EXPERIMENTAL

To determine the feasibility of trapping alkynes as urea inclusion compounds, the maximum cross-sectional diameters of several unbranched molecules were measured on Stuart-Briegleb scaler molecular models arranged as closely as possible to the planar zigzag conformation. These molecules along with their cross-sectional diameters and their abilities to form an inclusion compound are listed in Table II. In all cases the presence of an inclusion compound was verified by x-ray powder diffraction data (Table I).

2,4,6-Octatriyne, 2,4-hexadiyne, dipropargyl ether, and dipropargyl amine were obtained from Professor C. J. Marsel of New York University. The remaining compounds were purchased from the Farchan Research Laboratories in Cleveland, Ohio.

Preparation of urea inclusion compounds. A urea-methanol solution was prepared by dissolving 15 g. of urea in 100 ml. of absolute methanol. If the compound examined was a liquid, 30 drops of the compound was added to 4.5 ml. of urea-methanol solution, shaken, kept in a stoppered tube at 4° for 24 hr., suction filtered, and washed with 10 ml. of 4° absolute ethanol. The crystals were vacuum dried at 4° and 3 mm. for 24 hr. If the compound examined were a solid, 2.2 g. of the compound were added to 4.5 ml. of urea-methanol solution, heated to boiling or until the solid dissolved (whichever occurred first), and then cooled at 4° for 24 hr. The same procedure is then used for both liquids and solids.

Determination of X-ray powder diffraction pattern. The urea inclusion compounds were ground into a fine powder and applied to a roughened glass slide. The interplanar spacings and relative intensities were obtained using the North American Phillips x-ray Diffraction Apparatus operated at 35,000 volts and 15 milliamps with a scanning rate of 2° per min. using CuKα radiation.

CONCLUSION

The formation of urea inclusion compounds by both monoalkyl- and dialkylacetylene as well as substituted dialkylacetylene has been demonstrated.

All monoacetylenes examined which formed an inclusion compound contained nine or more carbon atoms. The relative stability of position isomers of monoacetylenes varied with the cross-sectional diameter of the molecule determined by scalar molecular models. When the triple bond occurred at or close to the center of the molecule, no complex formed. We attributed this to an insufficient number of consecutive —CH_2— groups. None of the polyacetylenes studied formed an inclusion compound.

Characteristic interplanar spacings occurring in the x-ray powder diffraction analysis of the inclusion compounds were used to determine the relative stability of the inclusion compound.

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[CONTRIBUTION NO. 371 FROM THE LABORATORY OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY]

On the Titrimetric Determination of the Configuration of Bridged Diels-Alder Adducts[1a]

HANS STOCKMANN[1b]

Received September 21, 1960

By means of several examples it is shown that mixtures of *exo-endo* isomers can be analyzed iodimetrically. The results obtained emphasize that even at room temperature the Diels-Alder reaction often does not proceed in a homogeneous manner as postulated by Alder's rule.

The Diels-Alder reaction between cyclic dienes and dienophilic substances, such as maleic anhydride, may lead to two stereoisomers Ia or Ib. These stereoisomers are called *endo* and *exo* according to the system of nomenclature introduced by Bredt[2] for derivatives of camphor. The steric course of the addition reaction can be usually predicted by applying Alder's rule[3]; however, exceptions also occur depending on the conditions of the reaction (solvent and temperature) and on the type of diene used. Accordingly, it was found desirable to have a fast and exact method for the determination of the configuration of Diels-Alder adducts. Two general methods are described in the literature both of which are based on gravimetric procedures. They can be illustrated by using the *endo-exo* isomers of bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid (IIa and IIb) as an example. The first method[4] consists of an oxidative degradation of the C=C double bond with the resulting formation of a diformylcyclopentanedicarboxylic acid (IIIa and IIIb). Of these only IIIa, a derivative of the *endo*-isomer IIa, can be converted into the neutral substance IVa. This proof of the configuration is unequivocal, but the method is tedious and gives satisfying results only if the steric homogeneity of a substance with unknown configuration is beyond question. Albeit this is some-

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(1) (a) This investigation was supported by grants of the U. S. Public Health Service and the National Science Foundation to Dr. F. F. Nord.

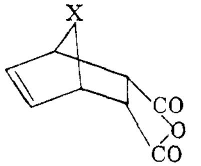
(1) (b) Postdoctoral Research Fellow from Germany.

(2)(a) J. Bredt, *Wüllner Festschrift*, Leipzig, 1905, pp. 119–120; quoted from A. Hesse *et al.*, *Chem. Ber.*, **35**, 1132 (1906); (b) J. Bredt, *J. prakt. Chem.*, 121, 153 (1929).

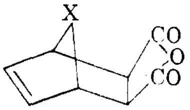
(3) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(4) K. Alder and S. Schneider, *Ann.*, **524**, 189 (1936).

times difficult to decide, as is indicated by the example of isocamphenilic acid.[5] In such or similar cases where the substance in question actually consists of a mixture of stereoisomers, the method permits only an approximate determination of the constituents, because the reactions concerned do not proceed quantitatively. The second method[6] utilizes the fact that a lactone VIa can be formed only from a hydroxy acid Va or Va′ in which both the hydroxyl group as well as the carboxyl group have the *endo*-configuration in regard to the methylene bridge. The formation of the hydroxy acid can be brought about by the addition of water to the double bond of bicyclo[2.1.1]5-heptene-2,3-dicarboxylic acid IIa and IIb catalyzed by sulfuric acid, whereby Va and Vb are obtained. Upon addition of hypobromous acid[7] to the double bond Va′ and Vb′ are formed. This reaction is stereospecific. The hydroxyl group is added to the double bond exclusively on the side of the plane opposite to the methylene bridge.[6] It is therefore justified to assume that the formation of (a) a hydroxy acid proves the *exo* configuration of the carboxyl group; and (b) the formation of a lactone proves the *endo* configuration.[8] However, occasionally difficulties are encountered arising from Wagner-Meerwein rearrangements of the carbonium ion intermediates whereby even *exo* acids form lactones.[6b,9,11a] These difficulties can be overcome by using hypoiodous acid instead of hypobromous acid by dissolving iodine in aqueous potassium iodide.[10] The inconvenience of this procedure is however that it calls for a gravimetric determination, since the lactone has to be separated from the acid. The application of a volumetric instead of a gravimetric method is made possible by consideration of the following facts. (a) *exo* Acids neither rearrange under the influence of hypoiodous acid nor do they add it.[5a,10,11] (b) The addition of hypoiodous acid to the *endo* isomer is quantitative and takes place at a sufficient rate to prevent side

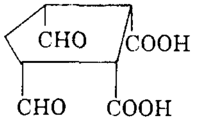


ENDO
Ia

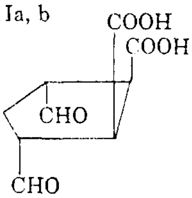


EXO
Ib

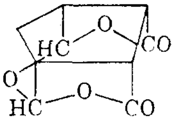
Ia, b. $X = CH_2$
Ia′, b′. $X = O$
IIa, b. free acid of Ia, b



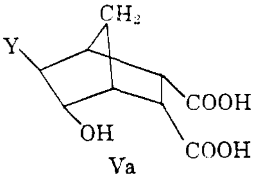
IIIa



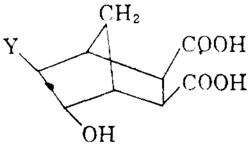
IIIb



IVa

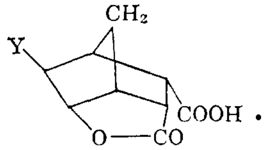


Va

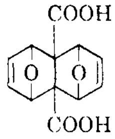


Vb

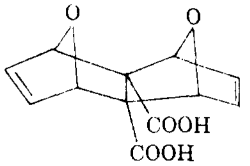
Va, b, VIa. $Y = H$
Va′, b′, VIa′. $Y = Br$



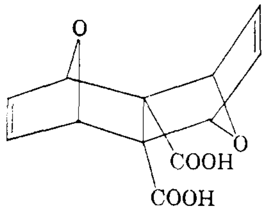
VIa



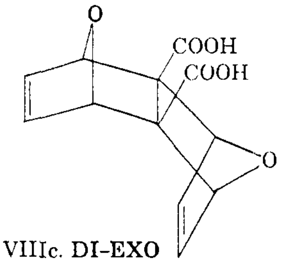
VIII



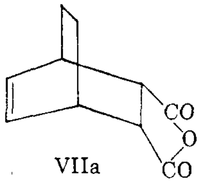
VIIIa. DI-ENDO



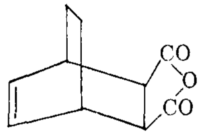
VIIIb. ENDO-EXO



VIIIc. DI-EXO



VIIa



VIIb

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(5)(a) K. Alder and W. Roth, *Chem. Ber.*, **90**, 1830 (1957); (b) Further literature cited in ref. 5a.

(6)(a) K. Alder *et al.*, *Ann.*, **504**, 216 (1933). (b) K. Alder *et al.*, *Ann.*, **514**, 1 (1934).

(7) The question whether the hypohalous acid or cationic halogen is the acting reagent has no bearing on this investigation.

(8) Other reagents used for the same purpose are: lead tetraacetate, leading to a dihydroxy acid or a dilactone,[3] and phenyl azide, leading to an aminohydroxy acid or an aminolactone *via* a cyclic imine. K. Alder, G. Stein, and S. Schneider, *Ann.*, **515**, 185 (1935).

(9) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948).

(10) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **77**, 3582 (1955).

(11)(a) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957); (b) K. Alder, R. Hartmann, and W. Roth, *Ann.*, **613**, 6 (1958); (c) Further examples in a later part of this paper.

reactions. While it is obvious that the titrimetric method enables the determination of an *endo* isomer, it is also possible to find the *exo* isomer as the differential of the total amount, if only these two substances are on hand. Other possible constituents present may be the unchanged α,β-unsaturated anhydride or polymeric addition products.[12] Both can be easily recognized, *e.g.*, by their different neutralization equivalents when compared with the normal addition products.

The usefulness of the titrimetric method can be demonstrated by several examples. Maleic anhydride or the corresponding acid was used as the dienophilic substance. But we believe that the method is applicable to all adducts with α,β-unsaturated acids.

Adduct of cyclopentadiene and maleic anhydride (Ia, b). This reaction was repeatedly studied and found to yield the *endo*-isomer exclusively. [6,13] In the present investigation the reaction was carried out in ether, and the resulting products were separated by fractional crystallization. The crops A and B amounted to more than 90% and consisted of the pure *endo*-isomer. Crop C represented an additional 6% possessing the same neutralization equivalent as A and B, but contained only 77% *endo*-isomer leaving the balance as the *exo*-isomer, which thus makes up 1.4% of the total yield. A residue of less than 1% was not investigated, and unchanged maleic anhydride could not be detected.

Adduct of 1,3-cyclohexadiene and maleic anhydride (VIIa,b). The addition reaction of these compounds did not proceed with the violence as above and required several hours for completion. Only the *endo* isomer was reported to be found[6b] and this in quantitative yield.[13] In the present work 78% was obtained as pure *endo*-isomer, whereas the next two fractions constituted 12.1 and 5.9%, respectively, and contained 84.1 and 73.6 respectively of *endo*-isomer.[14] Since the neutralization equivalents of all three fractions were identical, the balance represented the *exo*-isomer which is so obtained in a yield of 3.5%. A residue amounting to 1.5% was not further investigated but seems to contain some polymeric material as indicated by the neutralization equivalent. Maleic anhydride could not be detected.

Adduct of α-phellandrene and maleic anhydride. This diene not only reacts with maleic anhydride in the typical manner according to Diels and Alder,[13] but also yields appreciable amounts of polymeric material.[12] The structure of the main product has not been proved unequivocally, but seems to correspond to that of a normal adduct and is therefore a bicyclo[2.2.2]-6-methyl-8-isopropyl-5-octene-2,3-dicarboxylic anhydride. The configuration of this product is *endo* as shown by the formation of an iodolactone and its yield amounted to 58% (crop A). Crop B represents an additional 16% possessing an identical neutralization equivalent. 69% of this material consists of the *endo*-isomer, whereas the balance represents the *exo*-isomer. The residue consists of a complicated mixture from which 5% unchanged maleic anhydride could be removed by sublimation *in vacuo*. The remaining products contained considerable amounts of polymeric material as indicated by the lower neutralization equivalent and was not further investigated.

Adduct of furan and maleic anhydride (in ether) (Ia′, b′). The configuration of the maleic anhydride adducts of furan shows a remarkable dependence on the solvent employed in the addition reaction.[9] In ether the reaction between the addends yields the *exo*-isomer[9] and was believed to proceed homogeneously.[15] Applying the present method it was shown that the reaction in fact gave about 90% *exo*-isomer and 5.6% *endo*-isomer. The titrimetric method appears to have particular advantages for the investigation of maleic anhydride adducts in the case of furan for two reasons: (a) The usual treatment with hypobromous acid (*vide supra*) is not convenient for the differentiation of the two stereoisomers. With this agent the *exo*-isomer yields a bromo derivative of an acylated hemi-acetal as a result of a Wagner-Meerwein rearrangement[9] and this hemi-acetal has the same composition as the bromolactone formed by the *endo*-isomer.[16] (b) A separation of the stereoisomers is extremely difficult since the *endo*-isomer is not isolatable as such.[9,16]

Adduct of furan and maleic acid (in water) Ia′, b′). This reaction was shown to yield the *endo*-isomer[9] with the *exo*-isomer as a minor product.[17] The ratio between the two stereoisomers was dependent on the duration and the temperature of the reaction.[17] Because of the difficulties inherent in the simultaneous determination of both isomers as mentioned in the foregoing example, the separation was inconvenient and consisted in the fractional precipitation of the sodium salts in the cold, whereupon the determination by bromination could be carried out.[17] Using the present method, it could be demonstrated that a separation of the isomers is dispensable. A sample which was shaken three days at 26° and then kept at 0° for two months showed the following composition: 61% *exo*-isomer, 31% *endo*-isomer, and 3% maleic acid.

Adduct of two moles of furan and one mole of acetylenedicarboxylic acid (VIII). The reaction between two moles of furan and one mole of acetyl-

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(12) E. R. Littmann, *Ind. Eng. Chem.*, **28**, 1150 (1936).

(13) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(14) Because of the high symmetry of VIIa and VIIb no decrease of the melting point (6b) in a mixture was observed, and occlusion of the *exo*-isomer easily takes place.

(15) O. Diels and K. Alder, *Chem. Ber.*, **62**, 554 (1929).

(16) O. Diels *et al.*, *Ann.*, **490**, 243 (1931).

(17) J. A. Berson and R. Swidler, *J. Am. Chem. Soc.*, **75**, 1721 (1953).

enedicarboxylic acid was early described in the literature, but no proof of the structure of the reaction product was offered.[16] Recently the structure was established as being 1,4,5,8-diepoxy-1,4,4a,5,8,8a - hexahydro -4a,8a - naphthalenedicarboxylic acid VIII.[18] The addition of hypobromous acid yielded quantitatively a substance having the composition of a dibromodilactone.[19] This indicated that the adduct has to be considered as possessing the di-*endo* configuration (VIIIa). But this finding is contrary to all known experimental results regarding the steric course of the addition to the double bond in the bicyclo[2.2.1]-heptene system[20] and the main direction of the steric course of the Diels-Alder reaction of furan in ether[9] (*vide supra*). However, it is probable[19] that the formation of the "dibromodilactone" is due to a Wagner-Meerwein rearrangement of an *exo*-isomer which easily takes place in the 7-oxabicyclo[2.2.1]-heptane system.[9] Application of the iodimetric method demonstrated that the reaction product is actually a mixture of 91% *exo-endo* isomer VIIIb and 4% di-*endo*-isomer VIIIa. This was indicated by the formation of a monoiodolactone and of a diiododilactone, respectively. The di-*exo*-isomer VIIIc, the formation of which is very improbable, could not be detected.

The comparison of the adducts of the three isocyclic dienes shows an increasing ratio between the *exo*-isomer and *endo*-isomer when the reactivity of the diene is decreasing. As a result of this, longer reaction times are required. It was repeatedly observed that prolonged reaction times favor the formation of the *exo*-isomer at the expense of the presence of the *endo*-isomer.[17,21]

Furthermore, it was demonstrated that even in the case of adducts of isocyclic dienes formed at room temperature the steric course of the Diels-Alder reaction does not proceed in a homogenous manner as first assumed[3].

EXPERIMENTAL

General procedure. Preparation of the adducts. Maleic anhydride and the dienes were freshly distilled prior to use, the reactions being carried out in pressure bottles. Upon standing for the time stated, the reaction mixtures were kept for 12 hr. in the refrigerator, and the reaction products were separated by fractional crystallizations. The crystalline precipitate was filtered off (crop A) and washed with a small amount of ice cold ether. The filtrate and the washings were combined and yielded crop B after concentration. Here crop C and the residue were obtained. A Kofler micro melting point apparatus was used for the determination of all melting points.

Iodimetric determination. Usually, a solution containing 4 equivalents of sodium bicarbonate per equivalent of adduct was prepared. However, since the adducts of cyclohexadiene and its derivatives are resistant to this method of hydrolysis, the compounds were first dissolved in acetic acid whereupon water was added until turbidity persisted. This solution was allowed to stand 4 hr., and an excess of sodium bicarbonate was then added. In either case an excess of $0.1N$ iodine-potassium iodide solution was added, and the reaction mixture was allowed to stand 5 min. The excess of iodine solution was back-titrated with $0.1N$ arsenite solution using starch as indicator. A direct method may also be applied. In this case no indicator is used, and the endpoint of the titration is recognized by the color of free iodine in a few drops of chloroform added before starting the titration. The direct method gives less accurate results than the indirect one, the latter indicating an average deviation of ±1%. It should be noted that the adducts of cyclohexadiene and its derivatives can also be treated with iodine in suspension in a sodium bicarbonate solution without prior hydrolysis in acetic acid–water. In this case the reaction mixture has to stand for 0.75 hr.[22] However, the results are less accurate because minute amounts may remain unreacted, or side reactions may occur.

Pure samples of the *endo*-isomers of the adducts of maleic anhydride with cyclopentadiene,[13] cyclohexadiene,[13] and α-phellandrene[13] were prepared and found to take up between 99 and 101% of the theoretical amount of iodine solution. Likewise pure samples of the *exo*-isomers of the maleic anhydride adducts of cyclopentadiene,[23a] cyclohexadiene[23b] and furan[16] were prepared. None of them took up iodine.

Adduct of cyclopentadiene and maleic anhydride (Ia,b).[13] Cyclopentadiene (6.61 g.) was dissolved in an equal volume of absolute ether and added to a chilled solution of 9.81 g. of maleic anhydride in 75 ml. of absolute ether in a pressure bottle. The bottle was closed at once. After the initial violence of the reaction subsided, the bottle was rechilled.

Crop	Amount, g.	Yield, %	M.P.	Neutr. Equiv.	Iodine Requirement in % (Pure *endo*-isomer = 100)
A	13.26	80.8	164	81.5	100.0
B	1.64	10.0	163–164	81.1	99.9
C	1.00	6.1	138–140	82.0	77.3
Residue	0.12	0.7	Not further investigated		

Adduct of 1,3-cyclohexadiene (VIIa, b).[13] A solution of an approximately 80% pure cyclohexadiene preparation (13 g.) and 9.81 g. of maleic anhydride in 75 ml. of absolute ether was kept at 25° for 8 hr. All fractions were kept in a vacuum desiccator over paraffin prior to weighing and analysis.

Crop	Amount, g.	Yield, %	M.P.	Neutr. Equiv.	Iodine Requirement in % (Pure *endo*-isomer = 100)
A	13.88	77.9	147	88.7	101.0
B	2.16	12.1	149	88.4	84.0
C	1.05	5.9	150–151	88.8	73.6
Residue	0.25	1.4		82.7	

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(18) F. F. Nord and H. Stockmann, Abstracts 136th Meeting of the Am. Chem. Soc., 94P (1959).

(19) To be published.

(20) See among others: (a) K. Alder and K. Backendorf, *Ann.*, **535**, 106 (1938); (b) G. Stork, E. E. Van Tamelen, L. J. Friedman, and A. W. Burgstahler, *J. Am. Chem. Soc.*, **75**, 384 (1953); (c) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

(21)(a) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944); (b) K. Alder and R. Rühmann, *Ann.*, **566**, 1 (1950); (c) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951); (d) J. A. Berson, R. D. Reynolds, and W. M. Jones, *J. Am. Chem. Soc.*, **78**, 6049 (1956); (e) S. J. Cristol, W. K. Seifert, and S. B. Soloway, *J. Am. Chem. Soc.*, **82**, 2351 (1960).

Adduct of α-phellandrene and maleic anhydride.[13] α-Phellandrene (15 g.) was added to a solution of 9.81 g. of maleic anhydride in 75 ml. absolute ether, and the reaction mixture was allowed to stand at 26° for 24 hr. From the residue could be obtained by sublimation *in vacuo* at 75° 496 mg. maleic anhydride (5.1% of the starting material). The residue from the sublimation had a neutral equivalent of 103.2. All fractions were kept in a vacuum desiccator over paraffin prior to weighing and analysis.

Crop	Amount, g.	Yield, %	M.P.	Neutr. Equiv.	Iodine Requirement in % (Pure *endo*-isomer = 100)
A	13.52	57.7	126	117.7	100.7
B	3.65	15.6	118	117.1	77.0
Residue	5.18	22.1			

Adduct of furan and maleic anhydride in ether (Ia',b').[15] A solution of 6.81 g. of furan and 9.81 g. maleic anhydride in 75 ml. of absolute ether was kept at 26° for 6 hr. and then in the refrigerator for additional 12 hr. After filtration 13.22 g. (79.6%) of crystals were collected, m.p. 125°. While still cool, an aliquot volume of the mother liquor was extracted with ice cold sodium bicarbonate solution containing small pieces of ice. An aliquot volume of the extract was titrated with 0.1*N* iodine. The entire extract contained 5.61 mmoles (5.6%) of the *endo*-isomer. The unextracted ethereal mother liquor of the first crop was partially evaporated and filtered to remove the precipitated crystals. Taking into account the extracted volume, the total of the second crop of crystals amounted to 1.71 g. (10.3%), m.p. 122°.

Adduct of furan and maleic acid in water (Ia',b')[16]. A 6.81-g. sample of furan was shaken with a solution of 9.81 g. maleic anhydride in 30 ml. of water for 3 days at 26°. The mixture was then allowed to stand at 0° for 2 months. After filtering, the crystals were washed with a little ice water, until a sample of the washing did not react with hypoiodous acid after adding sodium bicarbonate, and dried in a vacuum desiccator over potassium hydroxide. A yield of 8.78 g. (47.7%) was obtained, m.p. 103–104°. The wash water and the mother liquor were combined and an aliquot volume treated with an excess of sodium bicarbonate at 0° and then titrated with 0.1*N* iodine. The total *endo*-isomer amounted to 31.1%. The rest of the aqueous solution was kept *in vacuo* at 55° for 3 hr. and then placed into the vacuum desiccator over potassium hydroxide and paraffin until dry. The residue contained 1.15 g. *exo*-isomer, bringing the total amount of that isomer in the aqueous solution to 12.5% and 1.63 g. of maleic acid, an excess of 3.3% over the amount to be expected from the degradation of the *endo*-7-oxabicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic acid.

Adduct of two moles of furan and one mole of acetylenedicarboxylic acid[16] *(1,4,5,8-diepoxy-1,4,4a,5,8,8a-hexahydro-4a,-8a-dicarboxylic acid)* VIII. An 11.41-g. sample of acetylenedicarboxylic acid was dissolved in 35 ml. of absolute ether, and 13.61 g. of furan was added. The solution was allowed to stand at 27° in a pressure bottle for 4 days and then kept in the refrigerator for another day. The crystals which were filtered off weighed 14.37 g. (57.4%). The m.p. 159° remained unchanged after repeated recrystallization from methanol. A 281.3-mg. (1.12 mmoles) sample required 22.48 ml. of 0.1*N* iodine whereupon a slight precipitate appeared. A 3.42-g. sample was treated in the same way and yielded the latter precipitate amounting to 0.21 g. of diiododilactone (3.0%), m.p. ~330°.

Anal. Calcd.: I, 50.6%. Found: 51.0%.

Upon acidification the mother liquor of the diiododilactone yielded 4.68 g. of monoiodolactonecarboxylic acid (91.0%), m.p. 220–221°.

Anal. Calcd.: I, 33.8%. Found: 34.3%.[24]

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(22) It should be noted that the hydrolysis of the anhydride ring, brought about by intramolecular reaction with the γ-OH group or the γ-carbonium ion, proceeded much faster than the intermolecular hydrolysis, effected by acetic acid-H_2O or by sodium bicarbonate.

(23)(a) K. Alder *et al.*, *Ann.*, **504**, 225 (1933). (b) K. Alder *et al.*, *Ann.*, **514**, 18 (1934).

(24) Determination of iodine according to C. W. Bacon, *J. Am. Chem. Soc.*, **31**, 49 (1909).

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION[1]]

The Diels-Alder Reaction of Levopimaric Acid and Its Use in Quantitative Determinations[2]

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The Diels-Alder reactions of levopimaric acid with maleic anhydride and quinone have been shown to give a single isomer, the kinetics of the reaction with maleic anhydride have been studied and the results of these investigations have been used to establish the validity of an analysis for levopimaric acid in pine oleoresin and to propose a complete structure of maleopimaric acid.

A current investigation of a process for the isolation of levopimaric acid from pine oleoresin in relatively large amounts made desirable the development of a less tedious analysis for the determination of levopimaric acid than the method of Fleck and Palkin[3] which is currently in use. Sandermann[4] proposed in 1938 that the change in optical rotation of a solution of resin acids upon treatment with maleic anhydride might be used to calculate the levopimaric acid content of the mix-

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented at the S. E. Regional Meeting of the American Chemical Society, Birmingham, Ala., November 3-5, 1960

(3) E. E. Fleck and S. Palkin, *Ind. Eng. Chem., Anal. Ed.*, **14**, 146 (1942).