chloride in water and neutralizing with 5% aqueous sodium carbonate, was purified by recrystallization from benzene; white needles, m.p. 118° dec.

Anal. Calcd. for $C_6H_8ClN_3$: C, 45.76; H, 5.12; N, 26.61. Found: C, 45.46; H, 5.12; N, 26.68.

The amines prepared by these two methods were shown to be identical by melting point and infrared spectra determinations.

3,4,5-Toluenetriamine.—Reduction of 4-amino-3,5-dinitrotoluene[7] in a similar manner afforded the triamine, which was purified by recrystallization from benzene; white needles, m.p. 105° (lit.[7] m.p. 105°).

This triamine was not identical with the amine prepared from II and hydrazoic acid.

5-Chloro-1,2,3-benzenetriamine.—Reduction of 4-chloro-2,6-dinitroaniline[4] in a similar manner gave the amine, which was purified by recrystallization from benzene; tan needles, m.p. 115° dec.

Anal. Calcd. for $C_6H_8ClN_3$: C, 45.76; H, 5.12; N, 26.61. Found: C, 45.46; H, 5.12; N, 26.68.

This triamine was not identical with the amine obtained by reduction of the product from I and hydrazoic acid.

4-Methyl-5(?)-(3-pentanedione-2,4)-*o*-phenylenedibenzenesulfonamide.—To a solution of 5.0 g. of 4-methyl-*o*-quinonedibenzenesulfonamide in 40 ml. of dioxane was added 1.87 g. of acetylacetone and about 40 mg. of sodium methoxide. After remaining at room temperature for one week, the reaction mixture was poured into 300 ml. of petroleum ether (b.p. 30–60°) to give an orange solid which weighed 2.5 g. (40%). The compound was purified by recrystallization from ethanol (Darco); white needles, m.p. 197–198°.

Anal. Calcd. for $C_{24}H_{24}N_2O_6S_2$: C, 57.70; H, 4.82; N, 5.60. Found: C, 57.99; H, 5.12; N, 5.57.

In the infrared spectrum an absorption band at 1610 cm.$^{-1}$ indicated the presence of a carbonyl group as a chelated, enolized diketone.

4-Chloro-5(?)-(3-pentanedione-2,4)-*o*-phenylenedibenzenesulfonamide.—By a procedure similar to that used for the corresponding methyl compound, acetylacetone was added to 4-chloro-*o*-quinonedibenzenesulfonimide. The product was obtained in only 16% yield. It was purified by recrystallization from ethanol (Darco); white needles, m.p. 180–181°.

Anal. Calcd. for $C_{23}H_{21}ClN_2O_6S_2$: C, 53.06; H, 4.07; N, 5.38. Found: C, 52.99; H, 4.02; N, 5.32.

In the infrared spectrum an absorption band at 1610 cm.$^{-1}$ indicated the presence of a carbonyl group as a chelated, enolized diketone.

4-Methyl-5(?)-(1-propanone-2)-*o*-phenylenedibenzenesulfonamide.—A solution of 3.0 g. of 4-methyl-5(?)-(3-pentanedione-2,4)-*o*-phenylenedibenzenesulfonamide in 200 ml. of 5% aqueous sodium hydroxide was boiled for 15 minutes. At the end of this time, the solution was filtered, cooled, and acidified with concentrated hydrochloric acid to give a white precipitate which weighed 2.0 g. (66%). The compound was purified by recrystallization from methanol; white needles, m.p. 125–126°.

Anal. Calcd. for $C_{22}H_{22}N_2O_5S_2$: C, 56.43; H, 4.83; N, 6.12. Found: C, 56.55; H, 5.10; N, 6.12.

In the infrared spectrum a carbonyl group was indicated by an absorption band at 1710 cm.$^{-1}$.

Dimerization of 4-Methyl-*o*-quinonedibenzenesulfonimide. Method A. To a solution of 5.0 g. of 4-methyl-*o*-quinonedibenzenesulfonimide in 50 ml. of dioxane was added 1.32 g. of nitromethane and about 40 mg. of sodium methoxide. After remaining at room temperature for 2 weeks, the reaction mixture was poured into 400 ml. of petroleum ether (b.p. 30–60°) to give an orange amorphous solid which weighed 2.5 g. (50%). The compound was purified by recrystallization from ethanol (Darco); orange crystals, m.p. 145°.

Method B.—To a solution of 1.5 g. of 4-methyl-*o*-quinonedibenzenesulfonimide in 100 ml. of chloroform was added 2 ml. of freshly distilled cyclopentadiene. After remaining at room temperature for 3 days, the chloroform was evaporated, leaving 1.0 g. (67%) of an orange residue. The compound was purified by recrystallization from ethanol; orange crystals, m.p. 145°.

Anal. Calcd. for $C_{38}H_{32}N_4O_8S_4$: C, 57.00; H, 4.03; N, 6.98; mol. wt., 800. Found: C, 56.74; H, 4.05; N, 6.86; mol. wt. (ebullioscopic), 847.

The infrared spectra of the dimers prepared by these two different methods were identical.

In the infrared spectrum the carbon–carbon double bond was indicated by an absorption band at 1665 cm.$^{-1}$.

Dimerization of 4-Chloro-*o*-quinonedibenzenesulfonimide. Method A.—By an identical procedure, 4-chloro-*o*-quinonedibenzenesulfonimide was dimerized with nitromethane. The product formed in 50% yield. It was purified by recrystallization from ethanol (Darco); orange crystals, m.p. 186°.

Method B.—4-Chloro-*o*-quinonedibenzenesulfonimide was dimerized with cyclopentadiene as described for the 4-methyl analog. The product was formed in 33% yield. It was purified by recrystallization from ethanol (Darco); orange crystals, m.p. 186°.

Anal. Calcd. for $C_{36}H_{26}Cl_2N_4O_8S_4$: C, 51.37; H, 3.11; N, 6.64; mol. wt., 841. Found: C, 51.24; H, 3.34; N, 6.51, mol. wt. (ebullioscopic), 762.

The infrared spectra of the dimers prepared by these two different methods were identical. In the infrared spectrum the carbon–carbon double bond was indicated by an absorption band at 1663 cm.$^{-1}$; the carbon–chlorine bond by an absorption band at 720 cm.$^{-1}$.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Reaction of β-Pinene with Dienophiles

BY RICHARD T. ARNOLD[1] AND JOHN S. SHOWELL[2]

RECEIVED AUGUST 30, 1956

β-Pinene has been found to react at 140° with a series of dienophiles including maleic anhydride, dimethyl maleate, dimethyl fumarate and methylenemalonic ester to form 1–1 adducts. In the three cases leading to the formation of a new asymmetric center, the 1–1 adduct consisted of a binary mixture of diastereoisomers in which one of these predominated. The adduct from β-pinene and methylenemalonic ester was synthesized independently. The data are consistent with a concerted mechanism involving a six-membered cyclic transition state.

Subsequent to the discovery by Alder and coworkers[3] that allylbenzene reacts thermally with maleic anhydride to form cinnamylsuccinic anhydride, many publications have appeared[4–7] which

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[1] Alfred P. Sloan Research Associate.

[2] Alfred P. Sloan postdoctorate Research Associate.

[3] K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943).

[4] K. Alder and Dorfmann, *ibid.*, **85**, 556 (1952), and previous papers.

[5] C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, THIS JOURNAL, **78**, 2637 (1956), and earlier papers.

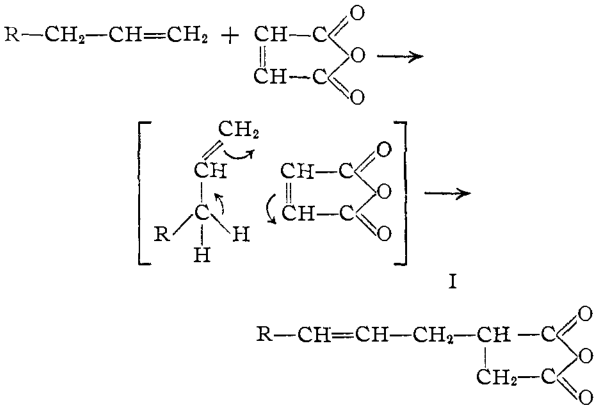
[6] C. S. Rondestvedt and A. H. Filbey, *J. Org. Chem.*, **19**, 548 (1954).

[7] R. T. Arnold and J. F. Dowdall, THIS JOURNAL, **70**, 2590 (1948).

describe the formation of 1–1 adducts from a variety of olefinic compounds and a host of readily available dienophiles.

A necessary structural feature of the olefinic compound appears to be the presence of at least one hydrogen atom on the carbon adjacent to the reactive carbon–carbon double bond. Invariably, a migration of the carbon–carbon double bond to an adjacent position in the olefin moiety is characteristic of this reaction.

It has been postulated[7] that formation of the above adducts occurs by means of a completely concerted mechanism imposed by a six-membered cyclic transition state (I).


I

β-Pinene was chosen for the present study because of the characteristic Wagner–Meerwein rearrangement or ring opening which occurs when the methylene carbon atom in this molecule reacts with active cations[8] or free radicals.[9,10]

Application of the above concerted mechanism to the reaction of β-pinene with maleic anhydride, methyl maleate, methyl fumarate and methylenemalonic ester, however, leads to the conclusion that the four-membered ring should remain intact and that the products formed should be represented by formulas II, III, IV, V and VI. The evidence available strongly supports this point of view.

Since in the reactions with maleic anhydride, methyl maleate and methyl fumarate, a new asymmetric center is introduced, one might suspect the simultaneous formation of two diastereoisomers. This proved to be correct although, in each case, one of these isomers was clearly present in preponderant amount. The reaction, therefore, exhibits considerable stereospecificity.

The diastereoisomeric pairs of compounds (II-III and IV-V) examined in this study exhibit remarkably similar although not identical infrared spectra, and some alternate means of analysis for these binary mixtures had to be found. This was accomplished in the following manner. From the reaction of β-pinene with maleic anhydride, one diastereoisomer (II) was isolated readily and easily purified by crystallization. This compound was hydrolyzed under mild conditions to a pure crystalline dibasic acid, and the latter, with diazomethane, gave the liquid dimethyl ester IV quantitatively. It is assumed that the conversion of pure II into IV proceeds with no alteration of the asymmetric centers present and that IV represents, therefore, a pure diastereoisomer. The optical rotation of IV is regarded as the sum of two contributions: one from the pinenyl radical and one from the newly introduced asymmetric carbon atom. The former value was obtained from observed rotations on the ester (VI). Solution of the appropriate simultaneous linear equations led to a calculated value for the specific rotation of the diastereoisomeric ester (V) of −54.9°.

For purposes of analysis, the mixture of isomeric anhydrides II and III, resulting from the reaction of β-pinene with maleic anhydride, was converted to the corresponding mixture of diastereoisomeric esters IV and V and compared with those derived directly from dimethyl maleate and dimethyl fumarate. The data are summarized in Table I.

TABLE I

Olefin	Dienophile	Rotation[a] (IV and V)	% IV	% V
β-Pinene	Maleic anhydride	− 6.12°	75	25
β-Pinene	Methyl maleate	−11.83	66	34
β-Pinene	Methyl fumarate	− 0.95	83	17

[a] Specific rotations, measured without solvent.

As anticipated, methylenemalonic ester is a very effective dienophile. This direct thermal route to monosubstituted malonic esters, as exemplified in the formation of VI, appears to be novel and should prove to be a valuable synthetic tool. The structure of VI was established rigorously by its independent synthesis from nopyl tosylate (VII) and malonic ester.[11]

Attempts to synthesize II, IV and several derivatives of these by alternative routes led to inseparable mixtures of diastereoisomers. The infrared spectra of these synthetic mixtures, however, were very similar to those of the desired products.

There can be little doubt concerning the formulas assigned to the 1–1 adducts derived from β-pinene. Catalytic hydrogenation led in each case to the absorption of one mole of hydrogen. The rapid reaction of (IV) with bromine to form a bromo-γ-lactone (as shown by its infrared spectrum) is very characteristic of γ,δ-unsaturated esters.[12]

Ozonization of the anhydride II produced no nopinone, establishing the fact that the double bond does not occupy an exocyclic position.

When warmed with methanol, II reacted to form a mixture of the two possible isomeric carbomethoxycarboxylic acids, neither of which could be isolated in a pure state due to their thermal instability. Attempts to fractionate this mixture resulted in partial elimination of methanol and reconversion to the anhydride II. The mixed isomeric half-esters reacted completely with diazomethane to give the diester IV.

α-Pinene did not react with maleic anhydride

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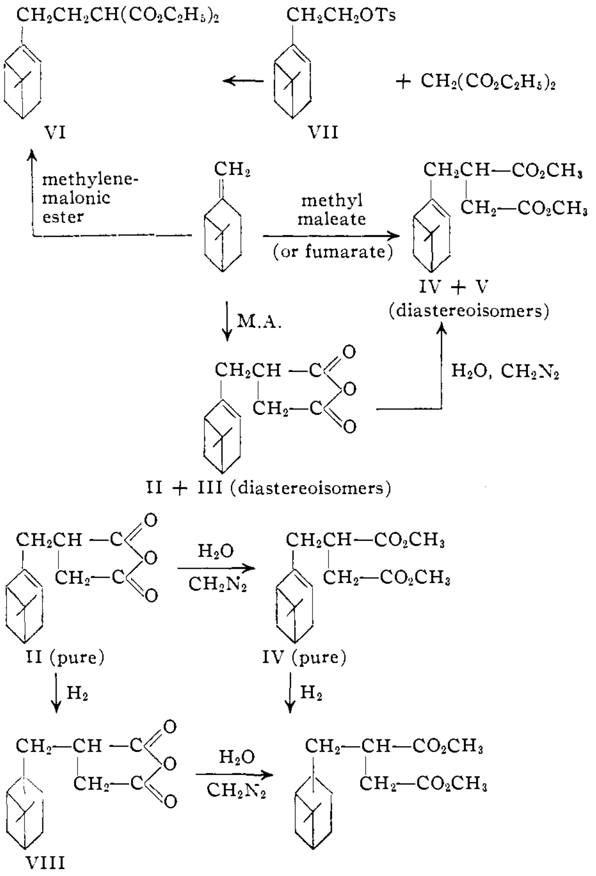
[8] R. T. Arnold and W. W. Lee, THIS JOURNAL, **75**, 5396 (1953).

[9] D. M. Olroyd, G. S. Fisher and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950).

[10] M. Vilkas, G. Dupont and R. Dulou, *Bull. soc. chim. France*, 799 (1955).

[11] We are indebted to Dr. John Jones of this Laboratory for a sample of VI used for purposes of comparison.

[12] R. T. Arnold, M. deM. Campos and K. L. Lindsay, THIS JOURNAL, **75**, 1044 (1953).



under the experimental conditions employed in this study.

Experimental

β-Pinene.—All β-pinene used in this study was obtained by careful fractionation of a commercial sample and had the following properties: b.p. 59° (20 mm.), $n^{25}\text{D}$ 1.4752, $[\alpha]^{26}\text{D}$ $-19.6°$ (10 cm. tube).

Reaction of β-Pinene with Maleic Anhydride.—(a) Maleic anhydride (150 g., 1.5 moles) was dissolved in boiling xylene (700 ml.) and β-pinene (217 g., 1.6 moles) was added. The solution was refluxed for 20 hr., cooled and the solvent removed under vacuum (60° (20 mm.)). The warm residue was dissolved in *n*-hexane (700 ml.) and the solution cooled overnight at $-5°$. The white crystalline solid (170 g., m.p. 73–75°) was recrystallized from *n*-hexane to give 10-pinen-2-ylsuccinic anhydride (II), m.p. 92–93°, yield 112 g. (31%). The analytical sample showed m.p. 92.5–93.5°, $[\alpha]^{26}\text{D}$ $-88.4°$.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.70; H, 7.54.

This product exhibited strong absorption at 5.41 and 5.63 μ characteristic of anhydrides. It readily decolorized bromine and was rapidly oxidized by potassium permanganate.

(b) In order to determine the amounts of the two diastereoisomeric 10-pinen-2-ylsuccinic anhydrides produced, the reaction was repeated as follows: β-Pinene (47.5 g.) was added to boiling xylene (150 ml.) containing maleic anhydride (34.5 g.), and the solution was heated under reflux for 16 hr. After removing the solvent under vacuum, the residue was dissolved in acetic acid (150 ml.) and heated for 0.5 hr. to form the mixed anhydride. Water (50 ml.) was then added and heating continued for 1 hr. The solvent was removed under vacuum (80° (20 mm.)) and the crystalline residue dissolved in potassium hydroxide (150 ml., 15%). This solution was extracted with ether and the aqueous phase was acidified with sulfuric acid. The acidic components were extracted with ether and approximately 10% of this solution was esterified with diazomethane. There was obtained by fractionation a mixture of diastereoisomers of dimethyl 10-pinen-2-ylsuccinate (IV and V) weighing 0.8 g., b.p. 110° (0.07 mm.), $n^{26}\text{D}$ 1.4778, $[\alpha]^{26}\text{D}$ $-6.12°$. The infrared spectrum of the mixed diastereoisomers was remarkably similar to but not identical with the pure ester IV.

10-Pinanylsuccinic Anhydride.—The 1–1 adduct from β-pinene and maleic anhydride, 10-pinen-2-ylsuccinic anhydride (11.7 g.), was dissolved in purified dioxane and hydrogenated at low pressure (3 atm.) with Adams catalyst (1 g.). Following an uptake of one mole of hydrogen, the catalyst was removed by filtration and the solvent evaporated under reduced pressure. The solid residue was dissolved in *n*-hexane and decolorized with Norite (1 g.). The filtered solution upon standing overnight at $-5°$ deposited crystalline 10-pinanylsuccinic anhydride, m.p. 92–93°, yield 7.5 g. (65%). An infrared spectrum (KBr pellet) exhibited strong anhydride bands at 5.45 and 5.65 μ. The product did not decolorize bromine.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.26; H, 8.64.

10-Pinen-2-ylsuccinic Acid.—This substance was prepared from the corresponding anhydride (23.4 g.) by heating the latter in acetic acid (40 ml.) for 20 minutes followed by the addition of water (60 ml.) and subsequent heating for 40 minutes. Upon cooling, the crystalline carboxylic acid separated, yield 20 g. (79%), m.p. 137–145° (decomp. to form anhydride).

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.82; H, 8.28.

Dimethyl 10-Pinen-2-ylsuccinate (IV).—10-Pinen-2-ylsuccinic acid (20 g.) was dissolved in ether (150 g.) and treated with an excess of diazomethane. The ether was evaporated and the residue flash distilled to obtain a colorless liquid ester, yield 16 g. (71%), $n^{24}\text{D}$ 1.4770, b.p. 160° (0.5 mm.), $[\alpha]^{26}\text{D}$ $+9.88°$. The infrared spectrum showed characteristic ester bands at 5.82 and 6.10 μ.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.55; H, 8.86.

Dimethyl 10-Pinanylsuccinate.—(a) The above unsaturated ester (16 g.) was reduced with hydrogen (3 atm.) and Adams catalyst (1 g.) in purified dioxane. Exactly one equivalent of hydrogen was consumed. Fractionation of the residue after removal of the catalyst and solvent gave the desired ester, yield 14.5 g. (90%), b.p. 160° (0.2 mm.), $[\alpha]^{26}\text{D}$ $+11.94°$ (10 cm. tube).

Anal. Calcd. for $C_{16}H_{26}O_4$: C, 68.05; H, 9.84. Found: C, 67.94; H, 9.49.

(b) Hydrolysis of 10-pinanylsuccinic anhydride (2 g.) in aqueous acetic acid gave 10-pinanylsuccinic acid, yield 2.02 g., m.p. 163–164° dec.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.29; H, 8.91.

Esterification of this with diazomethane in ether gave an ester identical in every respect with that obtained in part (a) above.

Reaction of β-Pinene with Methyl Maleate.—β-Pinene (40.8 g., 0.3 mole) was dissolved in xylene (150 ml.) containing dimethyl maleate (43.2 g., 0.3 mole) and the solution was heated under reflux for 90 hr. Fractionation led to recovery of dimethyl maleate (22.1 g.) and the isolation of the expected 1–1 adduct, yield 13 g. (32% based on maleate consumed), b.p. 130° (0.7 mm.), $n^{28}\text{D}$ 1.4758, $[\alpha]^{26}\text{D}$ $-11.83°$. This adduct (which is a mixture of diastereoisomers) had an infrared spectrum almost identical with that of the pure isomer IV.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.57; H, 8.57. Found: C, 68.24; H, 8.61.

Reaction of β-Pinene with Methyl Fumarate.—β-Pinene (40.8 g., 0.3 mole), dimethyl fumarate (43.2 g., 0.3 mole) and xylene (90 ml.) were heated together for 90 hr. at the boiling point. The resulting solution was cooled overnight at $-5°$ and dimethyl fumarate (13 g.) was recovered as a crystalline solid. The filtrate was concentrated under vacuum (70° (20 mm.)) and the resulting residue distilled in an oil-jacketed flask. There was obtained dimethyl 10-pinen-2-ylsuccinate as a mixture of diastereoisomers, yield 22 g. (37% based on fumarate consumed), b.p. 130° (0.5 mm.), $[\alpha]^{28}\text{D}$ $-0.95°$ (10 cm. tube). The infrared spectrum of this sample was almost identical with that obtained from dimethyl maleate.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.57; H, 8.57. Found: C, 68.32; H, 8.64.

Reaction of β-Pinene with Methylenemalonic Ester.—β-Pinene (8.3 g., 0.06 mole) and methylenemalonic ester[13] (10.3 g., 0.06 mole) were refluxed in xylene (200 ml.) under an atmosphere of nitrogen for 111 hr. The solvent was removed under vacuum (60° (20 mm.)) and the residue distilled in an oil-jacketed flask to give diethyl nopylmalonate, yield 9.5 g. (51%), b.p. 128° (0.2 mm.), n^{25}_{D} 1.4668, $[\alpha]^{26}_{D}$ −20.52°.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.13; H, 9.15. Found: C, 69.89; H, 9.35.

Diethyl Nopylmalonate.—Diethylmalonate (24 g.) was added to a solution of sodium (5.6 g.) in absolute ethanol (400 ml.). A solution containing nopyl tosylate (49.8 g.) and absolute ethanol (100 ml.) was added dropwise over 1 hr. to the stirred reaction mixture held at its boiling point. Heating and stirring were continued for 48 hr., and the cooled mixture was poured into water (2 l.) and extracted with ether (500 ml.). The ether solution was dried over magnesium sulfate, filtered and fractionally distilled to give diethyl nopylmalonate, yield 14 g. (28%), b.p. 127° (0.2 mm.), n^{25}_{D} 1.4678, $[\alpha]^{26}_{D}$ −21.5°.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.13; H, 9.15. Found: C, 69.97; H, 9.21.

All the physical properties of this substance, including its infrared spectrum, were indistinguishable from those for the material obtained directly from β-pinene and methylenemalonic ester.

Reaction of 10-Pinen-2-ylsuccinic Anhydride (II) with Methanol.—The anhydride (1 g.) was refluxed with anhydrous methanol (30 ml.) for 16 hr. The excess methanol was removed under partial vacuum and the oily residue was held at 70° at a pressure of 0.05 mm. for 3 hr. A value of 275 was obtained as neutral equivalent (calcd. for half acid-ester, 266). This residue showed no anhydride bands in the infrared but exhibited strong absorption at 5.8 (ester) and 5.9 μ (carboxylic acid). Following distillation of the oily residue (b.p. 155° (0.08 mm.)), the product exhibited strong anhydride bands at 5.43 and 5.63 μ in addition to those for the ester (5.8 μ) and carboxylic acid (5.9 μ). The undistilled crude half-ester reacted rapidly with diazomethane in ether to form dimethyl 10-pinen-2-ylsuccinate (IV).

NEW YORK, N. Y.

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[13] G. B. Bachman and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

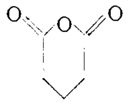
2*H*-Pyran-3,5(4*H*,6*H*)-Diones

BY MARY ANNE MORGAN[1] AND EARLE VAN HEYNINGEN

RECEIVED AUGUST 13, 1956

A synthesis is reported for the previously undescribed 2*H*-pyran-3,5(4*H*,6*H*)-diones.

In contrast to the many syntheses of 4,5-dihydro-2*H*-pyran-2,6(3*H*)-diones (I) appearing in the literature, there is no report of the synthesis of the isomeric 2*H*-pyran-3,5-(4*H*,6*H*)-diones (II). Gulland and Farrar[2] do mention their interest in compounds of this type as possible chemotherapeutic agents; they had prepared some substituted cyclotelluropentane-3,5-diones which had exhibited marked activity and the pyran-3,5-diones are their oxygen analogs. There is, however, no subsequent report of their preparation by these authors.



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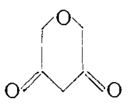


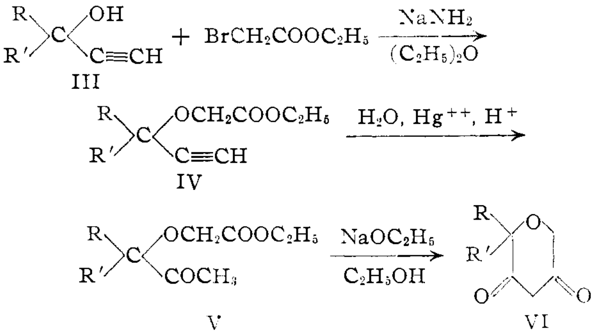
II

Our interest in their synthesis lay both in the compounds' intrinsic novelty as well as in the possibility that the β-hydroxyvinyl ketone grouping, common to their mono-enolic form and to salicylic acid, might impart to them the pharmacological activity of the salicylates.

The route chosen is indicated in Scheme I. Initial attempts to make the ketones V from acyloins and α-bromoesters *via* an ether synthesis were unsuccessful for no single, pure product could be isolated. But when the acetylenic alcohols III were used in the ether formation, acceptable yields of pure acetylenic ether-esters could be obtained.

In general, the hydration of the acetylene moiety to the methyl ketone proceeded as expected. However, in the hydration of 3-carbethoxymethoxy-1-hexyne (IV, R = H, R′ = C_3H_5) the solvent used was methanol, and transesterification occurred during the reaction to give as a product an inseparable mixture of methyl and ethyl esters. Since the alkoxyl group is lost in the ring closure, this mixture was as useful as a pure ester. The hydration of 3-carbethoxymethoxy-3-methyl-1-butyne (IV, R = CH_3, R′ = CH_3) gave a mixture which was not separated after repeated distillation, and the chemical tests for a terminal acetylene group were positive. One might anticipate that the steric hindrance afforded by the three groups on the carbon atom adjacent to the acetylene group would render the hydration of this compound more difficult than that of the others. The results seem to substantiate this conclusion.

SCHEME I



The ketoesters V were cyclized with sodium ethoxide in ethanol to give the pyrandiones VI in relatively poor yields. The diketones on distillation decompose to leave sizable residual distil-

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[1] University of Minnesota, Minneapolis, Minn.

[2] J. M. Gulland and W. V. Farrar, *Nature*, **154**, 88 (1944).