temperature overnight. Three different types of crystals resulted; these were separated manually. One type melted at 113–113.5°, another at 64–72°, and the third at 72–73.5°. The last was the dinitro ester A (mixed m. p. 72–74°). The bulk of the material was the mixture which melted at 64–72°, and no method was found whereby this mixture could be further separated into its components.

Nitration of the mononitro acid XII by the procedure described above also gave a mixture of nitro acids which could not be separated.

Summary

1. Nitration of methyl β-[3,5-dimethylphenyl]-isovalerate IV or the corresponding acid V in chloroform solution by action of potassium nitrate and sulfuric acid gives the 2,4-dinitro compounds. The ester also gave a sulfonic acid, but the structure of this has not been determined.

2. Action of ammonium sulfide converted one of the nitro groups in either the dinitro ester or dinitro acid to an amino group. The resulting aminonitro compounds could not be converted into hydrocarbostyrils; hence the amino group was not located in the 2-position, but must have been in the 4-position.

3. Nitration of the ester IV or of the acid V by fuming nitric acid in acetic anhydride gave the respective mononitro compounds; these products, on reduction, gave the same hydrocarbostyril. Hence the nitro group must have entered the 2-position. This result and that outlined in (2)

above, show that the dinitro compounds have the nitro groups in the 2- and 4-positions.

4. Nitration of the ester IV or of the acid V by sulfuric and fuming nitric acids gave the respective 2,4,6-trinitro compounds. No hydrocoumarin was formed during the nitration, but action of copper–chromium oxide catalyst upon a quinoline solution of the trinitro acid converted it into 5,7-dinitro-4,4,6,8-tetramethylhydrocoumarin VIII.

5. Condensation of 2,4-dimethylphenol with β,β-dimethylacrylic acid gave 4,4,6,8-tetramethylhydrocoumarin. This reaction constitutes a convenient and practical method for synthesis of 4,4-dialkylhydrocoumarins. When the tetramethylhydrocoumarin was nitrated, the product was the dinitro derivative VIII.

6. In contrast to the alkylphenol, 2,6-dimethylacetanilide failed to condense with either β,β-dimethylacrylic acid or methyl β-chloroisovalerate.

7. The nitro groups of these nitro compounds, but particularly those of the trinitro compounds, were extremely sensitive to alkaline reagents.

8. The fact that only nuclear nitro compounds were obtained in this work indicates strongly that the dinitro compound obtained in previous work from methyl β-[3,4,5-trimethylphenyl]-isovalerate is a nuclear dinitro compound.

The Rearrangement of Phenyl Allyl Ethers. VIII. Ethyl p-(γ,γ-Dimethylallyloxy)-benzoate[1]

BY WALTER M. LAUER AND OWEN MOE[2]

Earlier studies have shown that phenyl mono-alkyl-substituted allyl ethers in which the γ-position of the allyl group remains unsubstituted rearrange with inversion in accordance with the pattern outlined by Claisen. However, in the case of phenyl γ-monoalkylallyl ethers, the rearrangement becomes more complex and products in addition to those predicted on the basis of the pattern of Claisen are formed.[3] Very few pyrolysis studies have been carried out with γ,γ-dialkylallyl ethers: $\alpha,\alpha,\gamma,\gamma$-tetramethylallyl

phenyl ether was shown by Hurd and Cohen[4] to undergo cleavage to produce phenol and 2,4-dimethylpentadiene-1,3, but no substituted allyl phenol was obtained, and γ,γ-dimethylallyl phenyl ether was reported (but without experimental detail) by Claisen[5] to yield the cleavage products, isoprene and phenol, and the normal rearrangement product when heated with sodium carbonate. With the exception of the report of Claisen, the aforementioned studies concerning the influence of substitution on the course of the rearrangement led to the expectation that cleav-

(1) Paper VII, THIS JOURNAL, 65, 198 (1943).

(2) Abstract of Ph. D. thesis submitted in June, 1942.

(3) For an excellent discussion of the Claisen rearrangement, see D. Stanley Tarbell, Chem. Rev., 27, 495–546 (1940).

(4) Hurd and Cohen, THIS JOURNAL, 53, 1917 (1931).

(5) Claisen and Tietze, Ber., 59, 2344 (1926).

age and abnormal rearrangement products would result in the case of γ,γ-dialkylallyl phenyl ethers. Accordingly, the rearrangement of ethyl p-(γ,γ-dimethylallyloxy)-benzoate (I) was investigated. Isoprene and ethyl p-hydroxybenzoate, the cleavage products, and 2,2,3-trimethyl-5-carbethoxy-coumaran (II), produced by cyclization of the abnormal rearrangement product, were identified as the products of pyrolysis.

I

II
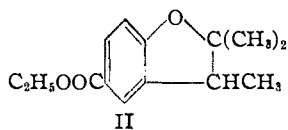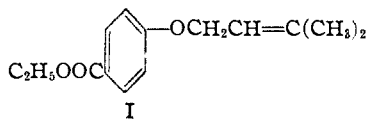
Apparently, as in all of the previously investigated cases, the formation of the abnormal product involved the establishment of an attachment of the aromatic residue to the beta carbon atom. In this case rearrangement was accompanied by cyclization, however.

The preparation of ethyl p-(γ,γ-dimethylallyloxy)-benzoate (I) was accomplished by the action of γ,γ-dimethylallyl bromide on ethyl p-hydroxybenzoate in the presence of potassium carbonate. The structure of this ether was established in two ways: (1) oxidation of the acid, produced by hydrolysis, gave p-carboxyphenoxy-acetic acid, and (2) catalytic reduction of p-(γ,γ-dimethylallyloxy)-benzoic acid, prepared by the hydrolysis of I, yielded p-isoamyloxybenzoic acid.

Pyrolysis of the ester gave mainly cleavage products as isoprene and ethyl p-hydroxybenzoate (weighed as the free acid) were isolated in 70 and 78% yield, respectively. The rearrangement product, 2,2,3-trimethyl-5-carbethoxy-coumaran (II), was isolated as the acid, the structure of which was established by the synthesis outlined below.

III

IV   V

VI

VII

VIII   IX
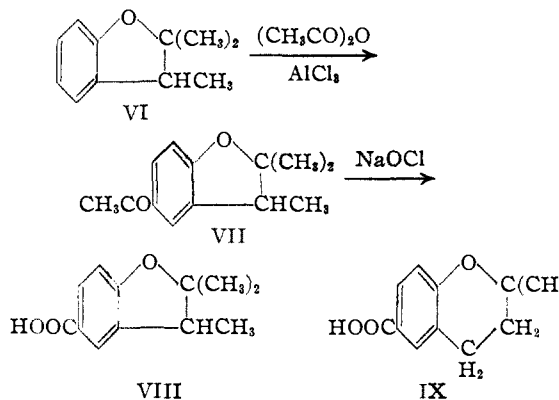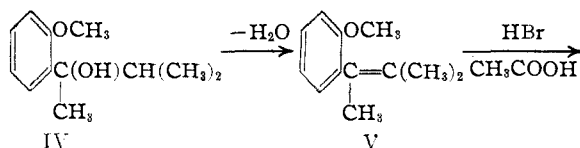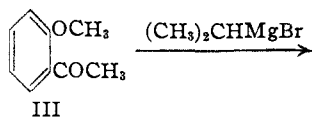
The dehydration product of methylisopropyl-o-methoxyphenylcarbinol (IV) was shown to be trimethyl-o-methoxyphenylethylene since oxidation yielded acetone and o-methoxyacetophenone (III). It is difficult to formulate the cyclization on any other basis than the formation of 2,2,3-trimethylcoumaran (VI). 2,2-Dimethyl-6-carboxy-chroman (IX), an isomer, differing from 2,2,3-trimethyl-5-carboxycoumaran (VIII), was prepared by the action of isoprene on ethyl p-hydroxybenzoate in the presence of zinc chloride, followed by hydrolysis.[6] This chroman was also prepared by hydrolysis of the ester frequently obtained as the main product of the action of γ,γ-dimethylallyl bromide on ethyl p-hydroxybenzoate in the presence of an alcoholic solution of sodium ethoxide. Presumably, direct allylation of the ethyl p-hydroxybenzoate, followed by cyclization, in accordance with Markownikoff's rule, was responsible for chroman formation in this second case.

Anomalous rearrangements of phenyl allyl ethers, in which an attachment of the aromatic residue to the β-carbon atom of the substituted allyl radical is established, are apparently of much more frequent occurrence than was previously recognized.

Experimental

(6) For examples of this type of reaction, see papers of Smith, et al., especially Chem. Rev., 27, 287-323 (1940).

(6a) The authors gratefully acknowledge their indebtedness to the United Gas Improvement Co. of Philadelphia for a generous supply of this material.

(7) Staudinger, Kries and Schilt, Helv. Chim. Acta, 5, 750 (1922).

Ethyl p-hydroxybenzoate (16.6 g.), dissolved in acetone (50 ml.), was placed in a three-neck flask fitted with a reflux condenser, a dropping funnel and a stirrer. Anhydrous potassium carbonate (14 g.) was added and while the mixture was stirred γ,γ-dimethylallyl bromide (14.9 g.) was dropped into the mixture during a period of fifteen minutes. The reaction mixture was then refluxed for six hours. After removing most of the acetone by distillation, water sufficient to dissolve the potassium salts was added. The water-insoluble layer was then removed and the aqueous solution was extracted repeatedly with ether. The combined ether extracts together with the water-insoluble layer were then washed with three portions of aqueous sodium hydroxide (10%) and finally with water. Crude ethyl γ,γ-dimethylallyloxybenzoate (17.9 g., 76%) was obtained from the ethereal solution.

The impure ester was hydrolyzed with an excess of methyl alcoholic potassium hydroxide, yielding p-(γ,γ-dimethylallyloxy)-benzoic acid (15 g.). Crystallization from a mixture of benzene and petroleum ether gave the pure acid (14.0 g., m. p. 150–151°).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 69.9; H, 6.7.

Oxidation of p-(γ,γ-Dimethylallyloxy)-benzoic Acid.— A sample (800 mg.), oxidized with aqueous potassium permanganate, yielded a solid product (m. p. 279–281°), p-carboxyphenoxyacetic acid, which was identical with a synthetic specimen prepared according to the general method of Koelsch.[8] Elkan,[9] who prepared this compound by the oxidation of p-formylphenoxyacetic acid, reported a melting point of 278°.

Reduction of p-(γ,γ-Dimethylallyloxy)-benzoic Acid.— Catalytic hydrogenation in the presence of a palladium (calcium carbonate) catalyst produced p-isoamyloxybenzoic acid (m. p. 141–142°). The melting point of the acid produced by catalytic reduction was identical with that of a specimen of p-isoamyloxybenzoic acid produced in the following manner. Ethyl p-hydroxybenzoate (1.66 g.) dissolved in dry acetone (20 ml.) was treated with isoamyl bromide (1.4 g.) in the presence of potassium carbonate (1.4 g.). After boiling under reflux four hours, most of the acetone was removed from the reaction mixture by distillation. Water was then added and ether extraction, followed by washing of the ether extract with a dilute alkali solution, yielded ethyl p-isoamyloxybenzoate (1.7 g.). Hydrolysis of this ester with methyl alcoholic potassium hydroxide produced, after acidification, p-isoamyloxybenzoic acid (1.4 g.). A sample, crystallized from a mixture of benzene and petroleum ether, melted at 140.5–142°.

Esterification of p-(γ,γ-Dimethylallyloxy)-benzoic Acid. —The purified p-(γ,γ-dimethylallyloxy)-benzoic acid (11.5 g.) was suspended in water and aqueous ammonia added dropwise until the acid was dissolved completely. The silver salt precipitated upon the addition of silver nitrate. After washing and drying, the silver salt was suspended in dry ether (200 ml.) and boiled with an excess of ethyl iodide for four hours. The silver iodide was removed and the ethereal solution was distilled. Two fractions of the desired ester were collected: (1) b. p. 90–92.5 at 0.1 mm., 1.1 g.; (2) 92.5–93.0 at 0.1 mm., 8.0 g. Fraction 2 was analyzed.

(8) Koelsch, THIS JOURNAL, **53**, 304 (1931).

(9) Elkan, *Ber.*, **19**, 3044 (1886).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.8; H, 7.7. Found: C, 71.6; H, 8.0.

Pyrolysis of Ethyl p-(γ,γ-Dimethylallyloxy)-benzoate.— Rearrangement was accomplished by boiling the ester under reduced pressure (50 mm.), making provision for the collection of any volatile products. The pressure was controlled by means of a manostat and heating was carried out in a metal-bath. The ester began to boil at 197° (50 mm.) and boiling was continued for three and one-half hours at the end of which time the boiling point was 224°. Upon cooling the pyrolysis mixture solidified and isoprene was present in the trap which was surrounded with dry-ice and acetone.

The isoprene (1.4 g. from 7.0 g. of the ester) was identified in two different ways: (1) by treatment with liquid sulfur dioxide according to the procedure of Staudinger and Ritzenthaler[10] which yields a solid derivative (m. p. 64°) (an authentic specimen of isoprene gave a derivative of the same melting point (mixed m. p. 64°)); (2) by treatment with maleic anhydride to produce the Diels–Alder addition product.

The solid pyrolysis products (obtained from 7.0 g. of the ester) were dissolved in ether and the ether solution was extracted with aqueous sodium hydroxide and finally with Claisen's alkali. The alkali-soluble portion was acidified and then extracted with ether. The ether extract yielded ethyl p-hydroxybenzoate (m. p. and mixed m. p. 117–118°; 3.2 g.). This substance was further characterized by conversion to the free acid (m. p. and mixed m. p. 210–212°). The ether solution of the pyrolysis products, after removal of the alkali-soluble material as described above, yielded an oil (2.0 g.), which on hydrolysis with methyl alcoholic potassium hydroxide gave a solid (1.6 g., m. p. 173–178°) after acidification. Repeated crystallization from petroleum ether and from aqueous ethyl alcohol gave 2,2,3-trimethyl-5-carboxycoumaran (m. p. 180–182°). Mixed with a specimen synthesized by the procedure described in this communication, the melting point remained unchanged.

The p-bromophenacyl ester of 2,2,3-trimethyl-5-carboxycoumaran, prepared from p-bromophenacyl bromide in the usual way, melted at 105–106°. A mixed melting point determination with a sample of ester prepared from synthetic 2,2,3-trimethyl-5-carboxycoumaran showed no depression.

Anal. Calcd. for $C_{20}H_{19}O_4Br$: C, 59.5; H, 4.7. Found: C, 59.7; H, 4.9.

B. The Synthesis of 2,2,3-Trimethyl-5-carboxycoumaran

o-Hydroxyacetophenone (136 g.), dissolved in aqueous alkali, was methylated with freshly distilled dimethyl sulfate. The o-methoxyacetophenone (130 g.; b. p. 115–117° at 10–12 mm.) resulting in this way was treated with isopropylmagnesium bromide.

Methylisopropyl-(o-methoxyphenyl)-carbinol.—Magnesium turnings (7.3 g.) and isopropyl bromide (37 g.) were converted to the Grignard reagent, to which was added o-methoxyacetophenone (44 g.). The reaction mixture was decomposed by the addition of iced hydrochloric acid. The ether soluble extract yielded the desired carbinol (41 g.; b. p. 90–91° at 1 mm.).

(10) Staudinger and Ritzenthaler, *ibid.*, **68**, 455 (1935).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 73.81; H, 9.28.

Trimethyl-(o-methoxyphenyl)-ethylene was obtained by the dehydration of the above carbinol. The carbinol (15 g.), dissolved in glacial acetic acid (*ca.* 35 ml.) was treated with concentrated sulfuric acid (2–3 ml.). After allowing the reaction mixture to stand for approximately one hour at room temperature, it was poured into water (200 ml.). The oil which separated was extracted with ether. The ether extract yielded trimethyl-(o-methoxyphenyl)-ethylene (9.5 g., b. p. 77–78° at 1 mm.).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.82; H, 9.09. Found: C, 81.86; H, 9.12.

Oxidation of a sample (4.0 g.) of this unsaturated compound, dissolved in acetic acid (10 ml.) with chromic anhydride (4.6 g. in 20 ml. acetic acid) yielded acetone and *o*-methoxyacetophenone. The acetone was separated from the reaction mixture by distillation and identified as the dibenzal derivative. The residue in the distilling flask, after dilution with water (100 ml.) was extracted with ether. The ether-soluble oil, upon treatment with semi-carbazide hydrochloride, sodium acetate and dilute alcohol produced *o*-methoxyacetophenone semicarbazone (m. p. 182–183°, 2.9 g.).

2,2,3-Trimethylcoumaran.—Demethylation and cyclization of trimethyl-(o-methoxyphenyl)-ethylene was accomplished by means of hydrobromic acid in acetic acid. A sample (9.0 g.) of the substituted ethylene dissolved in acetic acid (75–80 ml.) was treated with hydrobromic acid (48%, 36 g.) and heated under reflux for seventy minutes and then allowed to stand overnight. The reaction mixture was next poured into ice-water (350 ml.) and the oil which separated was extracted with ether. The ether extract yielded the coumaran (b. p. 62–63° at 1 mm., 5.3 g.).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.38; H, 8.43.

2,2,3-Trimethyl-5-acetylcoumaran.—The trimethylcoumaran (12 g.) dissolved in nitrobenzene was treated with acetic anhydride and aluminum chloride. The temperature was kept below 10° and the aluminum chloride was added over a period of thirty minutes. The reaction mixture, surrounded by an ice-bath, was stirred for an additional thirty minutes and then for two hours at room temperature, after which it was treated with ice and hydrochloric acid. The nitrobenzene layer was removed and the aqueous solution was extracted with ether. The combined ether–nitrobenzene extracts, after washing with alkali to remove phenolic substances, yielded the acetyl-coumaran (b. p. 140–142° at 4–5 mm., 9.2 g.).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.47; H, 7.84. Found: C, 76.31; H, 7.75.

The semicarbazone of 2,2,3-trimethyl-5-acetylcoumaran (m. p. 186–187°) was prepared in the usual way.

Anal. Calcd. for $C_{14}H_9O_2N_3$: C, 64.36; H, 7.28. Found: C, 64.36; H, 7.56.

2,2,3-Trimethyl-5-cinnamoylcoumaran (m. p. 108–109°) was obtained by the action of benzaldehyde on the 5-acetylcoumaran in the presence of alkali.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 81.91; H, 7.03.

2,2,3-Trimethyl-5-carboxycoumaran was prepared by the action of sodium hypochlorite on the acetylcoumaran. 2,2,3-Trimethyl-5-acetylcoumaran (0.40 g.), dissolved in methanol (5 ml.), was treated with aqueous sodium hypochlorite. The temperature of the reaction mixture increased, but was not allowed to exceed 48°. After about one hour, the reaction appeared to be complete. Further addition of hypochlorite no longer caused an increase in the temperature of the reaction mixture. The cooled solution was next extracted with ether and the aqueous alkaline solution, after treatment with a small amount of sodium bisulfite, was acidified in order to precipitate the desired product. The crude 2,2,3-trimethyl-5-carboxycoumaran melted at 172–177°, but crystallization from dilute alcohol raised this melting point to 182–183°. The melting point of this synthetic specimen, mixed with the acid obtained by the hydrolysis of the pyrolysis product of ethyl *p*-(γ,γ-dimethylallyloxy)-benzoate, remained unchanged.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.80. Found: C, 70.01; H, 6.85.

This same acid was also obtained by the oxidation of 2,2,3-trimethyl-5-cinnamoylcoumaran using potassium permanganate in aqueous acetone.

The *p*-bromophenacyl ester of the synthetic 2,2,3-trimethyl-5-carboxycoumaran melted at 105–106° after crystallization from alcohol.

C. 2,2-Dimethyl-6-carboxychroman was prepared in two ways. The action of alcoholic sodium ethoxide upon ethyl *p*-hydroxybenzoate and γ,γ-dimethylallyl bromide was investigated as a means of preparation for ethyl *p*-(γ,γ-dimethylallyloxy)-benzoate. Instead of uniformly obtaining this product, which upon hydrolysis yields the corresponding acid melting at 150–151°, the product frequently gave on hydrolysis an isomeric acid, which melted at 176–177°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.80. Found: C, 70.23; H, 7.00.

This acid (m. p. 176–177°) apparently was 2,2-dimethyl-6-carboxychroman and was also produced by the action of isoprene upon ethyl *p*-hydroxybenzoate in the presence of zinc chloride in the following way.

Ethyl *p*-hydroxybenzoate (4.0 g.), dissolved in acetic acid (18 ml.) to which fused zinc chloride (0.8 g.) had been added, was treated with isoprene (2.0 g.). After standing at room temperature for thirty-six hours, the reaction mixture was warmed for four hours at approx. 40°, and then added to cold water (90 ml.). The resulting mixture was subsequently extracted with ether. The combined ether extracts after washing with aqueous sodium hydroxide yielded an oil which was hydrolyzed with alcoholic potassium hydroxide. Acidification of the hydrolyzate gave the crystalline chroman (0.86 g., m. p. 176–177° after crystallization from alcohol).

The *p*-bromophenacyl ester of 2,2-dimethyl-6-carboxychroman (m. p. 147–148°) was prepared.

Anal. Calcd. for $C_{20}H_{19}O_4Br$: C, 59.5; H, 4.7. Found: C, 59.7; H, 5.2.

Summary

The thermal rearrangement of ethyl *p*-(γ,γ-dimethylallyloxy)-benzoate has been studied.

The main products are isoprene and ethyl *p*-hydroxybenzoate, which are produced by cleavage. 2,2,3-Trimethyl-5-carbethoxy-coumaran was also obtained, and its occurrence among the pyrolysis products is attributed to cyclization of

an abnormal rearrangement product. The abnormal rearrangement manifested in this case is consistent in character with those previously recorded.

NOTES

The Lead Chloride–Ethylene Glycol–Water System at 25°

BY A. B. GARRETT, M. V. NOBLE, GEORGE KIEFER AND RUSKIN BRYANT

In a thermodynamic study of lead chloride in mixed solvents[1,2,3] some interesting variations

TABLE I

SOLUBILITY OF PbCl₂ IN ETHYLENE GLYCOL–WATER SOLUTIONS

Glycol (by weight), %	N_2, mole fraction of glycol (water and glycol) $N_2 = n_2/(n_1 + n_2)$	Moles of PbCl₂ per 1000 g. of solvent
0.00	0.00	0.03905
5.44	.01642	.0386
6.54	.01992	.0386
7.62	.0234	.0384
8.72	.0300	.0383
9.80	.0306	.0383
10.00	.0313	.0381
10.00	.03125	.0380
10.88	.0342	.0384
11.97	.0380	.0383
13.07	.0418	.0384
20.00	.0677	.0383
21.75	.0747	.0383
30.00	.1106	.0388
40.00	.1621	.0398
42.57	.1772	.0340
50.00	.2251	.0411
60.0	.3034	.0426
60.0	.3034	.0419
62.4	.3234	.0430
70.0	.4039	.0441
80.0	.537	.0457
81.6	.563	.0465
85.4	.630	.0477
87.3	.666	.0479
89.4	.710	.0459
91.7	.762	.0427
93.3	.802	.0406
94.8	.841	.0385
96.5	.889	.0360
100	1.000	Av. .0309

TABLE II

SOLUBILITY OF LEAD CHLORIDE IN 1,2-PROPYLENE GLYCOL–WATER SOLUTION AT 25°

Glycol (by weight), %	N_2, mole fraction of glycol (water and glycol) $N_2 = n_2/(n_1 + n_2)$	Moles of PbCl₂ per 1000 g. of solvent
0.000	0.000	0.03905
20.5	.0577	.0292
40.8	.140	.0218
60.8	.270	.0173
80.5	.495	.0124
100.0	1.000	.0091

were observed in the solubility of lead chloride in solutions of ethylene glycol–water. These are shown in Fig. 1; the data are tabulated in Table I. The solubility of lead chloride in ethylene glycol was found to be 0.0309 (±0.0002) mole per 1000 g. of solvent, as averaged from nine determinations using lead chloride prepared and washed with conductivity water as well as lead chloride prepared and washed with pure ethylene glycol.
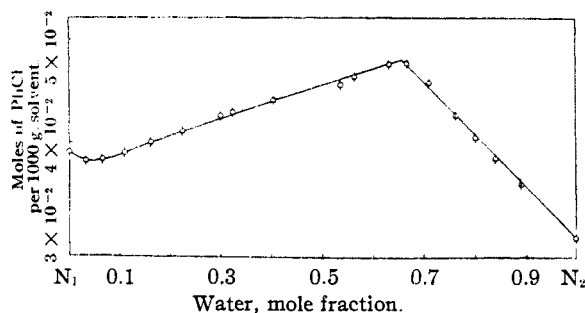

Fig. 1.

The general method of measuring the solubility was similar to that used in other work.[4,5]

The ethylene glycol used was from three different sources, namely, (a) Eastman Kodak best grade, (b) C. P. grade redistilled at low pressure and (c) C. P. grade dried over calcium oxide and redistilled at low pressure.

(1) M. V. Noble, Ph. D. Thesis, The Ohio State University, 1941.
(2) George Kiefer, M. S. Thesis, The Ohio State University, 1941.
(3) Ruskin Bryant, M. S. Thesis, The Ohio State University, 1941.
(4) Hogge and Garrett, THIS JOURNAL, 63, 1089 (1941).
(5) Garrett, Vellenga and Fontana, ibid., 61, 367 (1939).