fifth fractions were discarded; the boiling point of the collected material was 80.2° at 760 mm. pressure. The ethylene dichloride, Eastman Kodak Company practical grade, was stored for several days over anhydrous calcium chloride and distilled from anhydrous aluminum oxide. The fraction collected boiled at 83.5° under 768 mm. pressure. Its index of refraction was 1.4422 compared with the "International Critical Tables" value of 1.44225.

The resonance method as described by Wyman[6] was used for all the measurements, which were made at 25°.

The results of the measurements are shown in the table. Since density measurements were not available, it was not possible to calculate the polarization according to the relation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{(f_1M_1 + f_2M_2)}{\rho}$$

but it is hoped that this can be done at a later date.

The values for the dielectric constants of pure ethylene dichloride and benzene are in reasonable agreement with the values 10.235 and 2.267, respectively, found by Hooper and Kraus[7] at the same temperature. The data at low concentrations are also in good agreement with the previously determined values by Muller,[5] as nearly as can be judged by interpolation.

(6) Wyman, *Phys. Review*, **35**, 623–634 (1930).

(7) Hooper and Kraus, This Journal, **56**, 2265 (1934).

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NEW COMPOUNDS

Ethyl β-Keto-ε-phenoxyhexoate and Ethyl β-Keto-ζ-phenoxyheptoate

These β-keto esters have been prepared by carbethoxylation of the appropriate methyl ketones according to the procedure of Wallingford, Homeyer and Jones.[1]

γ-Phenoxypropyl Methyl Ketone.—Methylmagnesium bromide was prepared from 7.3 g. of magnesium and 29 g. of methyl bromide in 200 cc. of ether. The solution was cooled in an ice-bath while 29.3 g. of finely powdered anhydrous cadmium chloride (dried by heating in a stream of dry hydrogen chloride at 400–450° for three hours) was added. After stirring for two hours, 41.5 g. of γ-phenoxybutyryl chloride[2] was added slowly. After the initial reaction had subsided, the mixture was refluxed for two hours, with the separation of some solids. The reaction mixture was again cooled in an ice-bath and was decomposed by the slow addition of 300 cc. of 5% sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with ether. The ether extracts were dried over anhydrous sodium sulfate and were concentrated on the steam-bath. The product was distilled, and yielded 29 g. (78%) of the ketone boiling at 120–121° at 2 mm. This solidified upon cooling and melted at 48–50° A sample, recrystallized from methanol by cooling in a Dry Ice-bath, melted at 50–51°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.27; H, 7.92. Found: C, 74.40; H, 8.07.

The 2,4-dinitrophenylhydrazone, recrystallized from 95% ethanol, melted at 109–110°.

Anal. Calcd. for $C_{17}H_{18}O_5N_4$: N, 15.63. Found: N, 15.35.

Ethyl β-Keto-ε-phenoxyhexoate.—In an apparatus of the type described by Wallingford,[1] 2.6 g. of clean sodium was converted into dry sodium ethylate. With the oil-bath temperature at 50°, that of the heated fractionating column at 45°, and the pressure maintained at 130 mm., 70 cc. of diethyl carbonate and 20 g. of γ-phenoxypropyl methyl ketone in 10 cc. of diethyl carbonate were added. The bath was heated to 110° during thirty minutes and maintained there for one and one-half hours. Most of the alcohol which formed distilled during the first hour. The reaction mixture was then cooled and acidified with 125 cc. of 10% acetic acid. It was then extracted with ether and the ether extract was dried with anhydrous sodium sulfate. The diethyl carbonate was distilled at 20 mm. pressure and the residue fractionated at 1 mm. Four grams of forerun distilling between 130–156° and 9.0 g. (32%) distilling at 156–160° was obtained.

The N-phenylpyrazolone was prepared from 100 mg. of the keto ester and 50 mg. of phenylhydrazine by heating for fifteen minutes in 2.5 cc. of 80% ethanol with 0.1 cc. of acetic acid. After recrystallization from 90% ethanol, it melted at 115–117°.

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: N, 9.52. Found: N, 9.30.

The semicarbazone of the keto ester, after three recrystallizations from 50% ethanol, melted at 217–218°.

Anal. Calcd. for $C_{15}H_{21}O_4N_3$: N, 13.66. Found: N, 13.47.

The ethyl β-keto-ε-phenoxyhexoate was also prepared by the acylation of ethyl acetoacetate with γ-phenoxybutyryl chloride and hydrolysis of the phenoxybutyryl acetoacetate by shaking with 10% ammonium hydroxide.[3] The yield of the β-keto ester by this method was 5 to 9% and the product was difficult to purify. However, an N-phenylpyrazolone and a semicarbazone identical with those described above were obtained from the product synthesized by this method.

δ-Phenoxybutyl Methyl Ketone.—To 90 g. of sodium dissolved in 2 liters of absolute ethanol was added 520 g. of ethyl acetoacetate. The solution was stirred and heated to boiling and 860 g. of γ-phenoxypropyl bromide[4] was added over a period of two hours. The refluxing was continued for eight hours. The solution was cooled and decanted from the majority of the precipitated sodium bromide and the sodium bromide was washed with alcohol. The alcohol was removed by distillation on a steam-bath. To the crude ethyl α-aceto-δ-phenoxyvalerate, which weighed about 1300 g., was added a solution of 200 g. of sodium hydroxide in 4 liters of water and the mixture was stirred at room temperature for six hours. At the end of this time, about 250 g. of unsaponified oil remained. This layer was discarded and the aqueous layer was acidified by the drop-wise addition of 144 cc. of concentrated sulfuric acid in 300 cc. of water. The addition of the acid and accompanying decarboxylation was completed in two hours. The oily ketone was separated and the aqueous layer was extracted with ether and the ether extract was combined with the ketone. After drying briefly over sodium sulfate, the ether was removed and the ketone was distilled at 125–130° at 2 mm. The yield was 470 g. (61%) which solidified on cooling to 5°. It melted at 10°.

A sample which distilled at 127° at 2 mm. possessed n^{25}_{D} 1.5071; d^{20}_{20} 1.0164; M_D calcd. 55.67; found 55.95.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.81; H, 8.38. Found: C, 74.80; H, 8.54.

The 2,4-dinitrophenylhydrazone was recrystallized from 95% ethanol and melted at 100–101°.

Anal. Calcd. for $C_{18}H_{20}O_5N_4$:. N, 15.05. Found: N, 15.07.

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(1) Wallingford, Homeyer and Jones, This Journal, **63**, 2056, 2252 (1941).

(2) Hanford and Adams, *ibid.*, **57**, 921 (1935).

(3) Bouveault and Bongert, *Bull. soc. chim.*, [3] **27**, 1089 (1902).

(4) "Organic Syntheses," Coll. Vol. 1, 2nd ed., John Wiley and Sons, New York, N. Y., 1941, p. 435.

Ethyl β-Keto-ζ-phenoxyheptoate.—This compound was prepared by the procedure described for ethyl[1] β-keto-ε-phenoxyhexoate by the use of 6 g. of sodium, 175 cc. of diethyl carbonate, and 50 g. of δ-phenoxybutyl methyl ketone. The distillation of the residue from the concentration of the ether extract yielded 3 cc. of forerun to 158° and 18 g. (26.5%) which distilled at 162–164° at 1 mm. In another run, the product was distilled in a Hickmann vacuum still using a bath temperature of 100–120° at 0.02 mm. pressure. Three fractions possessing $n^{21}D$ 1.5009, 1.5020 and 1.5039 were collected. They totalled 28 g. (40%). The middle fraction possessed $d^{23}{}_{23}$ 1.0650, M_D calcd. (keto form) 71.19, (enol form) 72.23, found 73.10.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.12; H 7.63. Found: C, 68.45; H, 7.69.

The semicarbazone, after recrystallization three times from a large volume of water, melted at 212–214°.

Anal. Calcd. for $C_{16}H_{23}O_4N_3$: N, 13.08. Found: N, 12.99.

The N-phenylpyrazolone was prepared by warming 100 mg. of the keto ester and 50 mg. of phenylhydrazine for fifteen minutes in 5 cc. of 80% ethanol with 0.1 cc. of acetic acid. After recrystallization from 90% ethanol, it melted at 118.5–120°.

Anal. Calcd. for $C_{19}H_{20}O_2N_2$: N, 9.08. Found: N, 8.95.

Upon longer heating of the keto ester with an excess of phenylhydrazine in alcohol alone, a cleavage of the keto ester occurred and δ-phenoxyvaleryl phenyl hydrazide was obtained. After recrystallization from 75% ethanol, it sintered at 240° and melted at 285–287°.

Anal. Calcd. for $C_{17}H_{20}O_2N_2$: N, 9.85. Found: N, 9.87.

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Di-(β-phenoxyethyl) Oxalate

Incidental to a study of plasticizers, several aryloxyalkyl esters of oxalic acid have been prepared. Among these is di-(β-phenoxyethyl) oxalate. A search of the literature reveals that this particular ester has not been prepared previously.

The apparatus consisted of a 500-ml. 3-necked round-bottom flask equipped with a thermometer and gas leg in one side neck, an air condenser ($^3/_{16}$" inside diameter, 2 feet in length) in the other side neck and a mercury-sealed mechanical agitator in the middle neck. The flask was electrically heated.

The charge consisted of 63 g. of oxalic acid dihydrate, 138.2 g. of β-phenoxyethanol (phenol "cellosolve") and 2 ml. of a catalyst consisting of 50 g. of 95% sulfuric acid, 100 g. of phosphorous acid and 150 g. of methanol. The mixture was gradually heated under an atmosphere of inert gas, *i. e.*, carbon dioxide or nitrogen, to 150° and held at that temperature for four hours. On cooling, the solution solidified to a white, wax-like solid. The yield of crude product, m. p. 112.5–114.5°, was 156.5 g. or 95%. Crystallization from benzene and/or acetone resulted in a product melting sharply at 114°.

Anal. Calcd. for $C_{18}H_{18}O_6$: C, 65.5; H, 5.49; sapn. equiv., 165.2. Found: C, 65.7; H, 5.54; sapn. equiv., 164.8.

The ester is a hard, white wax-like solid and may find use as a synthetic wax.

Advance Solvents & Chemical
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α-Auromercapto-acetanilide

α-Carbamylmercapto-acetanilide was prepared in 60 and 80% yields by the procedures of Jaeger[1] and of Beckurts and Frerichs,[2] respectively. It crystallized from methanol or glacial acetic acid as plates or scales, m. p. 159° (cor.).[3] Heated with dilute ammonium hydroxide, α-mercapto-acetanilide was formed, m. p., after crystallization from methanol, 113° (cor.).

Procedure.—Sulfur dioxide was introduced into a solution of 10 g. of potassium auric bromide in 100 cc. of 95% alcohol. The potassium bromide which formed was removed by filtration and the light yellow solution added to an alcoholic solution of 3 g. of α-mercapto-acetanilide. A white precipitate formed at once. The mixture was diluted with water, the solid separated by centrifugation, washed repeatedly and successively with water, anhydrous ethanol and pentane, and dried *in vacuo* over phosphorus pentoxide. A yellowish gray powder insoluble in all common organic solvents was thus obtained. Upon heating, the compound darkened at about 230° and decomposed at 254°.

Anal.[4] Calcd. for C_8H_8NOSAu: C, 26.42; H, 2.23; N, 3.85; S, 8.82; Au, 54.3. Found: C, 26.57; H, 2.52; N, 3.89; S, 8.72; Au, 54.58.

α-Auromercapto-acetanilide, when treated with a 4% solution of $SeOCl_2$ in concentrated sulfuric acid, gives an intense purplish-red color. This reaction is given by other derivatives of α-mercapto-acetanilide, $C_6H_5NHCOCH_2SX$, where X = metal, -acyl, $-CONH_2$, $SCH_2CONHC_6H_5$, etc.

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(1) Jaeger, *J. prakt. Chem.*, [2] **16**, 18 (1877).

(2) Beckurts and Frerichs, *ibid.*, [2] **66**, 173 (1902).

(3) Jaeger[1] gives 148–152° and Beckurts[2] gives 147°.

(4) Microanalyses by Dr. Carl Tiedcke.

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Richmond Hill 18, New York
Ulrich Weiss

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June 10, 1945–July 10, 1945

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