

mann).—Phenylfluorenol methyl ether was prepared according to the directions of Schlenk and Bergmann.⁶ However, while they report fluorescence of the solution of the methyl ether, no trace of such fluorescence was shown by our solutions.

Five grams of sodium powder was allowed to react with 10 g. of 9-phenylfluorenol methyl ether in 150 cc. of absolute ether in a sealed flask. In less than half an hour the solution was red in color. When the reaction was complete the mixture was treated with benzyl chloride (3 cc.) until no more red sodium derivative remained. The mixture was hydrolyzed, the ether solution was well washed with water and the solvent was then removed under reduced pressure. The crystalline residue was digested with cold methyl alcohol and filtered; weight 11.10 g.; m. p. 136–136.5°. From the alcoholic filtrate an additional 0.32 g. was isolated, making the total yield equivalent to 99%. After being recrystallized from *n*-propyl alcohol, acetic acid or ligroin, the crystals melted at 138–138.5° (corr. 140.3–140.8°). When mixed with 9-benzyl-9-phenylfluorene made by the other methods the melting point remained the same.

In another experiment the mixture of the reactants was kept cold, and after hydrolysis the reaction product was obtained by allowing the ether to evaporate at room temperature. Only the compound melting at 138–138.5° was obtained.

Summary

9-Benzyl-9-phenylfluorene as prepared from phenylbiphenylenemethylmagnesium bromide and benzyl chloride is identical with the product formed by interaction of 9-bromo-9-phenylfluorene and benzylmagnesium chloride. Furthermore, the same compound was obtained in 99% yield from the action of benzyl chloride on 9-sodium-9-phenylfluorene, and no low-melting isomer was produced in this reaction.

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[CONTRIBUTION NO. 35 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. V. GLYCOL ESTERS OF OXALIC ACID

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RECEIVED APRIL 23, 1930

PUBLISHED AUGUST 5, 1930

Melting points ranging from 110 to 172° have been ascribed to ethylene oxalate.¹ Bischoff,² by distillation, prepared a form melting at 142–143°, which he showed to be monomeric. He observed that the melting points of this and higher-melting forms change spontaneously on standing, and he ascribed this change to reversible polymerization but without the support of any comparative molecular weight data. In connection with a study of glycol esters of dibasic acids³ we have made some further observations

⁶ Schlenk and Bergmann, *Ann.*, **463**, 202 (1928).

¹ (a) Bischoff, *Ber.*, **27**, 2939 (1894); (b) **40**, 2803 (1907); (c) Adams and Weeks, *THIS JOURNAL*, **38**, 2518 (1916); (d) Tilitcheev, *Ber.*, **56**, 2218 (1923).

² Bischoff, *ibid.*, **40**, 2803 (1907).

³ Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929); Carothers and Van Natta, *ibid.*, **52**, 314 (1930); Carothers and Dorough, *ibid.*, **52**, 711 (1930).

on ethylene oxalate and have also prepared some other alkylene oxalates.

Preparation of Ethylene Oxalate.—The ester was prepared by heating ethylene glycol and ethyl oxalate in a Claisen flask provided with a receiver. Alcohol distilled off fairly rapidly when the heating bath was kept at 180–190°. The residue was heated in a vacuum for a time to remove unchanged reactants. The distillate was found to contain some ethyl (β -hydroxyethyl) oxalate.

Ethyl (β -Hydroxyethyl) Oxalate.—Colorless liquid; b. p. (0.2 mm.), 108–110°; d_4^{20} 1.2241; n_D^{20} 1.4405.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.42; H, 6.22. Found: C, 44.01; H, 6.02.

The residue after crystallization from glacial acetic acid or from ethyl oxalate was a dusty white powder that usually melted at about 153°. This material was polymeric.

Anal. Calcd. for $C_4H_4O_4$: C, 41.38; H, 3.45; mol. wt., 116; saponification equivalent, 58. Calcd. for $C_{54}H_{58}O_{53} = C_2H_5O-(CO-CO-O-(CH_2)_2-O)_{13}H$: C, 41.70; H, 3.73; mol. wt., 1554; saponification equivalent, 59.4. Found: C, 41.66, 41.97; H, 3.76, 4.05; mol. wt. (in boiling acetonitrile), 1510, 1580, 1610; saponification equivalent, 59.0, 60.8, 61.0.

When this polymer was heated in a vacuum, distillation occurred and from the distillate Bischoff's 143° ester was obtained (observed m. p., 143–144°). Molecular weight determinations in boiling acetonitrile agreed with those in freezing acetic acid reported by Bischoff, indicating that this material is monomeric.

Anal. Calcd. for $C_4H_4O_4$: C, 41.38; H, 3.45; mol. wt., 116. Found: C, 41.42, 41.44; H, 3.56, 3.45; mol. wt. (in boiling acetonitrile), 118, 120, 123, 126.

Small samples of polymer, if distilled rapidly, gave better than 50% yields of the monomer. Under other conditions the yield was smaller owing to thermolysis^{1d} to ethylene, carbon dioxide, ethylene carbonate, carbon monoxide and other gaseous, liquid and tarry products.



Fig. 1.—Crystals of monomeric ethylene oxalate. $\times 94$. (These crystals were placed for observation in a microscopic culture plate and sealed against the access of air and moisture by means of a cover glass. Mechanical disturbances were avoided, and subsequent observations, except the last, were made from exactly the same position as the first.)

Properties of Ethylene Oxalate and its Polymers.—Monomeric ethylene oxalate is definitely macrocrystalline and shows a relatively high solubility (Table II). It is so readily hydrolyzed that it may be titrated directly with warm tenth normal alkali. On standing at room temperature, the sharply defined crystals of the monomer rapidly disintegrate (Figs. 1–3) with the appearance of having been violently disrupted, and finally are transformed into very minute crystals, which, if undisturbed, may become spontaneously oriented on a glass surface to thread-like aggregates (Fig. 4).

This transformation is due to polymerization. It is accelerated by

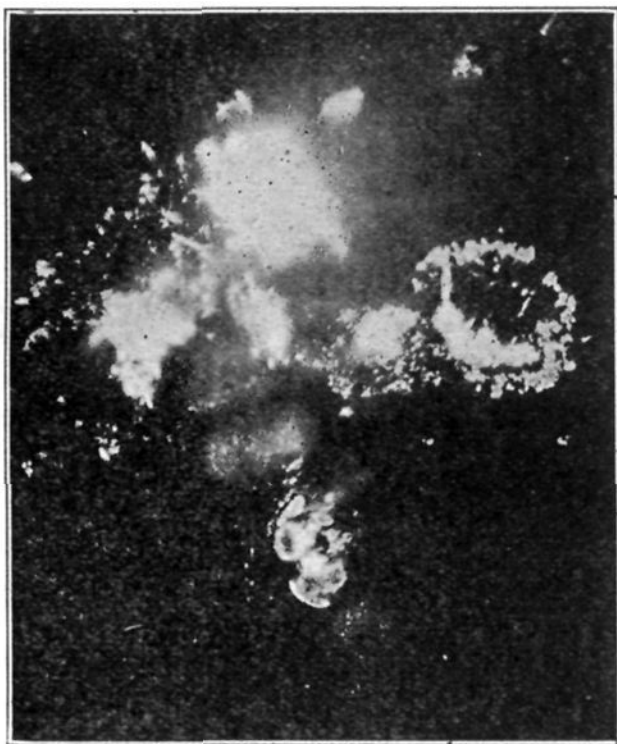


Fig. 2.—The crystals of Fig. 1 after five days at room temperature. $\times 94$.

moderate heat and catalyzed by acids or alkalies. The polymerization is accompanied by changes in melting point and solubility. In the first stages of the polymerization the melting point drops (*e. g.*, to 106–110°); higher-melting polymers are formed by heating the monomer in the presence or absence of solvents or catalysts, and the final product is an insoluble material melting at 172–173°.

A sample of monomeric ethylene oxalate was heated at 135–140° for seven hours, and then extracted repeatedly with cold acetone. The material that separated on evaporation of the acetone was identified as unchanged monomer. The

acetone-insoluble material was a dusty white powder which after drying melted at 171–172°. It was insoluble in all common organic solvents, so no molecular weight determinations could be made.

Anal. Calcd. for $(C_4H_4O_4)_x$: C, 41.38; H, 3.45; saponification equivalent, 58.0. Found: C, 41.48, 41.59; H, 3.71, 3.96; saponification equivalent, 58.45.

By fractional crystallization of polymerized monomer and of the 153° polymer formed directly from glycol and oxalic ester, a great variety of samples was obtained showing such melting points as 106–108°, 122–125°, 140–142°, 148–150°, 153°, 155–157°, 157–159°, 160–163°, 163–164°, 172–173°, as well as others having much wider melting ranges. Attempts to segregate homogeneous samples from these fractions met with difficulties

due to the rapidity with which spontaneous transformations occurred even in the absence of solvents and at room temperature. Portions of three sharply melting samples were stored in glass-stoppered bottles, and melting point determinations were made at intervals with the following results.

TABLE I

Nature and m. p. of sample	MELTING POINTS		
	M. p. after standing at room temperature		
	2 months	4 months	5 $\frac{1}{2}$ months
144° (monomer)	105–140°	105–135°	105–122° (A)
153° (polymer)	149–155°	149–155°	149–155° (B)
172° (polymer)	160–170°	160–170°	160–170° (C)

To avoid these changes during the process of fractionation, it was necessary to work rapidly and to use cold solvents as far as possible. Solubility data established the homogeneity of the monomer (144°) and the apparent homogeneity of the highest (172°) polymer. Intermediate fractions, unlike the 172° polymer, were completely soluble in warm acetonitrile, and since the solubility of the latter was not affected by the presence of monomer, intermediate polymers must have been present in these fractions. This led to the hope that it might be possible to isolate polymers sufficiently low for a study of structure.

The fractions A, B and C of Table I were recrystallized with the following results: extraction of A with cold acetone removed a small amount of monomer. The residue was treated with warm acetonitrile,

which dissolved all but a small amount of material that melted at 170–172° (high polymer). The material that separated from the acetonitrile solution, after recrystallization, melted at 157–159°. Similarly from B, fractions were isolated corresponding with monomer, high (172°) polymer, and 157–159° polymer. C yielded a small amount of material melting at 155–157°. The rest was unchanged 172° polymer. Extractions of various other samples were made, and in one case a small fraction melting at 106–108° and having an apparent molecular weight of about 900 was isolated.



Fig. 3.—The crystals of Fig. 1 after seven days at room temperature. $\times 113$.

There is still considerable doubt, however, concerning the homogeneity of this fraction.

The 153° material, which was the usual (recrystallized) product of the action of ethylene glycol on ethyl oxalate, was not homogeneous in spite of its fairly sharp melting point, for its apparent solubility changed with changing ratio of solute to solvent as shown below.

Sample, g.	Acetonitrile, cc.	Apparent soly. in g. per 100 g. at 25°
0.025	15	0.0821
.100	15	.2633
.500	15	.8644

A four-gram sample of the 153° material was then extracted repeatedly with 25-cc. portions of acetonitrile. With each extraction the apparent solubility decreased until a constant value was reached.

Extraction number	Apparent soly. in g. per 100 g. at 25°	M. p. of residue, °C.
1	1.4321	152-153
2	0.8111	152-155
3	.3240	155-159
4	.2390	155-160
5	.1729	157-160
6	.1315	157-159
7	.0894	157-159
8	.0891	158-159
9	.0890	158-159

The apparent solubility of the residue did not change on increasing the ratio of solute to solvent five-fold, so this material must be regarded as essentially homogeneous. Its apparent molecular weight in boiling acetonitrile was about 2380 (observed values, 2070, 2480, 2670, 2370, 2275, 2520).

One may conclude that at least two polymers of ethylene oxalate exist: a soluble form melting at 158-159° of molecular weight about 2400, and an insoluble form melting at 172° of unknown but probably much higher molecular weight. Either of these forms may arise spontaneously from the other, and both of them may be formed from the monomer. Definite evidence for the existence of other polymers of ethylene oxalate is lacking.

TABLE II
SOLUBILITIES OF ALKYLENE OXALATES

Nature of oxalate sample	M. p., °C.	Observed mol. wt.	Solvent		
			Acetonitrile	Acetone	Chloroform
Monomeric ethylene	144	118-126	11.29	4.13	0.35
Polymeric ethylene	159	2070-2670	0.0891
Polymeric ethylene	172	<0.01	<0.01	<0.01
Monomeric propylene	142	131-147	12.31	3.47	0.06
Monomeric ethylene	148-150	1620-1640	0.1823 ^a	0.1630 ^a	0.0390 ^a

heated at 90° for two weeks

^a These values have no quantitative significance since the sample was not homogeneous.

Chemical Properties of the Polymeric Ethylene Oxalates.—Monomeric ethylene oxalate is hydrolyzed with extraordinary rapidity. To a certain extent this property is shared by its polymers. Hence, although the polymers show acid reactions toward litmus in contact with water, this fact cannot be used to argue for the presence of long primary valence chains bearing carboxyl groups at the end. Attempts to prepare sodium salts from the polymers by the action of cold sodium bicarbonate solution led to the isolation of sodium oxalate and unchanged polymer. This ease of hydrolysis is associated with great sensitivity toward other reagents. The attempt to detect hydroxyl groups or carboxyl groups by heating polymeric ethylene oxalate with *m*-bromobenzoic anhydride and with phenylhydrazine led to the isolation of ethylene-*bis-m*-bromobenzoate and to the phenylhydrazide of oxalic acid. The latter reaction is what would be expected from an ester having the structure

—CO—CO—O—(CH₂)₂—O—CO—CO—O—(CH₂)₂—O—, etc., whether the chain is open or closed, but the first reaction requires the elimination of —CO—CO—O— residues. These fragments of the molecules appeared as carbon monoxide and carbon dioxide, which were observed to be evolved from the reaction mixture.

Ethylene *bis-m*-Bromobenzoate.—Prepared by the action of *m*-bromobenzoic anhydride on ethylene glycol or on ethylene oxalate; crystallized from a mixture of chloroform and alcohol; m. p. 78–79°.

Anal. Calcd. for C₁₆H₁₂O₄Br₂: C, 44.86; H, 2.80; Br, 37.38; mol. wt., 428. Found: C, 44.85, 45.06; H, 2.92, 2.98; Br, 37.26, 37.03; mol. wt. (in boiling benzene), 430.

Propylene Oxalate.—By heating propylene glycol and ethyl oxalate together and removing unchanged reactants in a vacuum, a colored viscous resin was obtained. In boiling acetonitrile this showed an apparent molecular weight of about 700 (observed, 670, 660). No crystalline material could be isolated from it. When this resin was strongly heated at a pressure of 5 mm., distillation occurred. A crystalline solid that separated

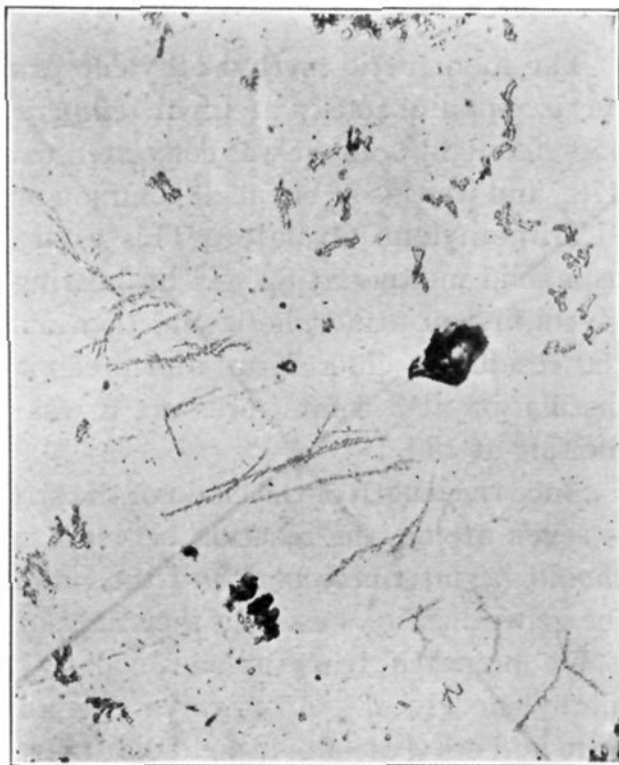


Fig. 4.—The crystals of Fig. 1 after two weeks at room temperature. $\times 185$.

from the liquid distillate melted at 142° after recrystallization from hot alcohol. This was identified as monomeric propylene oxalate.

Anal. Calcd. for $C_6H_8O_4$: oxalic acid, 69.24; saponification equivalent, 65; mol. wt., 130. Found: oxalic acid, 69.82; saponification equivalent, 64.5, 65.1; mol. wt. (in boiling acetonitrile), 131, 147.

Carbon and hydrogen values (Pregl method) were consistently low, perhaps owing to the loss of methane.

The monomeric methyl ethylene oxalate showed no tendency to polymerize spontaneously at room temperature, but on being heated to 140–150° for eight hours it was converted to a white powder that melted at 176–178° and was insoluble in all common organic solvents.

Trimethylene Oxalate.—This ester has been prepared by Tilitcheev⁴ as a solid melting at 82–84° by heating methyl oxalate with trimethylene glycol first at atmospheric and then under diminished pressure, dissolving the residue in chloroform, and precipitating it with methyl alcohol. On distillation at 3–4 mm. pressure it was converted into an "isomeric" form melting at 186–187°.

Since the length of the chain of the structural unit of trimethylene oxalate is seven atoms, the reaction between oxalic ester and trimethylene glycol should be intermolecular and the product polymeric, in accordance with the generalization based on the study of other similar reactions.^{5,3}

We prepared trimethylene oxalate by heating ethyl oxalate with trimethylene glycol. After three crystallizations from a mixture of chloroform and ethyl alcohol it melted at 87–88°. Its apparent molecular weight in boiling acetonitrile was about 2000 (observed value, 2040, 1980).

Anal. Calcd. for $C_6H_8O_4$: C, 46.15; H, 4.65. Found: C, 46.03, 46.34; H, 4.90, 4.95.

When this polymeric material was heated at 250° at 3–4 mm., thermolysis and distillation occurred. Gaseous, liquid and carbonaceous products were formed. The liquid distillate from 52 g. of polymer weighed 23.6 g., and on being cooled and treated with alcohol it yielded a small amount of crystalline solid, which after repeated crystallization melted at 186–187°. This was Tilitcheev's "isomeric" trimethylene oxalate.

Anal. Calcd. for $(C_6H_8O_4)_2$: C, 46.15; H, 4.65; mol. wt., 260. Found: C, 45.75, 46.12; H, 4.61, 4.69; mol. wt. in boiling acetonitrile, 282, 278; in freezing phenol, 272, 265.

The molecular weight determinations prove this material to be dimeric.

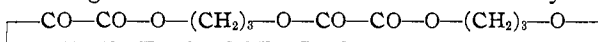
The liquid distillate from which the dimeric trimethylene oxalate was isolated was redistilled. It boiled from 70° at 20 mm. to 185° at 0.25 mm. From the higher-boiling fractions a considerable amount of trimethylene

⁴ Tilitcheev, *J. Russ. Phys.-Chem. Soc.*, **58**, 447 (1926); *C. A.*, **21**, 3358 (1927); *Chem. Zentr.*, II, 440 (1927).

⁵ Carothers, *THIS JOURNAL*, **51**, 2548 (1929).

carbonate was isolated. This is a product that Tilitcheev assumed to be intermediate in the thermolysis of trimethylene oxalate, but he was unable to isolate it. Saponification of the remaining liquid led to the isolation (as calcium oxalate) of about 1.5 g. of oxalic acid. Hence it is possible that some monomeric trimethylene oxalate may have been present in the mixture.

These results lead to the following conclusions. The action of trimethylene glycol on ethyl oxalate proceeds intermolecularly and leads to an ester of the type $-\text{CO}-\text{CO}-\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-\text{CO}-\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-\text{CO}-\text{O}-(\text{CH}_2)_3-\text{O}-$ etc. This on being heated to a high temperature undergoes thermal decomposition and yields a complicated mixture of products containing a small amount of the 14-membered cyclic ester



These reactions are analogous to those observed in the formation and decomposition of ethylene succinate⁶ and tetramethylene carbonate.⁷ No truly reversible relationship between a monomeric and polymeric form of trimethylene oxalate exists, as it does in ethylene oxalate and in trimethylene carbonate.⁷ The dimeric trimethylene oxalate shows no tendency to polymerize spontaneously.

Hexamethylene Oxalate and Decamethylene Oxalate.—From considerations which have already been set forth it is to be expected that these esters, by whatever method they are prepared, will be linear condensation polymers. They are readily prepared by heating ethyl oxalate with the corresponding glycols at first under atmospheric pressure and finally in high vacuum.

Hexamethylene Oxalate.—White powder purified by precipitation from chloroform by methyl alcohol, m. p. 66°.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_4$: C, 55.79; H, 7.03; mol. wt., 172. Found: C, 55.77, 55.58; H, 7.17, 7.08; mol. wt. (in boiling benzene), 1050, 1160, 1120.

Decamethylene Oxalate.—White powder purified by precipitation from chloroform by methyl alcohol, m. p. 79°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{O}_4$: C, 62.57; H, 9.63; mol. wt., 232. Found: C, 62.89, 62.73; H, 8.97, 8.90; mol. wt. (in boiling benzene), 1160, 1190.

Summary

Ethylene oxalate exists in three mutually interconvertible forms: a monomer (m. p. 144°), a soluble polymer (m. p. 159°), and an insoluble polymer (m. p. 172°). Ethylene oxalates showing other melting points are probably mixtures of these three forms, since evidence for the existence of any other individual forms is lacking. None of these forms are stable at ordinary temperature. The monomer polymerizes spontaneously, and the purified polymers are partially depolymerized.

⁶ Carothers and Dorough, *THIS JOURNAL*, **52**, 718 (1930).

⁷ Carothers and Van Natta, *ibid.*, **52**, 314 (1930).

Propylene oxalate exists in at least two mutually interconvertible forms: a monomer and a polymer. Monomeric propylene oxalate polymerizes much less rapidly than ethylene oxalate.

Trimethylene oxalate (m. p. 86°) prepared from ethyl oxalate and trimethylene glycol is a linear condensation polymer. It shows no tendency to depolymerize spontaneously. At high temperature it undergoes thermal decomposition, and one of the products of this reaction is the dimeric 14-membered heterocycle, m. p. 187°. This is stable and shows no tendency to polymerize further.

Hexamethylene oxalate and decamethylene oxalate prepared by the action of the glycols on ethyl oxalate are linear condensation polymers.

Ethyl(*p*-hydroxyethyl)-oxalate and ethylene-bis-*m*-bromobenzoate are described.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF McLAUGHLIN GORMLEY KING COMPANY]

STUDIES ON PYRETHRUM FLOWERS. IV. THE RELATIVE TOXICITY OF PYRETHRINS I AND II

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RECEIVED APRIL 23, 1930

PUBLISHED AUGUST 5, 1930

Staudinger and Harder¹ have shown that the two pyrethrins do not occur in *Pyrethrum* flowers in equal proportions. This conclusion has been confirmed by Tattersfield and Hobson.² The amount of pyrethrin II, in the flowers examined by these writers, was from 38 to 172% of the pyrethrin I content. If the two pyrethrins are equally toxic to insects, the proportion in which they are present is of little importance, and a determination of the total pyrethrin content would indicate the toxic value of a given sample. If, however, there is a considerable difference in the toxicity of the two pyrethrins, it would be necessary to determine the proportion of each present in a sample in order to establish its insecticidal value.

Staudinger and Ruzicka³ state that pyrethrin I is somewhat more toxic than pyrethrin II. Gnadinger and Corl⁴ also found that pyrethrin I is slightly more toxic. Tattersfield, Hobson and Gimingham⁵ found that pyrethrin I is about ten times more toxic than pyrethrin II, and they attempted to prove that the toxicity of *Pyrethrum* flowers depends almost entirely on the pyrethrin I content.

In view of the contradictory conclusions reached by different investi-

¹ Staudinger and Harder, *Ann. acad. sci. Fennicae*, **29A**, 1-14 (1927).

² Tattersfield and Hobson, *J. Agr. Sci.*, **19**, 433-437 (1929).

³ Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 449 (1924).

⁴ Gnadinger and Corl, *THIS JOURNAL*, **51**, 3054 (1929).

⁵ Tattersfield, Hobson and Gimingham, *J. Agr. Sci.*, **19**, 266-296 (1929).