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]

W. D. LLOYD AND G. W. HEDRICK

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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).

TABLE I

THE REACTION OF MALEIC ANHYDRIDE WITH LEVOPIMARIC ACID IN ACETONE SOLUTION

Run	Substrate	Temp.	Initial Concentration, M Maleic anhydride	Initial Concentration, M Levopimaric acid	k(l. mole^{-1} sec^{-1})
1	Levopimaric acid	25.4	0.4077	0.0943	0.00498
2	Levopimaric acid	25.0	.3941	.0483	.00493
3	Levopimaric acid	29.8	.2025	.0925	.00603
4	Levopimaric acid	40.2	.1981	.0879	.00997
5	Slash pine oleoresin	25.6	.3941	.1637	.00457
6	Slash pine oleoresin	25.4	.4077	.1112	.00457
7	Slash pine oleoresin	24.9	.3941	.0820	.00422
8	Slash pine oleoresin	25.3	.2039	.1036	.00464
9	Synthetic oleoresin	25.0	.3955	.0935	.00439
10	Synthetic oleoresin	25.0	.4677	.0729	.00447
11	Synthetic oleoresin	25.2	.3955	.0468	.00440

ture. Using the results of an acidimetric technique to calibrate the analysis of a resin acid fraction of oleoresin, he concluded that two isomers of maleopimaric acid were formed and introduced a factor into the calculations to correct for this; however, only one isomer of maleopimaric acid, m.p. 225–227°, $[\alpha]_D^{25}$ −25°, has been reported.[4–7]

The recent development of simple methods for the isolation of pure resin acids made it possible to use levopimaric acid as a standard for the determination. The specific rotation of maleopimaric acid formed *insitu* from pure levopimaric acid, m.p. 151–152°, $[\alpha]_D^{25}$ −276°, was found to be $[\alpha]_D^{25}$-24° (4% in acetone). The close correspondence of this value with the values reported for the presumably pure compound indicates that a single isomer is formed in the reaction. Apparently a single isomer is also formed in the reaction of levopimaric acid with quinone since the specific rotation, $[\alpha]_D^{25}$ −149° (4% in chloroform), of the quinone adduct formed *in situ* was found to agree well with the value reported by Weinhaus and Sandermann,[7] $[\alpha]_D^{25}$ −148° (in chloroform).

The following structure (Fig. 1) is proposed for maleopimaric acid, 6,14-α-ethano[21,22-dicarboxylic acid anhydride]-7-abietene-15-oic acid (the nomenclature of Klyne[8]) on the basis of molecular model studies. The configuration of the C_{13} position has not been definitely established in levopimaric acid. The observation that a single isomer is produced in the Diels-Alder reaction indicates that the angular C_{12} methyl inhibits the formation of one of the two possible isomers and this would be expected only in the case of a *trans* relationship between the C_{12} methyl and the C_{13} hydrogen. The low activation energy of the reaction, 8.7 kcal., reported later in this paper indicates the correctness of the proposed structure since all the other isomers possible would be expected to have some steric strain.

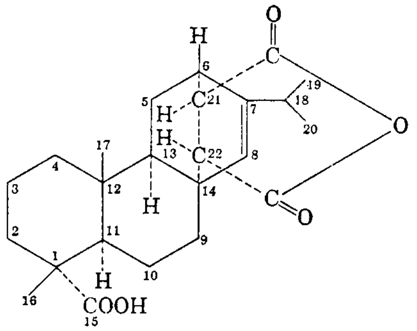

Fig. 1 Proposed structure of maleopimaric acid.

The kinetics of the reaction between maleic anhydride and either pure levopimaric acid, the oleoresin of slash pine (*pinus* Ellioti) or an artificial oleoresin composed of pure levopimaric acid, rosin and turpentine were determined (Table I) by following the change in rotation during reaction.

The exothermicity of the reaction and the thick glass walls of the polarimeter tube made temperature control difficult; however, the effect of changes in temperature was minor in the region studied. The rates from runs one through four were used to calculate the A and E factors of the Arrhenius equation, $k = Ae^{-E/RT}$, which were respectively $10^{5.1}$ l./mole^{-1} sec.$^{-1}$ and 8.7 kcal. These values are reasonable for a Diels-Alder reaction in the absence of strain. Bickford, *et al.*[9] found values of A and E of respectively $10^{4.3}$ l./mole^{-1} sec.$^{-1}$ and 12 kcal. for the reaction of maleic anhydride with β-eleosteric acid and Andrews and Keefer[10] found values of A and E of $10.^{4.7}$ l./mole^{-1}/sec.$^{-1}$ and 8.0 kcal., respectively, for the reaction between maleic anhydride and dimethyl anthracene.

The similarity of the rates of reaction calculated from rotation changes for pine oleoresin and arti-

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(4) W. Sandermann, *Ber.*, **71B**, 2005 (1938).

(5) B. A. Arbuzov, *J. Gen. Chem.* (*U.S.S.R.*), **2**, 806 (1932).

(6) L. Ruzicka and R. G. R. Bacon, *Helv. Chem. Acta*, **20**, 1542 (1937).

(7) H. Wienhaus and W. Sandermann, *Ber.*, **69B**, 2202 (1936).

(8) W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(9) W. G. Bickford, J. S. Hoffmann, D. C. Heinzelman, and S. P. Fore, *J. Org. Chem.*, **22**, 1080 (1957).

(10) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 6284 (1955).

ficial oleoresin solutions strongly suggests that the disappearance of levopimaric acid is being measured in both cases. The rosin and turpentine fractions of the artificial oleoresin gave no rotation change upon treatment with maleic anhydride. Solvent effects are usually small in the Diels-Alder reaction[10] and it was surprising that the presence of 3 to 5% of turpentine and rosin should reduce the rate by 10%. However, in runs five through eleven of Table I, the rate is relatively independent of the concentration. This indicates that the decrease in the rate of reaction of levopimaric acid may be due to the formation of a complex with some component of rosin or turpentine. Andrews and Keefer[10] reported, during a study of the reaction of maleic anhydride with anthracene, that a similar effect was caused by the formation of an unreactive complex between the reactants.

The chromatographic technique of Baldwin, Loeblich, and Lawrence[11] has been found to verify[12] the validity of levopimaric acid analyses obtained by the methods of Fleck and Palkin.[3] In the present work an optical procedure has been developed for the determination of levopimaric acid in pine oleoresin and this procedure has been checked by comparison with results obtained by the methods of Fleck and Palkin.[3] In the case of samples A and B of Table II, close correspondence of results by all three methods indicates the validity of the optical determination. In the case of oleoresin C, the result obtained by the gravimetric method of Fleck and Palkin[3] is significantly higher than results by the optical method developed here and the volumetric method of Fleck and Palkin.[3] This observation is in agreement with the suggestion by Davis and Fleck[13] that oxidized materials coprecipitate with the maleopimaric acid when this method is applied to oxidized oleoresin. Duplicate values obtained by the optical method proposed here usually agree within two tenths of a percent.

TABLE II

ANALYSIS OF PINE OLEORESIN FOR LEVOPIMARIC ACID AS A PERCENT OF THE TOTAL RESIN ACIDS

Oleoresin	Levopimaric Acid Content, %		
	Optical	Gravimetric[a]	Volumetric[a]
A[b]	30.7	30.0	31.0
B[c]	28.6	30.0	29.2
C[d]	25.5(25.3)	33.9(35.6)	26.7(27.2)

[a] The methods of Fleck and Palkin.[3] [b] Fresh slash oleoresin. [c] Fresh mixed (slash 60%, longleaf 40%) oleoresin [d] Year-old mixed (slash 60%, longleaf 40%) oleoresin.

EXPERIMENTAL

Materials. Levopimaric acid was prepared by a modification[14] of the method of Harris and Sanderson.[15] Eastman reagent grade maleic anhydride and Eastman laboratory grade quinone were used and the acetone was dried with calcium chloride before use. For the kinetic runs the oleoresin was diluted with pentane, chilled to 5°, dried with anhydrous sodium sulfate, and the pentane was removed under vacuum at 40°.

The rotation of maleopimaric acid. Levopimaric acid, $[\alpha]_D^{25}$ $-276°$ (0.3000 g., 0.00099 mole), was weighed into a volumetric flask, then dissolved in 2 ml. of acetone and diluted to 10 ml. with a 50% solution of maleic anhydride in acetone. The specific rotation, $[\alpha]_D^{25}$ $-24°$, was calculated after 15 min. using Equation 1:

$$[\alpha]_D^{25} = \frac{\alpha \times V}{(M_A/M_L)\, g \times D} \tag{1}$$

in which α is the observed rotation, V is the volume in milliliters, M_A and M_L are respectively the molecular weights of the adduct and levopimaric acid, g is the weight of levopimaric acid used in grams, and D is the length of the polarimeter tube in decimeters.

The rotation of the quinone adduct of levopimaric acid. Levopimaric acid, $[\alpha]_D^{25}$ $-276°$ (0.3000 g., 0.00099 mole), was weighed into a volumetric flask, then quinone (0.20 g., 0.0019 mole) was added in 2 ml. of chloroform and the contents of the flask diluted to 10 ml. with chloroform. After 6 hr. the specific rotation, $[\alpha]_D^{25}$ $-149°$, was calculated as above.

Determination of reaction rates. The substrate—levopimaric acid, pine oleoresin, or synthetic oleoresin—was placed in a 10-ml. volumetric flask, with enough acetone to give approximately 5 ml. of solution. An aliquot of a previously standardized acetone solution of maleic anhydride was added and the contents of the flask quickly diluted to the mark with dry acetone. The flask was agitated and its contents were placed in a jacketed polarimeter tube equipped with a thermometer. The reaction was slightly exothermic and the temperature dropped a few tenths of a degree after several half lives. A modification of the Biot formula was used to calculate the change in concentration of levopimaric acid, X, in Equation 2.

$$X = \frac{\{\alpha_t - \alpha_0\}\, 1000}{\{([\alpha]_D)_L - M_A/M_L\,([\alpha]_D)A\}\, M_L \times D} \tag{2}$$

in which α_t and α_0 are the observed rotations at time equals t and zero seconds respectively, $([\alpha]_D)_L$ is the specific rotation of levopimaric acid, $([\alpha]_D)_A$ is the specific rotation of maleopimaric acid, M_A and M_L are respectively the molecular weights of maleopimaric and levopimaric acids and D is the length of the polarimeter tube in decimeters. The rate, k, was determined by substituting the value X calculated above into Equation 3:

$$k = \frac{2.303}{t\,(b - a)} \log \frac{a\,(b - x)}{b\,(a - x)} \tag{3}$$

in which t is the time in seconds, a is the initial concentration of levopimaric acid, and b is the initial concentration of maleic anhydride. The initial rotation was determined by preparing a duplicate sample from which the maleic anhydride was omitted.

The analytical method. Pine oleoresin (12.5 g.) was diluted with 10 ml. of acetone, filtered with suction and transferred quantitatively to a 25-ml. volumetric flask and diluted to the mark with acetone. An aliquot of this solution was titrated in ethanol with 0.1N sodium hydroxide to the phenolphthalein end point. Two 5-ml. aliquots of the solution were placed in 25-ml. volumetric flasks and 5 ml. of a fresh 50% acetone

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(11) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *Chem. Eng. Data Ser.*, **3**, 342 (1958).

(12) R. V. Lawrence, unpublished studies.

(13) B. L. Davis and E. E. Fleck, *Ind. Eng. Chem.*, **35**, 171 (1943).

(14) W. D. Lloyd and G. W. Hedrick, to be published.

(15) G. C. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 334 (1948).

solution of maleic anhydride was added to one flask. After 15 min. the contents of both flasks were diluted to the mark and the rotations observed. The levopimaric acid content of the oleoresin, L, was calculated as a percent of resin acids using equation 4:

$$\% L = 100 \frac{(\alpha_M - \alpha_0)V}{W \{([\alpha]_D)_L - M_A/M_L([\alpha]_D)_A\}} \qquad (4)$$

in which α_M and α_0 are the observed rotations with and without maleic anhydride, V is the volume in milliliters, W is the weight in grams of resin acids in sample as calculated from the titer, $([\alpha]_D)_L$ and $([\alpha]_D)_A$ are the specific rotations of levopimaric acid and adduct, and M_A and M_L are the molecular weights of levopimaric acid and its adduct.

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OLUSTEE, FLA.

[CONTRIBUTION NO. 624 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND CO.]

4-(2-Cyano-3-maleimidyl)arylamines and Related Colored Compounds

E. L. MARTIN, C. L. DICKINSON, AND J. R. ROLAND

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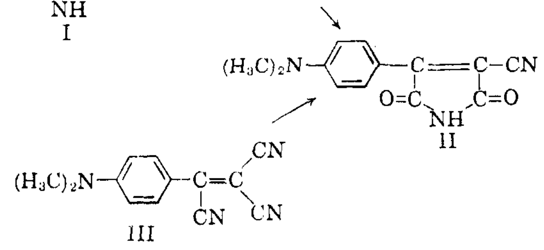
3-Chloro-2-cyanomaleimides react with tertiary arylamines by attacking the aromatic ring to give 4-(2-cyano-3-maleimidyl)arylamines, a new class of colored compounds. The same compounds can be obtained by the condensation of a dihalomaleimide and a metal cyanide in the presence of a tertiary arylamine. Dihalomaleic anhydrides and mucohalic acids can be substituted for the dihalomaleimides, and metal sulfinates can be used in place of metal cyanides to give analogous compounds.

Tetracyanoethylene reacts with primary and secondary aliphatic amines and with most primary and some secondary aromatic amines to give N-tricyanovinylamines.[1] However, the reaction of tetracyanoethylene and tertiary aromatic amines and certain secondary aromatic amines results in attack on the ring to give 4-tricyanovinylarylamines.[1] Tricyanovinyl chloride behaves much like tetracyanoethylene toward amines.[2] A recent publication[3] reported the reaction of 3-chloro-2-cyanomaleimide (I) with primary aromatic amines and a secondary aliphatic amine to give derivatives in which a hydrogen atom on the amine group had been replaced by a 2-cyano-3-maleimidyl residue. It has now been found that, like tetracyanoethylene and tricyanovinyl chloride, 3-chloro-2-cyanomaleimide (I) readily attacks the ring of tertiary atomatic amines to give 4-(2-cyano-3-maleimidyl)arylamines, a new class of colored compounds. For example, N,N-dimethylaniline and 3-chloro-2-cyanomaleimide (I) gave 4 - (2 - cyano - 3 - maleimidyl) - N,N - dimethylaniline (II), a bright red substance. N-Substituted 3-chloro-2-cyanomaleimides behave similarly.

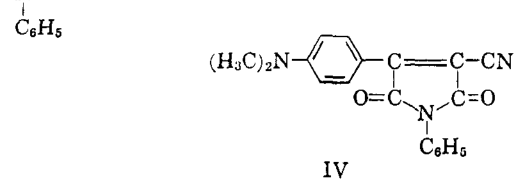


I

II

III

Compound II is identical with the product obtained by the acid hydrolysis[4] of 4-(tricyanovinyl)-N,N-dimethylaniline (III), a dye whose structure was established by an unequivocal synthesis.[1]



IV

4-(2-Cyano-3-maleimidyl)arylamines can be prepared also by the reaction of a dihalomaleimide, a tertiary aromatic amine, and sodium cyanide in a suitable solvent as illustrated in the preparation of 4-(N-phenyl-2-cyano-3-maleimidyl)-N,N-dimethylaniline (IV). Compounds of the formula VI are obtained conveniently by the addition of a salt of a sulfinic acid to a solution of a tertiary aromatic amine and a dibromo- or dichloromaleimide (V) in a suitable reaction medium. In these examples, the first step in the reaction

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(1) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

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(3) R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc.*, **80**, 1385 (1958).

(4) G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958).