The benzoate of the liquid isomer was recrystallized from alcohol; m. p. 178°.

Anal. Subs., 0.1284; CO_2, 0.2909; H_2O, 0.0513. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.59. Found: C, 61.78; H, 4.43.

Summary

1. *p*-Nitrobenzaldehyde condenses readily with ethylene glycol and 1,3-trimethylene glycol to give the corresponding cyclic acetals.

2. Preliminary experiments indicate that *p*-nitrobenzaldehyde readily condenses with glycerol to give an isomeric mixture of cyclic acetals.

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[Communication from the Department of Industrial and Cellulose Chemistry, McGill University]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIX. STRUCTURAL, GEOMETRICAL AND OPTICAL ISOMERISM OF THE PARA-NITROBENZYLIDENE GLYCEROLS AND THEIR DERIVATIVES

By Harold Hibbert and Neal M. Carter[1]

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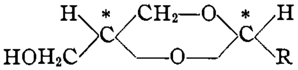
Introduction

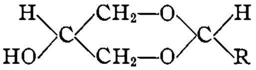
In previous communications[2] it has been pointed out that when an aldehyde (RCHO) condenses with glycerol, there results a "partition" of the aldehyde between the 1,2- and the 1,1′-hydroxyl groups, so that in the subsequent condensation structural isomers are formed, namely, five- and six-membered cyclic acetals.

An examination of these general types A and B

(A)



(B)



shows that the five-membered ring (A) should exist in two geometrically isomeric, optically resolvable racemic forms, due to the presence of the two asymmetric carbon atoms (*). On the other hand, the six-membered acetal, (B), representing as it does a case of pseudo-asymmetry, should exist only in two geometrically isomeric, non-resolvable modifications.

Only a few references to geometrical isomerism in *heterogeneous* ring systems are to be found in the literature. Among the better-known examples is its application to explain the difference between paraldehyde

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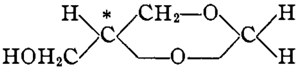
[1] Research Fellow, McGill University. This work was carried out under the auspices of the coöperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratory of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the support accorded them.

[2] Hibbert and coworkers, This Journal, **50**, (a) 2235, (b) 2242, (c) 3120 (1928).

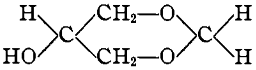
and metaldehyde.[3] Peacock,[4] in drawing attention to the existence of two optically active centers in cyclic acetals of type (A), mentions the possibility of geometrical isomerism, but his product was of such a character that the isomerism might well have been due to a double bond in the aldehydic residue. A recent paper by Böeseken and Felix[5] is also of interest in this connection. The five-membered cyclic acetals of glycerol (with the exception of that from formaldehyde) should therefore show the interesting property of possessing simultaneously all three types of isomerism: structural, geometrical and optical. The six-membered acetals cannot give rise to optical isomerism due to absence of an asymmetrical carbon atom.[6]

The substitution of HCHO for RCHO in the formation of acetals, for example, the condensation of formaldehyde with glycerol, results in the synthesis of the two structurally isomeric acetals (C) and (D) (methylidene glycerols) in which geometrical isomerism is no longer possible.

(C)



(D)



and the authors have shown[2c] that only two structural isomers are actually formed, one of which, however, the five-membered acetal, should be capable of further resolution into two optically active enantiomorphs, due to the asymmetric carbon atom (*).

Following this, attempts were made to find a suitable product capable of yielding *crystalline* glycerol acetals of both types (A) and (B) and, while this has proved unsuccessful, it has nevertheless been possible (as is shown

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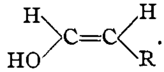
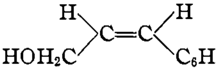
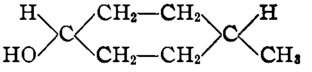
[3] Compare Baumann and Fromm, *Ber.*, **24**, 1426–1429, 1457 (1891).

[4] Peacock, *J. Chem. Soc.*, **107**, 816 (1915).

[5] Böeseken and Felix, *Ber.*, **61B**, 787–790 (1928).

[6] If the ring of formula (B), symmetrical about a line joining its terminal carbon atoms, be reduced to its simplest form, namely a double bond, a compound of the following type would be created:  . This, although unstable in itself, closely corresponds to the structure of cinnamyl alcohol:  , which is admittedly an inactive compound. Compare Perkin, Pope and Wallach, *J. Chem. Soc.*, **95**, 1790–1791 (1909), and the structure of hexahydroterephthalic acid.

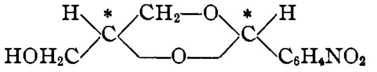
Confirmation of this view is found in the work of Gough, Hunter and Kenyon, *J. Chem. Soc.*, 2055 (1926), on the optical activity of secondary alcohols. In working with 2-, 3- and 4-methylcyclohexanols these authors found that the 2- and 3-isomers were resolvable while the 4-isomer, in accordance with the classical theory of symmetry, resisted all efforts at resolution. It will be observed that the structure of this compound



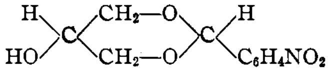
cis and *trans* forms, is quite analogous to the structure of a six-membered cyclic acetal of type (B).

in the experimental part) to isolate, in the case of the *p*-nitrobenzylidene glycerols, not only the two structurally different five- and six-membered ring isomers, but also to obtain, in the case of certain of their derivatives, the total number of isomers theoretically possible, namely, the two geometrically isomeric, racemic forms[7] of the five-membered ring type, (E), and the two geometrical isomers corresponding to the six-membered acetal, (F).

(E)



(F)



Preliminary experiments in this Laboratory[8] showed that the condensation of *p*-nitrobenzaldehyde with glycerol yielded two easily separable *p*-nitrobenzylidene glycerols, one crystalline and the other a slightly viscous oil. The former, even after repeated crystallizations, still exhibited a rise in melting point from 88°, when freshly crystallized, to 95–98° after standing for some days in a stoppered bottle. This change corresponds closely with that recorded by Irvine and coworkers[9] when investigating the benzylidene glycerols, and was attributed by them to partial decomposition.

The solid 1,1′-*p*-nitrobenzylidene glycerol (I) thus appeared to consist of a mixture of two geometrical isomers. Attempts to obtain the higher melting form in a pure state by recrystallization were unsuccessful due to the above-mentioned fact that the more stable derivative under these conditions again yields crystals with the lower melting point.[10] This change was at first attributed to a partial conversion of one ring structure into the other, but this did not explain why the melting-point of the crystals should *rise* if they tended to revert to the viscous, oily isomer. Work was therefore undertaken with the object of obtaining crystalline derivatives by replacement of the hydrogen in the remaining hydroxyl group of the free acetals, so as no longer to permit of such a *structural* change, thereby facilitating the isolation of the theoretically possible geometrical isomers. This has now been successfully accomplished and the synthesis and relationship of these derivatives is indicated below.

Isomeric Derivatives from 1,1′-*p*-Nitrobenzylidene Glycerol (I).—Methylation of the crystalline mixture of isomeric 1,1′-*p*-nitrobenzylidene glycerols (I) yielded two isomeric 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ethers (III and IV), the constitution of each being definitely

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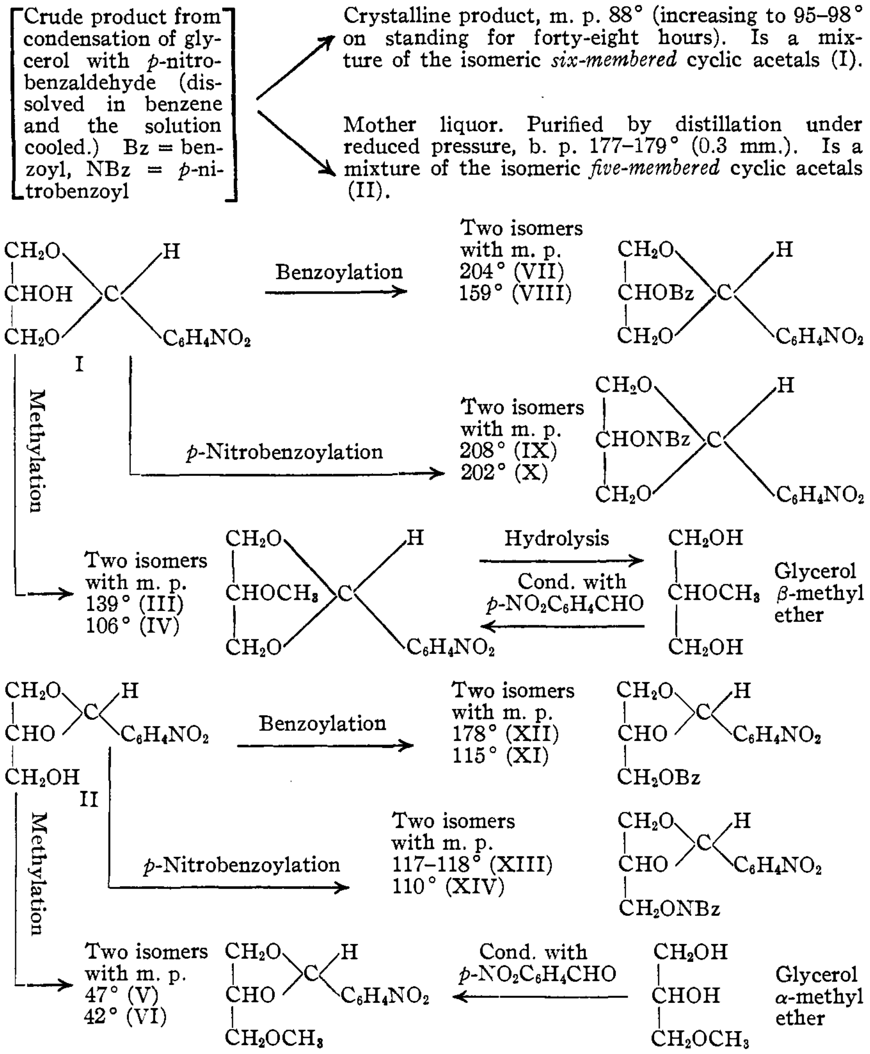
[7] The resolution of certain of these racemic forms will afford additional evidence of the ring structures, and is shortly to be undertaken.

[8] Hibbert and Sturrock, THIS JOURNAL, **50**, 3374 (1928).

[9] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 344 (1915).

[10] A similar case of conversion of geometrical isomers on solution occurs with iodoacrylic acid. The isomer melting at 65° is converted into that melting at 139–140° on recrystallization from ligroin [Stolz, *Ber.*, **19**, 542 (1886)].



Crude product from condensation of glycerol with p-nitrobenzaldehyde (dissolved in benzene and the solution cooled.) Bz = benzoyl, NBz = p-nitrobenzoyl

Crystalline product, m. p. 88° (increasing to 95–98° on standing for forty-eight hours). Is a mixture of the isomeric *six-membered* cyclic acetals (I).

Mother liquor. Purified by distillation under reduced pressure, b. p. 177–179° (0.3 mm.). Is a mixture of the isomeric *five-membered* cyclic acetals (II).

proved by their separate hydrolysis, and identification in each case of the resulting product by means of its physical properties (boiling point and refractive index), as glycerol β-methyl ether.

This result was further confirmed by condensing p-nitrobenzaldehyde with glycerol β-methyl ether (obtained by hydrolysis of 1,1′-benzylidene glycerol 2-methyl ether), and again identifying the resulting product as a mixture of III and IV. This latter experiment also served to definitely identify acetal I and its derivatives as belonging to the six-membered ring type.

In separating III from IV by fractional crystallization there was observed the same peculiar tendency for crystals of one form to commence growing on facets of the other that was experienced in separating other pairs of stereoisomeric derivatives of this acetal. In some cases when working initially with small quantities, the presence of two isomers of different melting points was only established by isolating the two forms by hand, using for the purpose a needle point under a lens. Ordinary careful recrystallization yielded a product of indefinite melting point unless the process was at least partially mechanical.

Following the isolation of the two isomeric methyl ethers, that of the corresponding benzoates VII and VIII and of the *p*-nitrobenzoates IX and X was accomplished.

Isomeric Derivatives from 1,2-*p*-Nitrobenzylidene Glycerol (II).—The 1,2-*p*-nitrobenzylidene glycerol (II) was purified by distillation under very low pressure (0.5 mm.). The distillate obtained was an apparently homogeneous, slightly viscous, amber-colored oil which resisted all attempts at crystallization. On methylation it was converted into a yellowish oil which crystallized only after inoculation with crystals of the two forms of the anticipated 1,2-*p*-nitrobenzylidene glycerol 1′-methyl ethers (V and VI), which were obtained by direct synthesis from glycerol α-methyl ether and *p*-nitrobenzaldehyde. Although two isomeric methyl ethers should be formed in the methylation of the 1,2-*p*-nitrobenzylidene glycerol II, it was only possible to isolate one of these (V) in appreciable amount, due probably to the further depression of their already low melting points (42 and 47°, respectively), by impurities in the mother liquor. It is also possible that in the distillation process, or during methylation, conditions exist which favor the formation of the one ether (V) at the expense of the other (VI). Nevertheless, it was found possible to obtain definite evidence of the presence of the second isomer (VI), and the simultaneous production of traces of 1,1′-*p*-nitrobenzylidene 2-methyl ether (III) showed that the method of purification of the 1,2-*p*-nitrobenzylidene glycerol (II) by distillation was not sufficient to free it from the last traces of its structural isomer, the 1,1′-*p*-nitrobenzylidene glycerol (I).

Both isomeric forms (XIII and XIV) of the *p*-nitrobenzoate of the five-membered acetal (II) were prepared from the latter, and one form (XI) of the benzoate. The second isomeric benzoate (XII) had been previously isolated[7] in this Laboratory in connection with work done on another phase of this general problem.

Failure to isolate the two stereoisomeric forms of each of the two free acetals (I and II) is possibly to be attributed to the influence of the higher polarity associated with the hydrogen of the free hydroxyl group in facilitating the conversion of the labile into the stable form.[11] The pro-

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[11] By conversion of the liquid acetal (II) into a mixture of its corresponding isomeric

duction, however, of both *cis* and *trans* isomers from apparently homogenous products upon treatment with certain reagents has been recorded.[3,12] The close similarity of the melting points of certain of the stereoisomers obtained in this investigation is in accord with other known cases.

	Cis isomer, m. p.	*Trans* isomer, m. p.
1,2-Cyclobutane	137–138°	131°
Limonene nitrosochloride	103–104°	105–106°
Menthylamine	207–208°	209–210°

No efforts have as yet been made to determine the exact configuration of the geometrical isomers. The repeated occurrence of one well-developed crystalline, yellow or greenish form, and one more or less amorphous, white form in the case of certain of the stereoisomeric pairs suggests that the former may be the *trans* form.[13]

Experimental Part

Preparation and Separation of the 1,1′- and 1,2-*p*-Nitrobenzylidene Glycerols I and II.—After several standard methods of acetal preparation had been attempted, a new procedure for this condensation was developed which is apparently applicable to any case where the aldehyde and polyalcohol have sufficiently high boiling (or melting) points.

One hundred and sixty-six g. of *p*-nitrobenzaldehyde (m. p. 106°, recrystallized from hot water) was heated for twenty minutes at 120° with 110 g. (3% excess over the theoretical amount) of glycerol and six drops of 40% sulfuric acid as catalyst. During this period suction was gradually applied to the reaction flask until toward the end a pressure of 15 mm. was reached. This removed the water formed in the reaction as fast as it was generated; loss of weight calculated as water, 20.1 g. (105% of theoretical). The resulting homogeneous, light reddish oil was dissolved in sufficient benzene to keep in solution at 30° the crystals that tend to separate. The solution was washed at this temperature with dilute aqueous sodium bicarbonate to remove the excess glycerol and the sulfuric acid, then with water, and finally dried over sodium sulfate. On cooling the benzene solution to 0° overnight, large yellowish needle-like prisms of 1,1′-*p*-nitrobenzylidene glycerol (I) formed, both in the benzene solution and in the reddish oil which settled out during the cooling. These were filtered off and on recrystallization from benzene melted initially at 88°. On standing for a week the melting point had risen to 95° and the clear crystals had lost their transparency. After some time a maximum melting point of 98° was apparently reached, although recrystallization from benzene, at any stage, yielded crystals with the original m. p. of 88°.

The product is readily soluble in alcohol, ether, acetone, ethylene bromide and warm benzene but insoluble in ligroin and water. It is odorless and exhibits no tendency toward hydrolysis even after exposure to the air for prolonged periods of time.

Anal. Subs., 0.1224: CO_2, 0.2411; H_2O, 0.0535. Calcd. for $C_{10}H_{11}O_5N$: C,

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benzoates XI and XII, and subjecting each of these separately to an alkaline hydrolysis involving only the benzoyl group, it is hoped to isolate the two forms of the acetal in a crystalline state.

[12] Wallach, *Ann.*, **252**, 113 (1899); Baeyer, *ibid.*, **245**, 103 (1888).

[13] Paal and Schulze, *Ber.*, **35**, 168 (1902).

53.35; H, 4.93. Found: C, 53.70; H, 4.84. *Mol. wt.* Subs., 0.3001; ethylene bromide, 39.50; ΔT, 0.404°. Mol. wt. found: 222. Theoretical: 225.

The mixture of reddish oil and benzene obtained as a filtrate in the separation of the above crystals became homogeneous on warming, and evaporation to one-fourth of its original bulk, followed by cooling yielded a second small crop of the crystalline isomer (I). This was removed by filtration and the oil thus obtained, when distilled under a pressure of approximately 0.5 to 1.0 mm., yielded at first a trace of unchanged *p*-nitrobenzaldehyde, later, a clear, amber colored, slightly viscous oil boiling between 195–215°. Redistillation of the latter under slightly lower pressure (approximately 0.3 mm.) yielded 95 g. of a similar oil boiling between 177 and 179°. Later experiments showed that this product still contained a small amount of the crystalline isomer (I). This distillate, which is the purest sample of 1,2-*p*-nitrobenzylidene glycerol (II) yet obtained, resisted all efforts at crystallization. When cooled to −70° a hard glass resulted, and a methyl alcohol solution, cooled to the same temperature, yielded an amorphous sludge which melted during the filtration at −20°. Other solvents proved equally ineffective as crystallizing media.

The liquid isomer is practically odorless and has the same solubilities as the crystalline isomer (I). Analysis, which would not be affected by contamination with (I), gave the following results.

Anal. Subs., 0.1833: CO_2, 0.3556; H_2O, 0.0810. Calcd. for $C_{10}H_{11}O_5N$: C, 53.35; H, 4.93. Found: C, 52.90; H, 4.94.

Total yield of mixed I and II (crude): 248 g. (99%); yield of I (crude): 121 g. (48%); yield of II (crude): 127 g. (51%).

It will be noted that this does not give the same ratio of I to II that was found in the interconversion experiment described later.

Synthesis of the Isomeric 1,1′-*p*-Nitrobenzylidene Glycerol 2-Methyl Ethers (III and IV)

(A) **Methylation of the Isomeric 1,1′-*p*-Nitrobenzylidene Glycerols (I).**—One hundred grams of 1,1′-*p*-nitrobenzylidene glycerol (I) was methylated with 160 g. of dry silver oxide and 100 g. of methyl iodide at 30° over a period of three hours, sufficient dry ether being added at intervals to keep the mass well mixed by the mechanical stirrer. The bulky reaction mixture was extracted five times with boiling benzene and once with boiling ethyl alcohol. Removal of both solvents under reduced pressure left 70 g. (68%) of the crude crystalline ethers. These were dissolved in warm ethyl alcohol (60°) and the flask was then allowed to cool until spontaneous crystallization set in at around room temperature, when the remaining solvent was poured off. If the cooling is too sudden, or the liquid is agitated, an apparently homogeneous, crystalline mass of needles with indefinite melting point (90°) results, which under a lens appears as small granules (m. p. 106°) growing from the facets of well-developed needles, melting at 139°. To obtain a satisfactory separation of the two isomers which appeared to be present, the following procedure was adopted.

The total yield of mixed ethers was dissolved in one liter of absolute alcohol at 70° and all traces of crystals removed by washing down the neck of the Erlenmeyer flask with hot alcohol. The flask was then surrounded by a large volume of water at 65–70° and the whole allowed to cool slowly until approximately one-fourth of the weight of the solid had crystallized out, which necessitated lowering the temperature to nearly 0°. The crystals were filtered off and the mother liquor was then evaporated down under reduced pressure to two-thirds its original bulk, and the same procedure of cooling followed. By repetition of this process until cooling of the final mother liquor to −10°

yielded only a negligible amount of crystals, four or five successive crystalline crops were obtained. The first two had a melting point of 137–139°, the middle crop an indefinite melting point around 90°, and the final crops a melting point of 102–105°.

By suitable recrystallization and combination of these fractions from the same solvent, the two pure 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ethers were isolated to the extent of 30 g. of III, 35 g. of IV and 5 g. of the unseparated isomers.

III was obtained as grayish needles (m. p. 139°), odorless, readily soluble in warm alcohol and ligroin, soluble in cold benzene, ether and acetone and insoluble in water.

Anal. Subs., 0.1937: CO_2, 0.3923; H_2O, 0.0938. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.21; H, 5.42. *Mol. wt.* Subs., 0.2144; ethylene bromide, 43.40; ΔT, 0.240°. Mol. wt. found: 243. Theoretical: 239.

IV preponderated as silky white needles (m. p. 106°), odorless, and slightly more soluble in organic solvents than its isomer, III.

Anal. Subs., 0.2030: CO_2, 0.4169; H_2O, 0.1007. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.38; H, 5.52. *Mol. wt.* Subs., 0.2089; ethylene bromide, 42.62; ΔT, 0.234°. Mol. wt. found: 251. Theoretical: 239.

That III and IV are two geometrical isomers is further substantiated by the following experiment.

(B) Condensation of Glycerol β-Methyl Ether with *p*-Nitrobenzaldehyde. Synthesis of 1,1′-*p*-Nitrobenzylidene Glycerol 2-Methyl Ethers.—One g. of glycerol β-methyl ether (prepared by hydrolysis of 1,1′-*benzylidene* glycerol 2-methyl ether)[2a] was condensed with 1.5 g. (slight excess) of recrystallized *p*-nitrobenzaldehyde, using a small drop of 40% sulfuric acid as catalyst. The reaction flask was placed under reduced pressure and heated to 120° for fifteen minutes. Spontaneous crystallization of the resulting material readily took place on cooling and from the crystalline product two isomers melting at 139 and 106° were obtained by careful crystallization from methyl alcohol, following the procedure outlined above. These proved to be identical with the previously prepared isomers (III and IV). Glycerol β-methyl ether obtained by hydrolysis of 1,1′-*methylidene* glycerol 2-methyl ether[2c] also yielded these same isomers (III and IV).

Hydrolysis of the Isomeric β-Methyl Ethers of 1,1′-*p*-Nitrobenzylidene Glycerol (III and IV).—The hydrolysis of the higher melting isomer III was effected by refluxing it for five hours with 60% ethyl alcohol in the presence of 2 cc. of concentrated hydrochloric acid, and subsequent removal of the acid with lead carbonate. The lower melting isomer IV was hydrolyzed by refluxing it for eight hours with 10% methyl alcohol and 2 cc. of concentrated hydrochloric acid, and removal of the acid by careful neutralization with potassium hydroxide solution. In both cases the neutral solution was then evaporated to less than one-fourth of its bulk. This removal of the alcohol, followed by cooling to a few degrees below 0°, brought about the separation of the greater part of the *p*-nitrobenzaldehyde formed in the reaction. This was filtered off, the filtrate evaporated under diminished pressure and the glycerol β-methyl ether distilled from the remaining solids under a pressure of 13 mm. with as low a bath temperature as possible. In both cases glycerol β-methyl ether, b. p. 122–3° (13 mm.), refractive index (n_D^{20} = 1.4480), was the sole liquid reaction product. The yield from isomer III was 8.3 g.; from isomer IV, 8.8 g., that is, approximately 90% in both cases.

Synthesis of the Isomeric 1,2-*p*-Nitrobenzylidene Glycerol 1′-Methyl Ethers (V and VI)

A preliminary methylation of a small quantity of 1,2-*p*-nitrobenzylidene glycerol (II) yielded only a non-crystallizable oil. It was therefore thought advisable to effect the synthesis of the expected methyl ethers by a more direct process in which, due to the use of fewer reagents, a purer product capable of crystallization might be obtained. The following procedure proved satisfactory.

(C) **Condensation of Glycerol α-Methyl Ether with *p*-Nitrobenzaldehyde.**—Twenty g. of glycerol α-methyl ether, prepared by hydrolysis of 1,2-*iso*propylidene glycerol 1′-methyl ether was condensed with the calculated amount (30 g.) of recryss tallized *p*-nitrobenzaldehyde under the influence of 2 drops of 40% sulfuric acid, by heating for twenty minutes at 110° under 20 mm. pressure. The resulting clear, amber-colored liquid was dissolved in ether, washed with dilute potassium carbonate solution and dried over solid potassium carbonate. On evaporation of the ether, a clear, light-colored oil remained which did not crystallize even on long standing at 0°. Fortunately, however, a single crystal had been obtained in a preliminary trial experiment where the product had been accidentally subjected to a temperature of −20° for some days. Inoculation with this crystal at 0° caused the immediate solidification of the above oil. Methyl alcohol was chosen as most suitable for recrystallization since on just dissolving the product in this solvent at 18°, crystallization rapidly begins below 0°. The process of deposition was carefully watched during the cooling from 0 to −20° and as soon as the characteristic formation of a lattice work of large yellow, prismatic crystals ceased (−10°), the mother liquor was then allowed to warm a few degrees and the crystals separated. Upon further cooling to −20° a deposit of white, feather-like crystals appeared on the sides and bottom of the container.

The yellow prisms proved to be 1,2-*p*-nitrobenzylidene gycerol 1′-methyl ether (V), m. p. 47°, soluble at 20° in all ordinary organic solvents except ligroin, but insoluble in water.

Anal. Subs., 0.1903: CO_2, 0.3856; H_2O, 0.0896. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.21; H, 5.26. *Mol. wt.* Subs., 0.2016; ethylene bromide, 42.42; ΔT, 0.217°. Mol. wt., found: 258. Theoretical: 239.

The white, feathery crystals retained their characteristics, even after recrystallization from the same solvent, thus sharply distinguishing them from the above yellow prisms. Analysis proved the compound to be 1,2-*p*-nitrobenzylidene glycerol 1′-methyl ether (VI), m. p. 42°, isomeric with the above ether (V). It is slightly more soluble in most solvents than its isomer.

Anal. Subs., 0.1926: CO_2, 0.3933; H_2O, 0.0927. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.65; H, 5.38. *Mol. wt.* Subs., 0.2759; ethylene bromide, 44.51; ΔT, 0.284°. Mol. wt., found: 257. Theoretical: 239.

These results, keeping in mind the difficulty experienced by Gilchrist and Purvis[14] in analyzing glycerol methyl ethers, and the confirmative results obtained in the following synthesis by direct methylation, leave no doubt that V and VI are the two geometrical isomers sought.

(D) **Methylation of the Isomeric 1,2-*p*-Nitrobenzylidene Glycerols (II).**—Twenty g. of the redistilled 1,2-*p* nitrobenzylidene glycerol (II) was methylated by the addition of 35 g. of dry silver oxide and 55 g. of methyl iodide over a period of three hours at 30°. The reaction mixture was extracted with boiling methyl alcohol and the extract dried over solid potassium carbonate. The alcoholic solution was evaporated to a volume of 30 cc. and then cooled to −20°, when a lower oily layer separated out. This could not be induced to crystallize until inoculated with a trace of the mixture of the two isomers obtained in synthesis (C), just described. The resulting sludge which formed at −20° was separated by filtration at this low temperature as a crystalline product which melted at room temperature (yield, 15 g., 75% of the theoretical). Careful

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[14] Gilchrist and Purvis, *J. Chem. Soc.*, **127**, 2744 (1925).

fractional crystallization from methyl alcohol at −20° yielded three distinct products. The first fraction, melting at 138°, proved to be identical with one of the 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ethers (III) obtained by methylation of the six-membered acetal (I), although the very small amount obtained (0.5 g.) indicated that its presence was due to the impossibility of completely separating the two structurally isomeric *p*-nitrobenzylidene glycerols (I and II) by distillation. The middle fraction consisted of 7 g. of yellow crystals melting at 47°, and was recognized by means of its melting point, crystalline form and solubilities as one of the two isomeric 1,2-*p*-nitrobenzylidene glycerol 1′-methyl ethers (V) synthesized in the previous experiment (C). The remaining fraction yielded 2 g. of white, fluffy crystals melting at 41–42°, identical in every respect with the second of the above two ethers (VI). The isolation of this product was rendered very difficult by its ill-defined crystalline form and the extraordinary tendency of remaining impurities in the last fraction to depress the melting point of the mixture to approximately room temperature.

Conversion of the Isomeric 1,1′-*p*-Nitrobenzylidene Glycerols (I) into the Two 1,1′-*p*-Nitrobenzylidene 2-Benzoyl Glycerols (VII and VIII).—Five g. of 1,1′-*p*-nitrobenzylidene glycerol (I) which had stood until its melting point had risen from 88 to 96° was benzoylated in the usual manner by mixing with 5 g. of anhydrous pyridine, then adding 3.1 g. of benzoyl chloride and allowing to stand for twenty-four hours at room temperature. The mixture was then treated for five minutes with 100 cc. of a 1% solution of sulfuric acid at 20° to remove excess pyridine. After washing with warm water, the apparently amorphous granular mass was dried at 70° and dissolved in ethyl acetate at 60°. On cooling slowly, the deposition of two crystalline forms was observed. To isolate these, the containing vessel was heated until the crystals had redissolved and was then immersed in a large volume of water at 60°, and the whole allowed to cool slowly to room temperature. A straw-colored mass of lustrous plates formed on the sides of the vessel, which increased in bulk until the temperature was lowered to 0°. Further lowering caused the separation of a white, fluffy precipitate in the body of the liquid, which redissolved on allowing it to warm to 0°. Separation and analysis of the first crystalline product showed it to be 1,1′-*p*-nitrobenzylidene 2-benzoyl glycerol (VII), m. p. 204°, soluble in ether, acetone, warm ethyl acetate, benzene and boiling ligroin, but insoluble in water; yield, 2 g.

Anal. Subs., 0.1388: CO_2, 0.2924; H_2O, 0.0524. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 61.92; H, 4.52.

By evaporation of the mother liquor from the above crystals to half its bulk and again cooling to 0°, a dense, white mass coagulated in the body of the liquid. Filtration yielded an almost amorphous, fluffy, lustrous white mass (m. p. 159°), which also proved to be 1,1′-*p*-nitrobenzylidene 2-benzoyl glycerol (VIII), isomeric with VII. It is slightly more soluble in organic reagents than its isomer; yield, 1.5 g.

Anal. Subs., 0.1385: CO_2, 0.3127; H_2O, 0.0564. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 61.60; H, 4.55.

From a sample of the freshly recrystallized 1,1′-*p*-nitrobenzylidene glycerol (I) only the benzoate melting at 204° (VII) was obtained.

Conversion of 1,1′-*p*-Nitrobenzylidene Glycerol (I) into the Two Isomeric 1,1′-*p*-Nitrobenzylidene 2-*p*-Nitrobenzoyl Glycerols (IX and X).—Twenty-five g. of *p*-nitrobenzylidene glycerol (I), which had stood until the melting point had risen from 88 to 96°, was dissolved in hot chloroform and 5 g. of pyridine added. This was run slowly into a mixture containing 21 g. of *p*-nitrobenzoyl chloride, 10 g. of pyridine and sufficient chloroform to keep the product liquid at 70°. An exothermic reaction took place, the product after standing overnight at room temperature changing into a solid mass. This was dissolved in more chloroform, washed with dilute sodium bicarbonate solution, dried over calcium chloride and the chloroform and pyridine removed as far as possible by heating under reduced pressure; yield, 32 g. The resulting amorphous product was shaken thoroughly with 0.1 *N* sulfuric acid to remove the remaining traces of pyridine, then washed with water and dried at 70°. Recrystallization from hot toluene yielded two distinct crystalline forms of the *p*-nitrobenzoate, which persisted in growing jointly from separate nuclei. It was not found possible, using this or other solvents, to obtain well-formed crystals. The separation of the two isomeric *p*-nitrobenzoates (IX) and (X) was effected by separating the crystals from appropriate nuclei by hand, using a hand lens. The higher melting isomer (IX) was obtained in the form of straw-colored, well-developed, brittle spicules (m. p. 208°). It dissolves to an appreciable extent in hot benzene, alcohol, carbon tetrachloride and chloroform, although solution only takes place slowly. It is readily soluble in ethyl acetate, ether, acetone and hot toluene, but is insoluble in water.

Anal. Subs., 0.2035: CO_2, 0.4072; H_2O, 0.0686. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.53; H, 3.77. Found: C, 54.68; H, 3.77.

The second isomer (X) was isolated by hand, in the same manner, in the form of rosets of microscopic, white needles, m. p. 202°, possessing similar solubility relations to those of the corresponding isomer (IX).

Anal. Subs., 0.1219: CO_2, 0.2446; H_2O, 0.0412. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.53; H, 3.77. Found: C, 54.72; H, 3.74.

Conversion of 1,2-*p*-Nitrobenzylidene Glycerol (II) into 1,2-*p*-Nitrobenzylidene 1'-Benzoyl Glycerol (XI).—Five. g of the redistilled 1,2-*p*-nitrobenzylidene glycerol (II) was benzoylated in exactly the same manner as its isomer I. The benzoylated product, after recrystallization from ethyl acetate, yielded only one benzoate in the form of greenish-yellow, granular crystals, m. p. 115°. Its behavior toward solvents was similar to that of the benzoate (VII) obtained from the six-membered acetal (I).

Anal. Subs., 0.1320: CO_2, 0.3001; H_2O, 0.0529. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 62.02; H, 4.48.

It was not possible to isolate the second, theoretically possible isomer, although investigation by another worker,[8] using the crude, undistilled acetal (II), yielded a product with m. p. 178°. This was soluble in warm benzene, and appears to be the second isomer (XII).

Anal. Subs., 0.1284: CO_2, 0.2909; H_2O, 0.0513. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 61.78; H, 4.43.

Conversion of 1,2-*p*-Nitrobenzylidene Glycerol (II) into the Two 1,2-*p*-Nitrobenzylidene 1'-*p*-Nitrobenzoyl Glycerols (XIII and XIV).—Twenty-five g. of undistilled 1,2-*p*-nitrobenzylidene glycerol (II) was *p*-nitrobenzoylated, using the same procedure as that adopted for the *p*-nitrobenzoylation of acetal I. The reaction mixture took much longer to crystallize prior to removal of the pyridine, and finally yielded 21 g. of a yellow, amorphous powder. The solubility of this mixed product in toluene is much greater than that of the structurally isomeric mixture of IX and X, hence benzene was used for recrystallizations. The same peculiar, simultaneous growth of two crystal forms from different nuclei was noted, as encountered when separating IX from X.

By manual separation under a lens, straw-yellow, brittle needles (smaller than those of the corresponding structural isomer IX) of m. p. 117–118° were obtained. These were soluble in toluene, ether, acetone, chloroform, hot alcohol or benzene, but insoluble in water. Analysis proved the product to be 1,2-*p*-nitrobenzylidene 1'-*p*-nitrobenzoyl glycerol (XIII).

Anal. Subs., 0.2033: CO_2, 0.4059; H_2O, 0.0676. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.53; H, 3.77. Found: C, 54.40; H, 3.72.

The isomeric 1,2-*p*-nitrobenzylidene 1'-*p*-nitrobenzoyl glycerol (XIV) was also isolated by manual separation as small, white nodules of microcrystalline structure with m. p. 110°, closely resembling the isomer (XIII) in solubilities and crystalline form. Only a very small amount was obtained, due to the laborious manipulation necessary to separate it from the corresponding isomer (XIII), since although considerable amounts of each were present, they were frequently too overgrown to permit of satisfactory separation.

The following summary of the properties of the *p*-nitrobenzoates of the two *p*-nitrobenzylidene glycerols shows the definite relationships existing between the pairs of corresponding isomers.

p-Nitrobenzoates of	Crystalline form	M. p.	Soluble in toluene
1,1'-*p*-Nitrobenzylidene glycerol (I)	Brittle, yellowish spicules (IX)	208°	Only when hot
	White, microcrystalline nodules (X)	202°	"
1,2-*p*-Nitrobenzylidene glycerol (II)	Brittle, yellowish spicules (XIII)	117–118°	In the cold
	White, microcrystalline nodules (XIV)	110°	"

Mutual Interconversion of the Five- and Six-Membered Acetals.—Addition of 0.01% by weight of dry hydrogen chloride to either 1,1'-*p*-nitrobenzylidene glycerol (I) or 1,2-*p*-nitrobenzylidene glycerol (II), followed by heating to 130° for a period of one and one-half hours, brought about the establishment of an equilibrium between I and II. Several experiments were carried out, varying the quantities of materials, but using the same amount of catalyst. The same proportions of I and II, in approximately the ratio of 1 to 5, were always obtained.

The separation of the equilibrium mixture into its components was carried out as previously described (p. 3381) by the use of warm benzene. Moreover, as an additional test of the permanence of this phenomenon, the two isomeric acetals (I and II), isolated from one equilibrium experiment, were each allowed once more to attain equilibrium separately. A similar ratio to that above was again obtained.

Summary

1. *p*-Nitrobenzaldehyde condenses with glycerol to give two different structural types of cyclic acetals: a five- and a six-membered *p*-nitrobenzylidene glycerol, respectively.

2. From the *five*-membered 1,2-*p*-nitrobenzylidene glycerol two isomeric 1,2-*p*-nitrobenzylidene glycerol 1'-methyl ethers, presumably corresponding to the two theoretically possible, geometrically isomeric, racemic forms, have been prepared.

3. From the structurally isomeric *six*-membered 1,1'-*p*-nitrobenzylidene glycerol two isomeric 1,1'-*p*-nitrobenzylidene glycerol 2-methyl ethers, corresponding to the two theoretically possible, non-resolvable, geometrically isomeric forms, have been isolated.

4. The corresponding benzoates and *p*-nitrobenzoates of the free five- and six-membered cyclic acetals have been prepared and identified.

5. The ready interconversion under the influence of a trace of dry hydrochloric acid of each of the two structurally isomeric acetals, namely,

1,2-*p*-nitrobenzylidene glycerol and 1,1′-*p*-nitrobenzylidene glycerol, into an equilibrium mixture has been shown.

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NOTE

A Temperature Regulator for Carius Furnaces.—The constant attention necessary to regulate the temperature of an ordinary gas-fired Carius furnace may be avoided by equipping it with a thermostat used to control the temperature of ovens on gas cooking stoves. Such a thermostat[1] is very easily installed, inexpensive and is accurate to about 5°. The approximate range of the device is 100–325°.

The only precaution to be observed is not to turn the burner on full if, for example, a temperature of 100° is required, for the heat from the walls of the furnace will raise the temperature above 100° even after the thermostat has reduced the flame. The burner should be turned on approximately as it would be if no regulator were being used.

Thermostats of this type should be satisfactory for controlling the temperature of other gas-fired furnaces used in chemical work.

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ADDITIONS AND CORRECTIONS

1922, VOLUME 44

The System Fe_2O_3–SO_3–H_2O, by E. Posnjak and H. E. Merwin.

P. 1984. In line 19 from the bottom read 1.681 instead of 1.618.

1927, VOLUME 49

Substituted O-Alkyl Hydroxylamines Chemically Related to Medicinally Valuable Amines, by Lauder W. Jones and Randolph T. Major.

The authors write as follows: "On p. 1531, line 9, the statement, 'Although O-methylhydroxylammonium chloride has been known for some time, the properties of the free base have not been described.' This statement is incorrect since the free base has been prepared by Traube and others, as described in *Ber.*, **53**, 1485 (1920). This reference was accidentally overlooked. On p. 1486 of the article by Traube, the preparation of methoxy-urea was also described. However, no analysis of the compound was given and the melting point ascribed to it, 82–83°, was lower than that found for it by us and given on p. 1537, line 17, of our article. On p. 1533, line 27, the statement is found, 'Pure formyl *p*-nitrophenylhydrazone forms red crystals;' this should be, 'Pure formaldehyde-*p*-nitrophenylhydrazone forms yellow crystals.' The heading 'α-Alkyl-β-methoxythiourea' near the top of p. 1539 should be 'α-Allyl-β-methoxythiourea.' In the next line the work 'alkyl' should be 'allyl.' "

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[1] Supplied by the Kraus Mfg. Co.