allowed to fall to −80° with the jacket at atmospheric pressure. At this temperature, evacuation of the jacket space to 0.1 mm. gave slow cooling, with probable formation of solid II, while evacuation to 100 mm. gave faster cooling, usually resulting in separation of solid I without detectable formation of solid II. If the sample was allowed to supercool more than about 15°, the halt corresponding to solid II was very brief, with a spontaneous rise in temperature and separation of solid I after a period of one-half to 3 minutes. Such supercooling could be prevented by momentarily tilting the f.p. tube, causing the stirrer to rub against the side of the tube inducing initial formation of solid II crystals.

From the available evidence, the change involved appears to be monotropic, solid II being the metastable form. The fact that no conclusive evidence for complete solidification of the sample to solid II has been obtained, and that no definite temperature is associated with the inception of change from solid II to solid I seems to indicate that solid II is continuously changing to solid I at a finite rate. It is not to be inferred that the rather sudden increase in temperature 2–7° below the f.p. of solid II necessarily corresponds to conversion of the solid II to solid I, but more probably that liquid remaining unfrozen in the necessarily unstirred sample is in contact with sufficient solid I to freeze directly to this form.

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N-Fluoroacetyl Derivatives of Carcinogenic Amines[1]

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In a previous paper[2] trifluoroacetyl derivatives of carcinogenic amines were described. The fluoroacetyl analogs were prepared for a comparative study of their carcinogenic and cancer therapeutic activity. It is probable that in animal metabolism these compounds would be hydrolyzed to the carcinogenic amine and fluoroacetic acid. Fluoroacetic acid and its derivatives are known convulsant poisons.[3] Essentially, fluoroacetic acid is a Krebs cycle poison.[4] It has been postulated[5–7] that activated fluoroacetic acid and oxalacetic acid molecules react to form a fluorocitric acid which blocks the conversion of citric acid to α-ketoglutaric acid in the body. On this basis the N-fluoroacetyl derivatives have been prepared to test their effect on living cells and malignant tumors. Table I lists these new fluoroacetyl derivatives.

TABLE I

Compound	M.p.,[a] °C.	Yield, %	Nitrogen, % Calcd.	Found
2-FA[b]-biphenyl	93–94	92	6.11	6.00
4-FA-biphenyl	179–180	95	6.11	6.06
4,4′-diFA-biphenyl	316–318 dec.	85	9.21	9.10
2-FA-naphthalene	106–107	90	7.82	7.60
2-FA-fluorene	168–169	97	5.81	5.99[c]
2,7-DiFA-fluorene	253–255	88	8.86	8.70
4-FA-2′,3-dimethyl-azobenzene	155–157	96	14.7	14.5

[a] All melting points are uncorrected. [b] FA = Fluoroacetylamino. [c] Calcd.: C, 74.69; H, 4.98. Found: C, 74.97; H, 5.11.

Experimental

General Procedure. (a).—Nine and seven-tenths g. (0.01 mole) of fluoroacetyl chloride[8] was added dropwise to an ice-cold stirred solution of 0.01 mole of the monoamine in 5 ml. of benzene and 2 ml. of pyridine. The stirred mixture was warmed for 5 minutes and then 20 ml. of water was added. The benzene was evaporated at room temperature under a vacuum and the crude crystals were crystallized from heptane.

(b).—Nineteen and four-tenths g. (0.02 mole) of fluoroacetyl chloride was added dropwise to a stirred ice-cold solution of 0.01 mole of the diamine in 20 ml. of pyridine. The mixture was stirred an additional half hour at 0–10° and then poured into 100 ml. of ice-cold 25% sulfuric acid. The precipitate was crystallized from methyl cellosolve.

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The Infrared Spectrum and Structure of Glycolate Nitrate Esters

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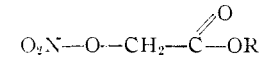
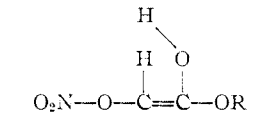
The structure of glycolate nitrate esters is expected to be mainly



but the possibility exists that some enol may be present.



If this is the case the infrared spectrum should have a frequency in the 3 μ region corresponding to the O–H vibration.

The esters[2] used in this study were: isopropylglycolate nitrate, n^{25}D 1.4163; *n*-butylglycolate nitrate, n^{25}D 1.4235; *s*-butylglycolate nitrate, n^{25}D 1.4270; isoamylglycolate nitrate, n^{25}D 1.4250. The spectra were determined on the pure liquids with a Perkin–Elmer Model 21 Infrared Spectrograph with a sodium chloride prism, using a sodium chloride cell without a spacer.

In Fig. 1 is the spectrum of *s*-butylglycolate nitrate. It is to be observed, that there is a strong band at 3.43 μ due to C–H but also a weaker but rather broad band with a peak at 2.93 μ which is evidence of the presence of O–H. It would appear that there is some enol present in this molecule. The spectra of the other three esters all show this band near 2.93 μ. For comparison the spectrum of ethyl acetoacetate which is known to have about 7.7% enol in the liquid is shown in Fig. 2. It is to be noted that it has a similar band with a peak

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