chloroform evaporated and the residual oil allowed to stand 18 hours with 5 ml. of acetic anhydride. The reaction mixture was diluted with water, extracted with chloroform and processed in the usual manner. The product was recrystallized from ethanol–water, yield 128 mg. (65%), m.p. 185–187°, specific activity: 13.2 cts./min./mg. $BaCO_3$, 32.3 cts./min./mg. $BaCO_3$ (cor.).[16]

Anal. Calcd. for $C_{27}H_{49}ON$: C, 80.33; H, 12.23. Found: C, 80.23; H, 12.16.

(16) The correction factor employed was 27/11 allowing for the methyl carbon lost and the two atoms of the acetyl derivative.

CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

The Infrared Spectra of Enolate Ions

BY MYRON L. BENDER AND JOHN FIGUERAS

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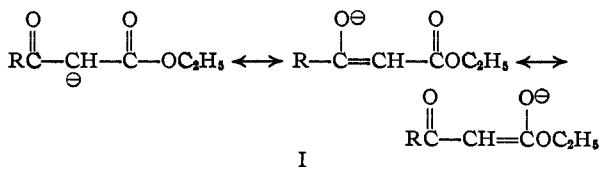
While studying the addition of sodium alkoxide to various esters,[1] the reactions of sodium ethoxide with ethyl acetoacetate, ethyl benzoylacetate and diethyl malonate in ethanol solution were investigated. These reactions did not result in addition to the carbonyl group[1] but rather in the production of enolate ions in all cases. The infrared spectra of the enolate ions exhibited a new band characteristic of the enolate anion as well as the absence of the original ester carbonyl and keto carbonyl absorption bands. These changes were not found in the system, ethyl levulinate and sodium ethoxide, which would not be expected to form an enolate ion. In addition, enolate ions were prepared in ethanol solution from the reaction of sodium ethoxide with acetylacetone and 2-nitropropane.

In the case of the β-keto esters, the enolate ion shows the disappearance of both the keto and ester carbonyl bands which indicates that the resonance hydrid of the enolate ion includes contributors involving the negative charge on the ester oxygen as well as the keto oxygen and the α-carbon as shown in I.



I

(1) M. L. Bender, THIS JOURNAL, **75**, 5986 (1953).

The enolate ion from diethyl malonate was formed only to the extent of 30–35% when equimolar quantities of sodium ethoxide and diethyl malonate were mixed, whereas the β-keto esters formed enolate ions under identical conditions to the extent of 95–100%. These results are in conformity with the relative stabilities of the resulting enolate ions. This is the first instance of the determination of the infrared spectra of enolate anions.[2,3]

Experimental

Materials.—Ethanol and sodium ethoxide in ethanol were prepared as described previously.[1] Ethyl acetoacetate ($n^{20}D$ 1.4198), ethyl benzoylacetate ($n^{20}D$ 1.5290), diethyl malonate ($n^{20}D$ 1.4143), acetylacetone ($n^{20}D$ 1.4511) and 2-nitropropane ($n^{20}D$ 1.3941) were Eastman Kodak Co. products which were fractionated before use.

Infrared Spectra.—Infrared spectra were determined by use of a Perkin-Elmer Model 21 Double Beam Recording Infrared Spectrophotometer. Matched sealed liquid absorption cells approximately 0.1 mm. in thickness were employed. Spectra of all compounds were determined in the region from 1200–2000 cm.$^{-1}$ using approximately 0.1 *M* solutions in absolute ethanol. Sodium ethoxide in ethanol was added to the compounds in equimolar amounts and the spectra of the resulting anions were determined. Table I indicates the absorption bands in the carbonyl region before and after the addition of ethoxide ion.

TABLE I

INFRARED ABSORPTION BANDS IN THE CARBONYL REGION OF SOME COMPOUNDS AND THEIR CORRESPONDING ENOLATE IONS IN ETHANOL

	Original bands (cm.$^{-1}$)[a]				
Compound	Ester C=O	Ketone C=O	Chelated conjugated C=O	Conjugated C=C	Enolate ion bands
Ethyl acetoacetate	1741 (s)[e]	1715 (s)	1650 (w)	1630 (w)[b]	1662 (1649, 1629) (s)
Ethyl benzoylacetate	1739 (m)	1686 (m)[c]			1656 (s)
Diethyl malonate	1740 (s)[d]				1666 (m)
Ethyl levulinate	1726 (s)	1721 (s)			
Acetylacetone		1726 (w)	1615 (s)[b]		1604 (s)
2-Nitropropane	1550 (s) (nitro)				1604 (s)

[a] These values are reliable to ±2 cm.$^{-1}$. [b] Compare assignments of R. S. Rasmussen and R. B. Brattain, THIS JOURNAL, 71, 1093 (1949); N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Peterson, *ibid.*, **74**, 4070 (1952). [c] The keto group is conjugated with the benzene ring as in acetophenone. [d] This band is unusually broad (25 cm.$^{-1}$). [e] Relative intensity symbols determined by per cent. transmission as follows: vw, 95–100; w, 90–95, m, 60–90; s, 20–60; vs, 5–20; vvs, 0–5.

(2) C. Duval, R. Freymann and J. Lecomte, *Compt. rend.*, **231**, 272 (1950); *Bull. soc. chim. France*, 106 (1952), reported the infrared spectra of several metal chelates of acetylacetone. They observed no normal carbonyl band and suggested that the metal acetylacetonates exist solely in the enolic form, that the C=O and C=C bands may undergo large shifts because of perturbations and that in general the infrared spectra of the acetylacetonates resemble those of complexes rather than those of salts.

(3) M. Kubota, *J. Chem. Soc. Japan*, **62**, 214 (1941), reported the ultraviolet absorption spectra of the sodium salts of acetylacetone and ethyl acetoacetate in alcohol solution. He observed a shift from the parent compounds toward the longer wave lengths.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS

Aryloxyketones

BY CHARLES K. BRADSHER, FRANCES C. BROWN AND R. JACK GRANTHAM

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In view of the reported fungistatic activity of pentachlorophenoxyethanol[1] and related compounds, it seemed of interest to prepare and test some aryl-

(1) C. W. MacMullen (to Röhm and Haas), U. S. Patent 2,416,263; Felton and McLaughlin, *J. Org. Chem.*, **12**, 298 (1947).

TABLE I

ARYLOXACETONES

Phenoxyacetones	Yield,[a] %	M.p., °C.	Formula	Analyses,[c] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	*A. niger* inhibition, % at 250 p.p.m.
Cl_5	94.5	106.5–107	$C_9H_5O_2Cl_5$	33.53	33.67	1.56	1.57	72
2,4-Cl_2	15.5[b]	55.5–56.5	$C_9H_8O_2Cl_2$	49.35	49.40	3.68	3.84	84
2-CH_3-3,4,5,6-Br_4	84[b]	149.5–150.5	$C_{10}H_8O_2Br_4$	25.03	25.35	1.68	2.01	17
2-Br-4-C_6H_5	24[b]	88.5–89	$C_{15}H_{13}O_2Br$	59.05	59.07	4.26	4.54	15
4-$C_6H_5CH_2O$	70	73.5–75	$C_{16}H_{16}O_3$	74.97	75.24	6.29	6.57	17
Naphthoxyacetones								
1-Br-2	97	69.5–70.5	$C_{13}H_{11}O_2Br$	55.93	56.19	3.97	3.91	
1,6-Br_2-2	95	109.5–110.5	$C_{13}H_{11}O_2Br$	(Br Calcd.: 28.63.		Found: 28.58)		6
1,6-Br_2-2	90	151.5–152.5	$C_{13}H_{10}O_2Br_2$	43.61	43.72	2.81	3.07	0
2,4-Cl_2-1	94	87–88	$C_{13}H_{10}O_2Cl_2$	58.02	58.06	3.75	3.82	0

[a] All yields are for products with melting points not more than two degrees below that of the analytical sample. [b] No potassium iodide added. [c] Analyses by Clark Microtechnical Laboratories.

oxyketones. Most of these ketones were prepared by the Hurd and Perletz[2] modification of the method of Bradsher and Rosher.[3] Fungistatic action of the compounds against *Aspergillus niger* was determined essentially as described by Leonard and Blackford,[4,5] and as may be seen from Table I none of the aryloxyacetones completely inhibited growth of the fungus at 250 parts per million.

1-(6-Bromo-2-naphthoxy)-2-hexanone was prepared from 1-chloro-2-hexanone[6] by the same general procedure, yielding white flakes from alcohol, m. p. 67–68° (48% yield). The analytical sample melted at 68.5–69°. At 250 p.p.m. it inhibited the growth of *A. niger* by only 23%.

Anal. Calcd. for $C_{16}H_{17}O_2Br$: C, 59.82; H, 5.34. Found: C, 59.46; H, 5.65.

(2) C. D. Hurd and P. Perletz, THIS JOURNAL, **68**, 38 (1946).
(3) C. K. Bradsher and R. Rosher, *ibid.*, **61**, 1524 (1939).
(4) J. M. Leonard and V. L. Blackford, *J. Bact.*, **57**, 339 (1949).
(5) We are indebted to Mrs. Rita S. Kardon and Mrs. Barbara Bayless for carrying out these tests.
(6) J. Cason, THIS JOURNAL, **68**, 2078 (1946).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.

Aromatic Esters of Fluorocarbon Acids

BY REGINALD F. CLARK AND J. H. SIMONS

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A series of aromatic esters of fluorocarbon acids were prepared and their physical properties studied.

Several reactions were attempted in order to prepare these compounds; however, only one gave favorable results.

The reactions and yields in the case of trifluoroacetic acid were

$$C_6H_5ONa + CF_3COCl \longrightarrow CF_3COOC_6H + NaCl \quad 20\% \text{ yield}$$

$$C_6H_5OH + CF_3COOH \xrightarrow{H_2SO_4} \text{N.R.}$$

$$C_6H_5OH + \text{excess } CF_3COOH \longrightarrow CF_3COOC_6H_5 + CF_3COOH\cdot H_2O\ (1)\ (\text{azeotrope}) \quad 15\% \text{ yield}$$

$$C_6H_5OH + (CF_3CO)_2O \longrightarrow CF_3COOC_6H_5 + CF_3COOH \quad 95\% \text{ yield}$$

(1) Swarts, *Bull. soc. chim. Belg.*, **48**, 176 (1939); *C. A.*, **33**, 8172 (1939).

The esters were soluble in ethyl ether, ethyl alcohol, benzene and dibutforyl oxide. The esters were found slightly soluble in water, 50% sulfuric acid, 10% sodium bicarbonate and concentrated sulfuric acid, after standing a period of two weeks. With 10% sodium hydroxide they underwent saponification. The solubility and rate of saponification decreased proportionally from phenyl trifluoroacetate to phenyl caproforate.

Experimental

Preparation of Anhydrides.—The anhydrides used in the preparation of the esters were prepared by heating the corresponding acid with phosphorus pentoxide. The physical properties of the anhydrides are listed in Table I.

TABLE I

Compound	B.p., °C.	$n^{25}D$	d^{25}_4	F Analyses, % Theory	F Analyses, % Found
$(CF_3CO)_2O$[1]	39.5–40.5	1.269	1.490	...	...
$(C_2F_5CO)_2O$	71.5–72.0	1.273	1.571	76.16	75.86
$(C_3F_7CO)_2O$[2]	107–107.5	1.285[a]	1.665[a]	...	...
$(C_4F_9CO)_2O$	137–137.5	....	....	67.05	66.78
$(C_5F_{11}CO)_2O$	175–176	1.295	1.769	68.51	68.38

[a] Determined at 20°.

Preparation of Esters.—The esters were prepared by adding the anhydrides dropwise to phenol, maintained at 120° with constant stirring. A slight excess of phenol was used with the anhydrides. The quantities of anhydrides taken were: $(CF_3CO)_2O$, $(C_2F_5CO)_2O$, $(C_3F_7CO)_2O$ (0.05 *M*) and $(C_4F_9CO)_2O$, $(C_5F_{11}CO)_2O$ (0.001 *M*).

The reaction products were then fractionated through a 50-cm. column, 8-mm. i.d. packed with 1/16-inch glass helices. In the case of the preparation of phenyl valerforate, after the anhydride was added to the phenol, the reaction mixture was fractionated to remove valerforic acid and the residue washed three times with 50-ml. portions of hot water to remove phenol. The remaining ester was dried over anhydrous magnesium sulfate and fractionated. The yields obtained are listed in column 2 of Table II.

The authors wish to acknowledge the sponsorship of the Minnesota Mining and Manufacturing

(2) "Heptafluorobutyric Acid," Technical Bulletin, Minnesota Mining & Mfg. Co. (1949).