will result in only the oxygenated radical being detected. This was probably the case in work by Bijl and Rose-Innes.

It therefore appears that the diffusion processes in solids may be separated kinetically into two classes with rates of a very different order : (1) very slow diffusion of organic free radicals and their oxygenated derivatives ; (2) much more rapid gaseous diffusion. The effects described by Wilson[1] appear likely to occur only in the case of the former processes.

If this unusual behaviour in nylon films is due to oxygenated radicals, one would expect it to be a fairly general phenomenon, although it may be unique for solids since a rigid medium is necessary to prevent processes of radical termination. Similar effects have been reported for polystyrene by Reiney et al.[5]. But it was then thought that a different product was obtained in the dark from that in the light, and therefore their results were interpreted differently. However, no new band was clearly resolvable in their spectra, which leaves their interpretation open to doubt.

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A Simplified Method of preparing Pure Mono-, Di- and Tri-glycerides

GLYCERIDES of known structure are usually prepared by blocking one or two hydroxyls of glycerol and esterifying the remaining hydroxyl or hydroxyls with fatty-acid chlorides. Thus monoglycerides are obtained by the action of a fatty-acid chloride on acetone–glycerol according to the well-known method of Fischer et al.[1], whereas mixed di- and tri-glycerides have been synthesized by Verkade and co-workers[2] by the use of triphenyl-chloro-methane.

However, the greater reactivity of primary hydroxyls of glycerol, as compared with that of secondary hydroxyl, makes possible a selective esterification without recourse to blocking. This technique has been employed to a limited extent in the past[3]. Selective esterification has now been developed in this laboratory into a general method covering the whole range of glyceride syntheses. One of the difficulties has been to bring into a homogeneous solution glycerol, fatty-acid chlorides and chloroform (used commonly as solvent in such reactions). The difficulty has been overcome by the addition of N,N-dimethyl formamide, which ensures the miscibility of glycerol with other components.

Monoglycerides can now be prepared directly from fatty-acid chlorides and a large excess of glycerol (5–10 mol. of glycerol per 1 mol. of fatty-acid chloride). To obtain monoacid $\alpha\alpha'$-diglycerides, 1 mol. of glycerol is esterified with 2 mol. of a fatty-acid chloride in a single step. In both cases sufficient

dimethyl formamide is employed to obtain a homogeneous mixture at about 10° C., with pyridine as catalyst. Diacid diglycerides are produced in the reaction between a monoglyceride and another fatty-acid chloride used in approximately equimolar proportions. By extending this procedure to the preparation of mixed triglycerides, all three isomers of triglyceride containing stearic, palmitic and oleic acid radicals have been obtained in good yields by three-stage direct esterification. Their characteristics conformed with those of the triglycerides synthesized by Prof. P. E. Verkade[4], who kindly supplied samples of his products. Although Fischer's and Verkade's methods have been indispensable in establishing the configuration and properties of synthetic glycerides, for preparative purposes selective direct esterification of glycerol might be useful.

It is hoped to publish experimental details of this work elsewhere.

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Molecular Orbital Theory of the Relative Reactivities of Substituted Aromatic Molecules towards Radical Addition

THE results obtained recently by Farenhorst and Kooyman[1] on the relative reactivities of substituted anthracenes towards radical attack lend support to the validity of the simple molecular orbital theory of radical reactions. The results show (Table 1) that substitution at the 9-position enhances the activity towards radical attack at the 10-position irrespective of the polarity of the substituent group.

Two theoretical criteria have been used for the description of radical reactions : first, the free valence F_r at atom r in the unperturbed ground-state[2], and secondly the radical localization energy ΔE_r required to localize a free electron at position r, calculated according to the technique introduced by Wheland[3]. Now it has been shown[4] that in the simplest molecular orbital theory the change in free valence δF_r in passing from a parent alternant hydrocarbon to the mono-substituted derivative is an even function of the electronegativity of the substituent group. That is to say, the sign of the change in free valence at any atom of the conjugated molecule is independent of the sign of the electronegativity of the substituent group referred to a conjugated carbon atom. In the present case, the free valence F_{10} at atom 10 increases in passing from the parent hydrocarbon to any of the 9-substituted derivatives of Table 1. Thus the pre-

Table 1

Anthracene	Relative rate-constants for 10-position	
	55° C.	70° C.
Unsubstituted	1·00	1·00
9-Methyl	2·06	2·06
9-Ethyl	1·48	—
9-Cl	1·64	1·62
9-Br	1·33	1·28
9-OCH$_3$	2·09	2·06
9-CN	4·24	3·94