(2) 0.44 g. (95–110°) and (3) 0.20 g. (110–115°). Fraction 3 (ketoalcohol V) solidified on standing and after recrystallization from benzene–hexane melted at 177–180°.

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.34; H, 10.39.

The infrared spectra of all three fractions had a strong carbonyl band at 5.85 μ. Only fraction 3 absorbed appreciably in the hydroxyl region (peaks at 2.75 and 2.85 μ).

B.—Diol IVb (409 mg.), m.p. 172–175°, was oxidized as in part A. The crude product (375 mg.) crystallized and after several recrystallizations melted at 183–185°. The filtrates from the recrystallizations containing most of the oxidation product (324 mg.) were treated with potassium hydroxide in methanol as in part A to yield V, m.p. 177–180° identical with the previous preparation. The melting point of a mixture of V and the crystalline product,[12] m.p. 183–185°, was 155–185°.

Structure Proof for V.—A solution of V (787 mg.) in ether (40 ml.) was added to methylmagnesium iodide prepared from methyl iodide (9.4 g.), magnesium (1.6 g.) and ether (50 ml.). The reaction mixture was processed as in the attempted structure proof of III. The product (756 mg.) crystallized on standing but was directly dehydrogenated without further purification. The first dehydrogenation with 5% palladium-on-charcoal and no solvent was incomplete. A portion (366 mg.) of the partially dehydrogenated mixture was dehydrogenated as in the previous case using freshly prepared palladium-on-charcoal (17%) and diphenylamine (2 g.) as a solvent. The main crystalline fraction of the dehydrogenation product (48 mg.) was recrystallized from ethanol to yield 1-methylphenanthrene which melted at 121–122°. The melting point of a mixture of this sample with authentic 1-methylphenanthrene (m.p. 118–119°)[13] was 118–120° (capillary). The picrate of this compound crystallized from ethanol as orange needles which melted at 136–139° (reported[13] 136–136.5°).

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[12] This is believed to be an isomer of V in which rings B and C are *cis*.

[13] Kindly furnished by Prof. R. C. Elderfield from the collection of the late Prof. W. E. Bachmann; W. E. Bachmann and A. L. Wilds, This Journal, **60**, 624 (1938).

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Monocyanoethylation of Certain Ketones

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Other investigations in this Laboratory have required the preparation of relatively large quantities of γ-acetylvaleric acid (II) or of its derivatives. Trial of previously reported[1,2] procedures for the synthesis of II revealed that these procedures were lengthy, utilized costly starting materials and resulted in low over-all yields. Indeed, the most attractive procedure for the synthesis of II appeared to be the monocyanoethylation of methyl ethyl ketone to give γ-acetylvaleronitrile (I) followed by acid hydrolysis to II. However, as pointed out by Yoho and Levine,[3] numerous investigators have found that cyanoethylation of simple ketones leads to the formation of polycyanoethylated derivatives as the main reaction products or to very low yields of the monocyanoethylated derivatives in those few cases in which monocyanoethylation has been observed. In fact, the best yield of I thus far reported was 6% (obtained by Barkley and Levine[4] from the reaction of methyl ethyl ketone anion with β-chloropropionitrile).

$$CH_3COCH_2CH_3 + CH_2{=}CHCN \longrightarrow$$

$$\underset{\text{I}}{CH_3COCH(CH_3)CH_2CH_2CN} \xrightarrow[HCl]{H_2O} \underset{\text{II}}{CH_3COCH(CH_3)CH_2CH_2CO_2H}$$

As far as we have been able to determine, most of the previously reported cyanoethylation reactions have been run with the stoichiometric quantities of both reactants (*e.g.*, equimolar quantities for attempted monocyanoethylations) although it seems reasonable that the use of a large excess of ketone over acrylonitrile might lead to a larger yield of the monocyanoethylated derivative. In support of this thesis we found that, when a 10 to 1 molar ratio of methyl ethyl ketone to acrylonitrile was used (with benzyltrimethylammonium hydroxide as catalyst), the yield of I was 24–30%.[5] The hydrolysis of I with concentrated hydrochloric acid gave II in 91% yield. Although the over-all yield of II is not high by the usual standards, the relative low cost of the starting materials (the unused methyl ethyl ketone may be recovered and reused) recommends this procedure over those previously employed for the preparation of II.

Cyclohexanone has been reported[6] to react with a molecular equivalent of acrylonitrile to give a 10% yield of the monocyanoethyl derivative. With a 5 to 1 ratio of ketone to acrylonitrile, cyclohexanone gave a yield of 47% of the monocyanoethyl derivative. Acetone has been reported to give an 8% yield of the monocyanoethyl derivative when either a 1 to 1 ratio[7] or a 2 to 1 ratio[8] of ketone to acrylonitrile was used, although in the former instance the product was not isolated in the pure state. With a 10 to 1 ratio of ketone to acrylonitrile, acetone gave an 18% yield of the monocyanoethyl derivative.

Experimental

γ-Acetylvaleronitrile (I).—In a typical experiment a mixture of 2160 g. (30 moles) of methyl ethyl ketone and 5 ml. of a 40% aqueous solution of benzyltrimethylammonium hydroxide was cooled to 5° in a 5-l. three-necked flask fitted with a stirrer, dropping funnel, thermometer and reflux condenser. To the cooled and well-stirred mixture 159 g. (3 moles) of acrylonitrile was added at such a rate that the temperature did not rise above 10° (about 15 minutes was required). Stirring was continued for five minutes after addition was completed and the mixture was neutralized with dilute hydrochloric acid to congo red. The excess methyl ethyl ketone (and acrylonitrile, if any) was removed by distillation at atmospheric pressure through a 15-in. Vigreux column. The residue was fractionated under reduced pressure and the fraction boiling at 110–120° (15 mm.) was taken leaving a considerable quantity of higher boiling product in the stillpot. The recovered methyl ethyl ketone was dried over potassium carbonate for reuse in similar reactions. Occasionally subsequent reactions were a little harder to control due to the presence of some unreacted acrylonitrile in the recovered methyl ethyl ketone. The product from three runs was fractionated through the same Vigreux column, giving 330 g, (29.4%) of γ-acetyl-

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[1] F. March, *Ann. chim.*, [7] **26**, 295 (1902).

[2] F. Lions, *J. Proc. Roy. Soc., N. S. Wales*, **771**, 192 (1938).

[3] C. W. Yoho and R. Levine, This Journal, **74**, 5597 (1952).

[4] L. B. Barkley and R. Levine, *ibid.*, **72**, 3699 (1950).

[5] The remainder of the acrylonitrile appeared as the dicyanoethyl derivative, yield *ca.* 70%.

[6] H. A. Bruson and T. W. Riener, This Journal, **64**, 2850 (1942).

[7] O. W. Shannon, U. S. Patent 2,381,371; *C. A.*, **40**, 350 (1946).

[8] A. P. Terent'ev and S. M. Gurvich, *Vestnik Moskov. Univ.*, **5**, No. 5, Ser. Fix.-Mat. i Estest. Nauk No. 3, 47 (1950); *C. A.*, **45**, 7005 (1951).

valeronitrile, b.p. 114–115° (15 mm.), n^{25}_{D} 1.4332, d^{25}_4 0.951.

Anal. Calcd. for $C_7H_{11}NO$: C, 67.15; H, 8.85; N, 11.19. Found: C, 66.97; H, 9.07; N, 11.05.

Starting with quantities of from 0.1 to 3.0 moles of acrylonitrile and 10 molecular equivalents of methyl ethyl ketone, other experiments gave yields of γ-acetylvaleronitrile of 24–30%. After distillation of the product the residue in the flask solidified on cooling and could be recrystallized (two or three times) from ethanol to give a *ca.* 70% yield of γ-acetyl-γ-methylpimelonitrile, m.p. 66–67°. The reaction could be run starting at room temperature (*ca.* 25°) and maintaining the temperature of the reaction mixture below 50° without any appreciable effect on the yield. Under these conditions the addition of acrylonitrile required 60 to 90 minutes, and it was necessary to use two large capacity condensers and to provide a means for very rapid cooling to prepare for those occasional reactions which became suddenly and vigorously exothermic.

When 178 g. (1.0 mole) of γ-acetyl-γ-methylpimelonitrile was added in small portions to a well-stirred mixture of 1440 g. (20 moles) of methyl ethyl ketone and 10 ml. of the benzyltrimethylammonium hydroxide catalyst at 27° and later warmed to 60° for two hours, none of the monocyanoethyl derivative (I) could be found in the distillates from the reaction mixture, nor could the yield of the monocyanoethyl derivative in the typical procedure be increased by adding varying amounts of the dicyanoethyl derivative at the start of the reaction.

γ-Acetylvaleric Acid (II).—To 160 ml. of concentrated hydrochloric acid was added 70 g. (0.64 mole) of freshly distilled γ-acetylvaleronitrile. The solution became red and boiled gently. A white solid appeared (amide?) which slowly disappeared as the solution was heated under reflux for four hours. The cooled mixture was diluted with enough water to dissolve the precipitated ammonium chloride (extraction at this point with five portions of ether gave *ca.* 60% of the desired product). The solution was neutralized with strong sodium hydroxide solution, made just acid to congo red with hydrochloric acid, saturated with sodium chloride, and extracted ten times with 50-ml. portions of ether. The ethereal solution was dried over magnesium sulfate and distilled from a Claisen flask, giving 74 g. (91%) of γ-acetylvaleric acid, b.p. 160–162° (16 mm.), semicarbazone m.p. 160–161° (dec.) (lit.[2] m.p. 159–162° (dec.)).

2-(Cyanoethyl)-cyclohexanone.—To a mixture of 370 g. (3.78 moles) of cyclohexanone and 10 ml. of a 40% aqueous solution of benzyltrimethylammonium hydroxide in a flask fitted with a stirrer, reflux condenser and dropping funnel and heated on the steam-bath to 60° was added dropwise with stirring 40 g. (0.76 mole) of acrylonitrile, the addition requiring about 20 minutes. The temperature of the reaction mixture rose above 60° but the mixture did not boil nor was there any appreciable amount of acrylonitrile condensing in the condenser. The mixture was allowed to stand until the temperature fell to 40°, the catalyst was neutralized with hydrochloric acid to congo red, and the mixture was washed with water, dried over magnesium sulfate, and distilled through the 15-in. Vigreux column, giving 52 g. (47%) of 2-(cyanoethyl)-cyclohexanone, b.p. 147–150° (14 mm.), 5 g. of material boiling at 150–200° (1 mm.), and 49 g. of residue.

When the above reaction was attempted at room temperature (26°) for a period of two hours, only traces of the above products were obtained.

γ-Acetylbutyronitrile.—A mixture of 580 g. (10 moles) of acetone and 5 ml. of 40% aqueous benzyltrimethylammonium hydroxide was heated to boiling under reflux and to the hot solution was added 53 g. (1.0 mole) of acrylonitrile dropwise over a period of one hour. The mixture was heated an additional hour under reflux. The catalyst was neutralized with hydrochloric acid to congo red and the solution was distilled through the 15-in. Vigreux column, giving 20 g. (18%) of γ-acetylbutyronitrile, b.p. 108–112° (14 mm.), 2,4-dinitrophenylhydrazone m.p. 154–155° (lit.[9] m.p. 154–155°).

When the above reaction was attempted at room temperature for two hours, the yield of the product indicated was 7%.

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(9) N. F. Albertson, THIS JOURNAL, **72**, 2594 (1950).

Fluorinated Esters. V. Surface Tension and Parachor Studies[1,2]

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The surface tensions of a number of fluorocarbons have been reported by Simons and Pearlson[3] and by Fowler and co-workers.[4]

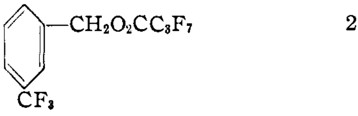
The values for these compounds are the lowest known and are considerably lower than those of analogous hydrocarbons. Schulman and Zisman[5] have recently reported the surface tensions of several fluorinated compounds including a number of perfluoroamines, chlorofluorocarbons and "pseudoperfluoroalcohols" of the type $H(CF_2)_xCH_2OH$.

In a continuation of the study of the relation of structure to physical properties of fluorine-containing esters and diesters,[6] the surface tensions of several of these esters were measured and the influence of fluorine on this property was noted.

In Table I are listed the surface tensions of eleven fluorinated esters and diesters and these are correlated with the percentage of fluorine in the molecule. The measurements were made by the ring method and the corrections for this method[7] included the use of the extended tables recently de-

TABLE I

SURFACE TENSIONS OF FLUORINATED ESTERS

Compound	γ, dynes/cm.	*t*, °C.	Fluorine, %
$C_2H_5O_2C(CF_2)_4CO_2C_2H_5$	22.7	27.0	43.9
$C_3H_7CH_2O_2C(CF_2)_4CO_2CH_2C_3H_7$	22.2	26.0	37.8
$C_3F_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	20.4	25.8	52.2
$C_3H_7CO_2CH_2(CF_2)_4CH_2O_2CC_3H_7$	23.9	26.0	37.8
$CF_3CO_2(CH_2)_5O_2CCF_3$	24.4	26.2	38.5
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	20.6	26.2	53.6
$C_3F_7CO_2(CH_2)_6O_2CC_3F_7$	22.2	26.2	52.2
$C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$	19.1	26.2	63.6
$C(CH_2O_2CC_3F_7)_4$[a]	18.5	26.0	57.8
	24.8	26.5	51.1
$C_3F_7CO_2CH_2CH_3$[b]	17.0	26.0	55.0

[a] Courtesy Minnesota Mining and Manufacturing Co., St. Paul, Minn. [b] This value is undoubtedly low since the density of the vapor of this compound (b.p. 96°) was neglected in the correction.

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[1] Part of the data in this paper was presented before the Fluorine Symposium at the 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

[2] Opinions expressed are those of the author and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[3] J. H. Simons and W. H. Pearlson, Fluorine Symposium, 112th Meeting of the American Chemical Society, New York, September, 1947.

[4] R. D. Fowler, J. M. Hamilton, Jr., J. S. Kasper, C. E. Weber, W. B. Burford, III, and H. C. Anderson, *Ind. Eng. Chem.*, **39**, 375 (1947).

[5] F. Schulman and W. A. Zisman, NRL Report 3950, April 1952.

[6] M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, THIS JOURNAL, **75**, 87 (1953); R. Filler, J. F. O'Brien, J. V. Fenner and M. Hauptschein, *ibid.*, **75**, 966 (1953); R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien and M. Hauptschein, *ibid.*, **75**, 2693 (1953); G. Rappaport, M. Hauptschein, J. F. O'Brien and R. Filler, *ibid.*, **75**, 2695 (1953).

[7] W. D. Harkins and H. F. Jordan, *ibid.*, **52**, 1751 (1930); B. B. Freud and H. Z. Freud, *ibid.*, **52**, 1772 (1930).