

valeronitrile, b.p. 114–115° (15 mm.), n_D^{25} 1.4332, d_4^{25} 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 monocycanoethyl derivative (I) could be found in the distillates from the reaction mixture, nor could the yield of the monocycanoethyl derivative in the typical procedure be increased by adding varying amounts of the dicycycanoethyl 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.³ m.p. 159–162° (dec.)).

2-(Cycanoethyl)-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-(cycanoethyl)-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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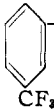
The surface tensions of a number of fluorocarbons have been reported by Simons and Pearson³ and by Fowler and co-workers.⁴

The values for these compounds are the lowest known and are considerably lower than those of analogous hydrocarbons. Schulman and Zisman⁵ have recently reported the surface tensions of several fluorinated compounds including a number of perfluoroamines, chlorofluorocarbons and "pseudo-perfluoroalcohols" 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 method⁷ 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
 $-CH_2O_2CC_3F_7$	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.

(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. Pearson, 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*, **76**, 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).

scribed by Fox and Chrisman⁸ for liquids of high density and low surface tension.

The difference in surface tension between a fluorinated diester and its hydrogen-containing analog is illustrated by diethyl octafluoroadipate (22.7 dynes/cm.) and diethyl adipate (28.0 dynes/cm.). This difference is comparable to that observed for fluorocarbons and hydrocarbons. It will also be noted that, with the exception of *m*-trifluoromethylbenzyl heptafluorobutyrate,⁹ the surface tension generally decreases with increasing fluorine content. A corollary to this observation may be drawn by noting the effect of increasing numbers of $-CF_2$ groups. While the addition of a methylene group is normally attended by an increase in surface tension (as illustrated by 1,5-pentanediol diheptafluorobutyrate and the corresponding 1,6-hexanediol ester), the value is lowered by the addition of $-CF_2$ groups, though this decrease becomes much smaller with increasing length of the fluorinated chain. This may be seen in the homologous series, $CF_3CO_2(CH_2)_5O_2CCF_3$, $C_3F_7CO_2(CH_2)_5O_2CC_3F_7$ and $C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$. Similar results were reported by Schulman and Zisman.⁵

In Table II are listed the experimental parachors of a few of these compounds, which were calculated from the surface tensions by the Sugden equation.¹⁰ These values are compared with those calculated from the atomic and structural constants of Sugden¹⁰ and of Mumford and Phillips.¹¹

TABLE II
PARACHOR DATA

Compound	Calcd. parachor		Expl. parachor	P_F
	Sugden	M.p., °C. ¹¹		
$C_3H_7O_2C(CF_2)_4CO_2C_3H_7$	544.6	530.0	538.0	24.9
$C_3F_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	752.2	750.6	728.7	24.0
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	713.2	710.6	704.8	25.1
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	752.2	750.6	753.8	25.8
$C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$	1162.8	1192.2	1114.0	24.1

The atomic parachor for fluorine (P_F), obtained from the experimental values using the Sugden constants (except for fluorine), range from 24.0 to 25.8. If the more recent constants given by Vogel¹² are employed, values from 22.2 to 24.0 are obtained. Schulman and Zisman⁵ found similar variances in the few examples they studied. Fowler⁴ reported values of 24.4–24.8 for P_F in fluorocarbons, which are lower than those assigned by Sugden¹⁰ (25.7), Mumford and Phillips¹¹ (25.5) or Vogel¹² (26.1).

It is therefore difficult with the data now available to assign a definite value or a narrow range for the atomic parachor for fluorine, though what data have been accumulated seem to indicate that the earlier values may be somewhat high. It may, perhaps, be advisable to assign a parachor value to the CF_2 group instead of to a single fluorine atom. This system of assigning values to whole groups

(8) H. W. Fox and C. H. Chrisman, Jr., *J. Phys. Chem.*, **56**, 284 (1952).

(9) This compound has not been described previously. Physical constants include: b.p. 52–53° (0.8 mm.), n_D^{20} 1.3824 and d_4^{20} 1.491.

(10) S. Sugden, "The Parachor and Valency," Routledge and Sons, Ltd., London, 1930.

(11) S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112 (1929).

(12) A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

rather than to individual atoms has been suggested by Gibling.¹³ It also takes into account the slight increase in parachor of the methylene group as the number of carbon atoms increases. This might also be applied to the CF_2 group. The bond parachors suggested by Vogel¹⁴ may also prove useful. In this system a preliminary value of 28.2 has been assigned for the C–F bond. The present diesters give C–F bond parachors varying from 24.4 to 26.2.

Experimental

Measurements were made with a Du Noüy Interfacial Tensiometer (Precision direct reading model), using a platinum-iridium ring with a circumference of 6.015 cm. and $R/r = 53.8$.

Acknowledgment.—The author wishes to thank Mr. Ray Robinson for his assistance with the measurements.

(13) J. W. Gibling, *ibid.*, 299 (1941); *ibid.*, 661 (1942); *ibid.*, 146 (1943).

(14) A. I. Vogel, W. T. Cresswell, G. J. Jeffery and J. Leicester, *Chemistry and Industry*, 358 (1950).

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The Compounds Formed between Nickel(II) and Dimethylglyoxime by Alkaline Oxidation

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The determination of traces of nickel by dimethylglyoxime in the presence of alkaline oxidizing agents is established analytical practice. Difficulties still encountered, in particular the formation^{2a} of a "metastable" complex, are largely explained by the discovery by Hooreman^{2b} of two complexes with markedly different absorption spectra, and containing nickel and dimethylglyoxime (DMGOH) in the ratio 1:2 and 1:4. (For brevity we shall refer to them as complexes I and II, respectively.)

Isolation in the solid state of these complexes is very difficult and we believe that the substances isolated and analyzed by authors such as Feigl,³ Kuras and Ruzicka⁴ or Okac and Polster⁵ are not the same as those present in solution during analytical methods for traces of nickel. Whilst disagreeing with the findings of Babko,⁶ we do agree that techniques such as spectrophotometry are the most reliable for elucidating the formulas of compounds of this type and we have used such methods exclusively.

Experimental

Absorption Spectra.—The absorption spectra of complex I and complex II, were obtained at $3.75 \times 10^{-5} M$ concentrations.

Complex I had two peaks in the visible, the molar extinction coefficients being 1.16×10^4 (442 $m\mu$) and 0.52×10^4 (530 $m\mu$). The oscillator strength, f , of the main peak was approximately 0.16 per nickel atom. The single broad peak of complex II had a molar extinction coefficient of $1.28 \times$

(1) The British Columbia Research Council, Vancouver 8, Canada.

(2) (a) N. H. Furman and B. McDuffie, Atomic Energy Commission Classified Report AEC-M-4234 (1947); (b) M. Hooreman, *Anal. Chim. Acta*, **3**, 635 (1949).

(3) F. Feigl, *Ber.*, **57**, 758 (1924).

(4) M. Kuras and E. Ruzicka, *Chem. Listy*, **45**, 100 (1951).

(5) A. Okac and M. Polster, *Collection Czechoslov. Chem. Commun.*, **18**, 561 (1948).

(6) A. K. Babko, *Zhur. Anal. Khim.*, **3**, 284 (1948).