fluorescent material, 40 binary mixtures involving 25 different compounds have been chromatographed. Detailed descriptions of the resulting separations are given in Table I. Satisfactory visibility of the adsorbed compounds was obtained in every case by illuminating the column with the hydrogen lamp from a Beckman Spectrophotometer, which provides continuous illumination to below 220 mμ. A Purple X bulb (General Electric Co.) was usable in some cases, but not in others, where the spectral absorption of the zones occurred at very low wave lengths. Zones visible with either light source were almost invariably seen more readily with the hydrogen lamp. Because of the discontinuous nature of the radiation afforded, a quartz mercury lamp was of little value; a few compounds gave excellent shadows, but most were invisible.

Acetone was employed in preliminary experiments as an additive agent for increasing the strength of the petroleum ether developer, but was discarded in favor of diethyl ether when the latter was found to be markedly superior in producing certain separations. Benzene was not

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(1) This paper was presented before the Division of Analytical and Micro Chemistry at the 113th Meeting of the American Chemical Society, Chicago, April, 1948.

(2) H. Brockmann and F. Volpers, *Ber.*, **80**, 77 (1947).

(3) J. W. Sease, THIS JOURNAL, **69**, 2242 (1947).