[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION OF CYANO-ACETIC ESTERS TO ESTERS OF GLUTACONIC AND β-METHYLGLUTACONIC ACIDS

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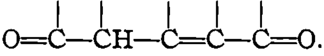
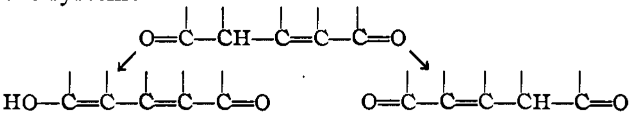
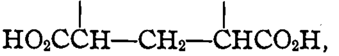
Glutaconic acid and those of its homologs which have at least one alpha hydrogen atom contain the uncommonly interesting unsaturated system,



$O{=}\overset{|}{C}{-}\overset{|}{C}H{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O$. Any substance containing this system would be expected to be capable of undergoing a great variety of reactions, because the hydrogen which is in combination with a carbon atom flanked by unsaturated groups should be more reactive than that of the methylene group in cyclopentadiene, and have a mobility approaching that of the same group in β-ketonic acids. Moreover, this hydrogen atom can undergo the usual 1,3- shift of tautomerism in two directions without materially altering the degree of the conjugation and, consequently, that of the saturation of the system:



The work of a number of investigators, notably that of Perkin,[1] Henrich[2] and Feist,[3] and especially that of Thorpe and his collaborators,[4] has shown not only that these acids are even more versatile than could have been anticipated, but also that it is extremely difficult to account for all of their peculiarities on the basis of conventional structural formulas. Thus, as early as 1905 Perkin and Tattersall[5] suggested the symmetrical formula,



$HO_2C\overset{|}{C}H{-}CH_2{-}\overset{|}{C}HCO_2H$, for glutaconic acid in order to account for their inability to prepare its geometrical isomer. Later in the same year Thorpe and Rogerson published the first of the long series of papers describing the work of Thorpe and his collaborators on the chemistry of the glutaconic acids and supporting the belief "that the formulas of glutaconic acid and those of its derivatives which contain a mobile hydrogen atom must differ from those of ordinary unsaturated dicarboxylic acids in some fundamental manner."

The experimental facts which have led to this conclusion need not be reviewed here because Feist[3b] has given an excellent summary in his latest

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[1] (a) Perkin and Smith, *J. Chem. Soc.*, **83**, 8, 771 (1903); (b) **85**, 155 (1904). (c) Perkin and Tattersall, *ibid.*, **87**, 361 (1905).

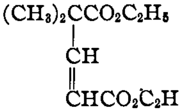
[2] Henrich, *Ber.*, 31, 2103 (1898); *Monatsh.*, **20**, 539 (1899); *Ber.*, **35**, 1663 (1902). Henrich and Thomas, *Ber.*, **40**, 4927 (1907).

[3] Feist, (a) *Ann.*, **370**, 41 (1909); (b) **428**, 25 (1922).

[4] A long series of papers in *J. Chem. Soc.* beginning with **87**, 1669 (1905).

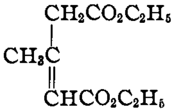
[5] Ref. 1 c, p. 363.

article on the chemistry of the glutaconic acids. The method of representation which has been adopted by Thorpe and others is, in essentials, that of Perkin and Tattersall. The acids that have no mobile hydrogen behave like typical α,β-unsaturated compounds; they are, therefore, represented by conventional formulas (I). Acids that have a mobile hydrogen atom may exist in modifications (called the labile acids) that can likewise be represented in this manner (II); but the stable forms of these acids (called the normal acids) are to be represented as structural and not as geometrical isomers (III).[6]



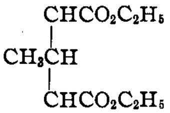
$$\begin{array}{l}(CH_3)_2CCO_2C_2H_5\\ \quad\;\;\mid\\ \quad\;\;CH\\ \quad\;\;\|\\ \quad\;\;CHCO_2C_2H_5\end{array}$$

I



$$\begin{array}{l}\quad\;\;CH_2CO_2C_2H_5\\ \quad\;\;\mid\\ CH_3C\\ \quad\;\;\|\\ \quad\;\;CHCO_2C_2H_5\end{array}$$

II



$$\begin{array}{l}\quad\;\;CHCO_2C_2H_5\\ \quad\;\;\mid\\ CH_3CH\\ \quad\;\;\mid\\ \quad\;\;CHCO_2C_2H_5\end{array}$$

III

After a critical examination of the many interesting facts discovered by Thorpe and others, Feist reached the conclusion that these can be accounted for without resorting to special formulas. He made no attempt, however, to explain the peculiar behavior of these substances in certain addition reactions. Thorpe and Wood[7] found that whereas α,α-dimethylglutaconic ester (I), as had been shown by Perkin,[8] combines with cyano-acetic ester in the usual manner of α,β-unsaturated esters, glutaconic ester itself offered a peculiar resistance to addition and, under the conditions of their experiment, gave but 6% of addition product. Moreover, they found that while they met with no difficulty in adding cyano-acetic ester to the "labile" modification (II) of β-methylglutaconic ester, which gave 60% of a product that was formed by addition to the double linkage, the "normal" ester under similar conditions offered even greater resistance than glutaconic ester, gave no addition product of this type, and yielded instead a small quantity (5%) of a substance which could result only from 1,3-addition to a substance represented by III.

The proof of the structure of these addition products seems conclusive. When boiled with sulfuric acid they gave isomeric butane-tricarboxylic acids. The structure of the acid (V) that was obtained by starting with the ester of the "normal" acid was known, because it had previously been synthesized by Perkin.[9] From β-methylglutaconic ester an acid of this structure could be formed only as a result of 1,3-addition.

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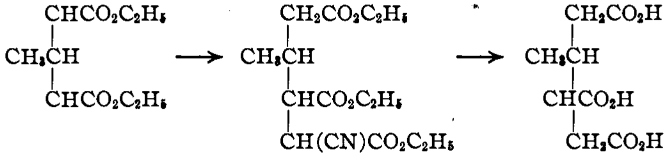
[6] The implications of this formula have changed somewhat from time to time as the knowledge of the glutaconic acids has progressed. For these the reader is referred to (a) Thorpe and Rogerson, *J. Chem. Soc.*, **87**, 1685 (1905). (b) Thole and Thorpe, *ibid.*, **99**, 2187 (1911). (c) Goss, Ingold and Thorpe, *ibid.*, **123**, 327 (1923). (d) Verkade, *Verhandel. Akad. Wetenschappen Amsterdam*, **24**, 1527 (1916). (e) Verkade and Coops, *Rec. trav. chim.*, **39**, 586 (1920).

[7] Thorpe and Wood, *J. Chem. Soc.*, **103**, 1597 (1913).

[8] Perkin, *ibid.*, **81**, 246 (1902).

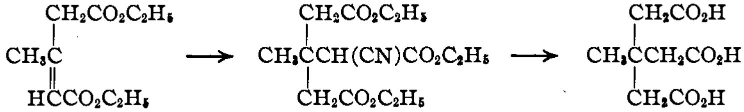
[9] Hope and Perkin, *ibid.*, **99**, 766 (1911).



$$\begin{array}{l} \quad CHCO_2C_2H_5 \\ \quad | \\ CH_3CH \\ \quad | \\ \quad CHCO_2C_2H_5 \end{array} \longrightarrow \begin{array}{l} \quad CH_2CO_2C_2H_5 \\ \quad | \\ CH_3CH \\ \quad | \\ \quad CHCO_2C_2H_5 \\ \quad | \\ \quad CH(CN)CO_2C_2H_5 \end{array} \longrightarrow \begin{array}{l} \quad CH_2CO_2H \\ \quad | \\ CH_3CH \\ \quad | \\ \quad CHCO_2H \\ \quad | \\ \quad CH_2CO_2H \end{array}$$

III IV V

The acid obtained by starting with the "labile" ester might be a stereoisomer of Perkin's acid (V), but in view of the fact that addition in this case appeared to occur quite normally Thorpe correctly decided that this is a structural isomer of Perkin's acid.



$$\begin{array}{l} \quad CH_2CO_2C_2H_5 \\ \quad | \\ CH_3C \\ \quad \| \\ HCCO_2C_2H_5 \end{array} \longrightarrow \begin{array}{l} \quad CH_2CO_2C_2H_5 \\ \quad | \\ CH_3CCH(CN)CO_2C_2H_5 \\ \quad | \\ \quad CH_2CO_2C_2H_5 \end{array} \longrightarrow \begin{array}{l} \quad CH_2CO_2H \\ \quad | \\ CH_3CCH_2CO_2H \\ \quad | \\ \quad CH_2CO_2H \end{array}$$

II VI VII

At the time our work was begun, these results constituted the most convincing evidence against a conventional formula for the "normal" glutaconic acids. Differences in the relative ease with which geometrical isomers add other substances are well known, and it was conceivable that the conditions under which Thorpe and Wood had operated might enhance such differences, but the *mode* of addition to unsaturated compounds is not determined by experimental procedure, and the formation of a 1,3-addition product would have to be accepted as conclusive proof of a symmetrical formula like that advocated by Thorpe. We decided, therefore, to test these results.

We began with glutaconic acid but used the methyl instead of the ethyl ester because we happened to have methyl cyano-acetate on hand. In our first experiments we also operated under somewhat different conditions from those selected by Thorpe and Wood for the following reason. It is well known that the Michael reaction is reversible and that, when the equilibrium is unfavorable or the reactants are sensitive to bases, the best results are frequently obtained by employing only a small quantity of condensing agent. We found that under these conditions there is no difficulty whatsoever in adding methyl cyano-acetate to dimethyl glutaconate; with pure esters and dry solvent the normal addition product is obtained in a yield of about 82%. This yield is about the same as that which is obtainable from methyl cinnamate, and in so far as it is possible to judge without accurate rate measurements, which it is almost impossible to secure, the rate of addition is also not materially different from that of the cinnamate.

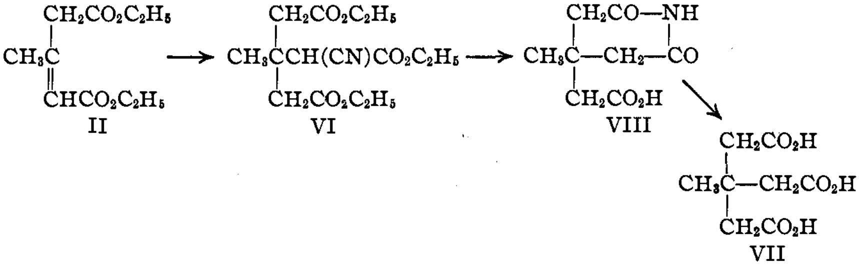
It is, of course, impossible to account with certainty for the great discrepancy between our results and those of Thorpe and Wood. That it is not due to our substitution of methyl for ethyl esters is clear, because the same discrepancy appeared in the work on the β-methylglutaconic acids, where we used ethyl esters. It is, doubtless, partly accounted for by the difference in the amount of condensing agent employed. When we used only enough methylate to produce definite alkalinity, the methyl alcoholic solution immediately assumed an amber-yellow color, which changed but little on prolonged boiling. When, in accordance with the procedure of Thorpe and Wood, one equivalent of methylate was used, the solution, which likewise was yellow at the outset, turned brown on boiling and gradually became so dark in color as to make it advisable to stop the process after three hours (half the time employed by Thorpe and Wood); but even this gave 46% of addition product. In an experiment in which we used an old preparation of methyl cyano-acetate without careful repurification we found it necessary in order to maintain alkalinity to add relatively large amounts of methylate and our yield fell to about 10%. We believe, therefore, that the difficulties experienced by Thorpe and Wood were due largely to the presence of water or acid in their cyano-acetic ester.

After convincing ourselves that there is nothing peculiar in the behavior of glutaconic ester in the Michael reaction we turned to the esters of the isomeric β-methylglutaconic acids. These were made by esterifying the pure acids and carefully purified by distillation under very low pressures. Here the method of bringing about addition by employing only a trace of condensing agent failed completely, the resistance of two groups in the β-position being sufficient, as usual, to prevent addition under these conditions. It was necessary, therefore, in this case to resort to the more effective procedure employed by Thorpe and Wood, and we followed this as closely as possible. We found that our isomeric esters behaved exactly alike, each giving about 60% of addition product. The experiments were repeated a number of times but the outcome was always the same: no difference in the relative ease with which the esters of the "normal" and "labile" add ethyl cyano-acetate could be detected.

We have not been able to account for this great difference between our results and those reported by Thorpe and Wood. It cannot have been due to accidental variations in procedure because our results were invariable. There remained the possibility that one or the other of our esters had, by chance, undergone isomerization during its preparation, but we found that when both of our esters were hydrolyzed with very dilute acid each gave, almost exclusively, the acid from which it had been made. We are compelled to believe, therefore, that the results reported by Thorpe and Wood are erroneous.

Our results differ from those of Thorpe and Wood not only with respect to the ease of addition but also (and this is much more important) with respect to the products. Each ester gave a liquid that boiled at 180–185° (5 mm.). On digestion with concd. hydrochloric acid these liquids were transformed into a solid acid, $C_8H_{11}O_4N$, which was easily purified, m. p. 156°, and was obtained in almost the calculated quantity. *The addition product from both esters invariably gave the same acid; the mode of addition to the two esters is therefore the same.*

When the acid melting at 156° was boiled with alkalies it lost ammonia and passed into a solid acid, m. p. 165–170°, and formed an anhydro acid; m. p., 99°. This, therefore, was the butane-tricarboxylic acid which Thorpe and Wood had obtained only from the labile ester, the transformation being represented as follows.



Since the imido acid (VIII) was not obtained in quite the calculated quantity, there remained the possibility that the ester boiling at 185° might contain a small amount of 1,3 addition product. We hydrolyzed a relatively large quantity of this ester (58 g.), therefore, and evaporated the mother liquors from VIII to complete dryness. They contained, besides a little of this acid (VIII), only ammonium chloride (1.5 g.) and a corresponding amount (5 g.) of Thorpe's acid (VII). We found no evidence whatsoever of 1,3 addition.

Glutaconic acid reduces permanganate immediately;[10] it is more rapidly reduced by hydrogen and palladium than either fumaric or cinnamic acid;[11] it readily combines with ozone[3b] and with bromine;[6e] and its ester combines with cyano-acetic esters like any other α,β-unsaturated esters. It may safely be concluded, therefore, that if it or the other "normal" glutaconic acids have a peculiar structure, this does not reveal itself in addition reactions.

I. Experiments with Glutaconic Acid

Preparation of Dimethyl Glutaconate.—Glutaconic acid was made by the following modification of the method of Conrad and Guthzeit[12] which gives reliable results.

In a 5-liter flask fitted with a mechanical stirrer, a long reflux condenser and a dropping funnel, 45 g. of sodium was dissolved in 700 cc. of absolute ethyl alcohol. To this solution 128 g. of diethyl malonate was added slowly from the dropping funnel and

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[10] Buchner, *Ber.*, **23**, 707 (1890).

[11] Korevaar, *Chem. Weekblad,* **13**, 98 (1915).

[12] Conrad and Guthzeit, *Ann.*, **222**, 250 (1884).

then, while the mixture was still hot, as rapidly as was possible without losing control of the reaction, 65 g. of chloroform. The solution boiled so vigorously that it was usually necessary to cool the upper part of the flask, but cooling the liquid or adding the chloroform more slowly greatly diminished the yield. The liquid was allowed to stand overnight, when a mixture of the sodium derivative of the ester of dicarboxyglutaconic acid and sodium chloride separated. This was collected on a suction filter, washed with ether and turned into the free ester by stirring it with an excess of 5% hydrochloric acid. After the liquid ester had been washed with water it was hydrolyzed and cleaved by boiling it with aqueous alcoholic hydrochloric acid (3 volumes of 6 *M* hydrochloric acid and 1 volume of alcohol) until solution was complete. The glutaconic acid, isolated by evaporating this solution under diminished pressure, was sufficiently pure for esterification. The average yield, based on malonic ester, was 64.5%. The dimethyl ester, obtained by esterifying this acid with sulfuric acid and methyl alcohol, boils at 105–110° (5 mm.).

Addition of Methyl Cyano-acetate to Dimethyl Glutaconate.—The methyl cyano-acetate used in the experiment given below had been freed from water and free acid by distillation from a small quantity of magnesium methylate, the methyl alcohol used as solvent had been dried in the same manner and the apparatus in which the reaction took place was protected with a tube containing phosphorus pentoxide. The reaction mixture contained 28 g. of dimethyl glutaconate, 30 g. of methyl cyano-acetate, 20 cc. of methyl alcohol and 5 drops of a sodium methylate solution made by dissolving 1.8 g. of sodium in 20 cc. of methyl alcohol. This mixture was boiled for 12 hours. In order to insure alkalinity 5 drops of the same methylate solution were added every two hours. The mixture, which had been left at the ordinary temperature overnight, was neutralized with 4 drops of glacial acetic acid and then fractionated under diminished pressure. It gave 33.4 g. of a colorless liquid; b. p., 203–205° (11 mm.).

The addition was also carried out by the procedure selected by Thorpe and Wood. The reacting mixture in this case consisted of 16 g. of dimethyl glutaconate, 10 g. of methyl cyano-acetate and 2.3 g. of sodium in 25 cc. of methyl alcohol. By the time that this mixture had been boiled for three hours it had become so dark in color that it seemed advisable to stop the operation. The liquid was chilled and poured into 100 cc. of 4% hydrochloric acid. The resulting oil was extracted with ether, the ethereal solution was freed from acids by washing with a solution of sodium bicarbonate, dried over sodium sulfate and fractionally distilled under diminished pressure. It gave 12 g. of a colorless liquid; b. p., 172° (2 mm.).

The effect of small quantities of acid and water is shown by the following experiment in which the materials were the same as before, but the cyano-acetate had not been distilled from magnesium methylate, and the methyl alcohol had been dried over lime. The reacting mixture was composed of 50 g. of dimethyl glutaconate, 32 g. of methyl cyano-acetate and 75 cc. of methyl alcohol. It was necessary to add 70 drops of the methylate solution to secure alkalinity. The rest of the procedure was the same as that employed in the first experiment. The result was a large, low-boiling fraction (52 g.) and 11 g. of crude product which on redistillation gave 8 g. of colorless liquid; b. p., 185° (4 mm.); yield, 14% of crude and 10% of pure product.

The Nature of the Addition Product.—All these methods of addition, and a number of others which we do not regard as worth while to describe, gave the same addition product. This was established by transforming these liquid products into methane-triacetic acid, which is a solid. The most satisfactory way to accomplish this is as follows.

The liquid is suspended in ten times its volume of constant-boiling hydrochloric acid contained in an open flask provided with an efficient mechanical stirrer. The mixture is heated on a steam-bath for several hours more than is necessary to dissolve the liquid addition product. The solution is evaporated to dryness under diminished pressure, the acid extracted from the residue with acetone and finally purified by recrystallization from dry ether. The yield is nearly quantitative. All samples of our addition product gave a nitrogen-free acid; m. p., 126°, when pure. As this is 11° higher than the melting point of methane-triacetic acid (115°) reported by Thorpe and Wood[13] and confirmed by Ingold[14] who had obtained the acid in an entirely different manner, we analyzed our acid and transformed a sample of it into the dianilic acid, which is likewise a solid.

Anal. Calcd. for $C_7H_{10}O_6$: C, 44.2; H, 5.3. Found: C, 44.3; H, 5.5.

The **dianilic acid** was made and purified as directed by Ingold,[14] but it melted at 206° instead of at 192°, the melting point reported by Ingold.

Anal. Calcd. for $C_{19}H_{20}O_4N_2$: C, 67.0; H, 5.9. Found: C, 66.8; H, 6.0.

Synthesis of α,β,δ-Butane-tricarboxylic Acid.—Inasmuch as both our acid and its aniline derivatives had much higher melting points than those previously reported for these substances, it became necessary to prepare the isomer that might be formed as a result of 1,3 addition. This was accomplished without difficulty by the method of Kay and Perkin.[15] The acid melted at 115–116° as reported and the melting point of a mixture of this acid and ours was very much lower. Dreifuss and Ingold[16] have since made methane-triacetic acid in quantity by still another method and they likewise have found that the melting point of the pure acid is 126°. The proof is therefore complete that dimethyl glutaconate adds methyl cyano-acetate in the usual manner of α,β-unsaturated esters.

II. Experiments with the Isomeric β-Methyl-glutaconic Acids

Preparation.—*iso*Dehydro-acetic ester was made from aceto-acetic ester by the method of Goss, Ingold and Thorpe[17] which we found to be excellent.

Fifteen hundred g. of aceto-acetic ester gave 717 g. of *iso*dehydro-acetic ester; b. p., 140–160° (4 mm.). This ester was converted into a mixture of the methylglutaconic acids in accordance with the directions of Feist,[18] the average yield of crude acids being 90%. Of the various methods for getting the isomers out of this mixture we found that of Fichter and Schwab[19] much the most satisfactory. The melting point of slightly impure "normal" acid that we used in esterification was 145°, that of the pure labile acid 115°. The ethyl ester of the "normal" acid boiled at 94–96° (3 mm.), that of the labile acid at 97–100° (3 mm.).

Addition of Ethyl Cyano-acetate.—The materials used in the following experiments were the pure esters made as has been described, ethyl cyano-acetate which had been distilled under diminished pressure from a small quantity of sodium and alcohol that had been distilled from calcium alcoholate. All methods of addition were tried with both isomers. After using a small quantity of sodium alcoholate and the procedure that had

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[13] Ref. 7, p. 1581.

[14] Ingold, *J. Chem. Soc.*, 119, 352 (1921).

[15] Kay and Perkin, *ibid.*, **89**, 1643 (1906).

[16] Dreifuss and Ingold, *ibid.*, **123**, 2967 (1923).

[17] Ref. 6 c, p. 348.

[18] Feist, *Ann.*, **345**, 78 (1906).

[19] Fichter and Schwab, *Ann.*, **348**, 252 (1906).

been found excellent with dimethyl glutaconate, we could find no evidence of any addition to either ester. Attempts to add with the assistance of piperidine were equally futile. Solid sodium cyano-acetate, suspended in benzene, gave a small quantity of higher-boiling product but in this case also most of the ester was recovered. We turned, therefore, to the method of Thorpe and Wood, operating as follows.

A mixture containing 14 g. of dimethyl glutaconate, 8 g. of ethyl cyano-acetate and a solution of 1.7 g. of sodium in 24 cc. of ethyl alcohol was boiled for five hours. The dark brown liquid was chilled and poured into excess of cold 2% hydrochloric acid, the oil extracted with ether, the ethereal solution washed with sodium bicarbonate, dried and distilled under diminished pressure. The product from each ester distilled without leaving more than a trace of tarry residue. Each gave a small quantity of low-boiling distillate (about 3 g.) composed of unaltered esters and then about 14 g. (64%) of a colorless or very pale yellow, oily liquid; b. p., 180–185° (5 mm.). This accounts for nearly 80% of the material, the balance being lost by hydrolysis.

Hydrolysis and Cleavage of the Addition Product.—*The oil was suspended in 60* cc. of concd. hydrochloric acid and the mixture heated on a steam-bath until all of the oil had dissolved. The solution was then evaporated to 20 cc., and set aside. It deposited 6 g. of a solid acid of which 2 g. more was obtained after further evaporation, making a total yield of about 90%. After one crystallization from 20% hydrochloric acid, the acid melted at 155–156° and this melting point was not changed by repeated recrystallizations from this and other solvents. As this was the melting point (155°) which Thorpe and Wood found for the acid which they obtained on hydrolyzing the small quantity of addition product from the "normal" ester, and which they identified with Perkin's acid (V), we synthesized the latter in accordance with Perkin's[9] directions. We obtained in this way an acid that melted at almost exactly the same temperature as ours (155°) but a mixture of the two melted much lower. This led to the discovery that our product contained nitrogen and an analysis showed that it was an imido acid.

Anal. Calcd. for $C_8H_{11}O_4N$: C, 51.9; H, 5.9. Found: C, 52.0, 52.2; H, 6.0, 5.6.

Hydrolysis of the Imido Acid.—An 8g. sample of the acid was boiled with 150 cc. of 10% sodium hydroxide solution until the odor of ammonia was no longer detectable. The solution was acidified with hydrochloric acid and evaporated to dryness. From the residue, acetone extracted an acid, m. p. 165–169°, and this remained the same after repeated recrystallization from other solvents.

Anal. Calcd. for $C_8H_{12}O_6$: C, 47.1; H, 5.8. Found: C, 47.6; H, 5.8.

The analysis shows that the substance has the same composition as the acid that Thorpe and Wood obtained from the addition product of the "labile" ester (VI) for which they reported a melting point of 172° and which when heated at 200° formed an anhydro acid melting at 99°. Our acid, when heated in the same way, likewise lost water. The anhydro acid melted at 99°, and had the other properties described by these authors; the two acids are, therefore, identical.

Proof of the Integrity of the Isomeric Esters.—A sample of each ester was boiled with water containing a few drops of hydrochloric acid until solution was complete. The resulting solutions were then evaporated to complete dryness on a steam-bath. The residues were washed once with a little ether and then used for melting-point determinations without further purification; the one from the ester which had been prepared from the normal acid melted at 145°; that from the ester of the labile acid, at 112–113°. The melting points of mixtures with the original acids completed the proof that these had been esterified without isomerization.

Summary

1. Methyl cyano-acetate can be added without difficulty to dimethyl glutaconate. The mode of addition is the same as that to any other α,β-unsaturated ester.

2. There is no appreciable difference in the ease with which cyano-acetic ester combines with the esters of the "normal" and labile forms of β-methylglutaconic acid; the addition product from both esters is the same, and the mode of addition is that of α,β-unsaturated esters.

3. The addition reactions of glutaconic acids cannot be properly used to support the view that the "normal" forms of these acids cannot be represented by conventional formulas.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRUM OF MOLTEN NAPHTHALENE

BY FREDERICK K. BELL

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Introduction

In view of a proposed study of the infra-red absorption spectra of the naphthylamines and alkyl naphthylamines it seems particularly desirable that information concerning the absorption spectrum of naphthalene in this region be available.

Coblentz,[1] taking advantage of the high solubility of naphthalene in carbon tetrachloride, studied the absorption of the saturated solution between 2.0 and 5.0μ and found that the 3.25μ band of benzene was present, indicating that the vibration of the benzene nucleus in that region had not been disturbed by the naphthalene structure.

Stang[2] measured the absorption of solutions of naphthalene and several of its alpha and beta mono-derivatives in both carbon tetrachloride and carbon disulfide. These measurements extended from 2.7 to 10.0μ.

In studying the absorption of solid substances in the infra-red region two methods of procedure have been employed. Either a film of the solid substance or a solution of the solid in a suitable solvent may be used. In either case the absorption curves obtained leave much to be desired and this becomes at once apparent when such curves are compared with those obtained with pure liquids.

With solid films there is a considerable loss of energy due to scattering of light which, in effect, greatly reduces the resolving power of the optical

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[1] Coblentz, *Carnegie Inst. Publ.*, **35**, 127 (1905).

[2] Stang, *Phys. Rev.*, **9**, 542 (1917).