TABLE IV

PHYSICAL CONSTANTS OF REDUCED INDOPHENYL ESTERS

Compound No.	Appearance	M.P.[a]	Infrared,[b] μ
1	Pale grey microcrystals	119–121	2.84, 2.99, 5.77, 8.16, 8.37
2	Pale pink microcrystals	137–141	2.85, 2.99 (shoulder), 5.67, 5.76, 8.12, 8.38
3	Brown needles	128–129	2.85, 2.97, 5.72, 8.10, 8.23 (shoulder), 8.38
4	Pale tan microcrystals	155–157	2.87, 2.95, 3.00, 5.68, 5.83, 8.17, 8.40
5	Pale tan needles	181	2.86 (shoulder), 2.96, 5.72 (shoulder), 5.79, 8.12, 8.30
6	Tan needles	83–84	2.71, 2.78 (shoulder), 2.89, 5.70, 8.10, 8.32 (broad)
7	Pale tan needles	224–225	2.94, 2.99 (shoulder), 5.78, 8.12, 8.31
8	Tan plates	203–204	2.83, 5.61, 8.17 (shoulder), 8.43
9	White needles	164–165	3.00, 5.67, 5.79, 8.17, 8.35–8.50
10	White plates	174–175	2.94, 5.66, 5.71 (shoulder), 8.11, 8.36
11	Yellow-white needles	178–179	2.97, 5.60 (shoulder), 5.68 (shoulder), 5.71, 8.16, 8.43
12	Tan needles	192–193	2.94, 5.70 (shoulder), 5.73, 8.17, 8.47
13	White needles	168	2.96, 5.57 (shoulder), 5.64 (shoulder), 5.71, 8.3 (broad)
14	Tan needles	164–165	2.95, 5.71, 5.84 (shoulder), 8.35
15	Pale yellow microcrystals	192–196	2.95, 5.65 (shoulder), 5.72, 8.20 (broad), 8.45
16	Light grey plates	119–120	2.94, 5.76, 8.18, 8.39
17	White plates	166–168	2.93, 5.72, 8.20, 8.40

[a] All melting points are uncorrected. Determined using Fisher-Johns melting point apparatus. [b] Potassium bromide pellet. Absorption peaks due to amine, hydroxy, carbonyl, and ester functions are the only ones reported.

catalyst. The ester (0.005 *M*) was dissolved in glacial acetic acid and stirred under a hydrogen atmosphere until no further hydrogen was taken up. The catalyst was filtered and the solvent removed under vacuum. It was recrystallized from ethanol–water.

Preparation of 4,4′-diacetoxydiarylamines.—The 4-hydroxy-4 -acetoxydiarylamine was dissolved in 5 mole excess of acetic anhydride containing one equivalent of pyridine. The solution was stirred for 15 min. and the product isolated as above. These compounds are also listed in Tables III and IV.

Spectra.—Infrared absorption spectra were obtained with a Perkin-Elmer Infracord using a sodium chloride prism and potassium bromide pellets. The NMR spectra at 60 Mc. were obtained by Varian Associates using deuterochloroform as a solvent.

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Pyrolysis of Esters. XX. Pyrolysis of Cyclohexenyl Acetates[1,2]

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Pyrolysis of methyl *cis*-2-acetoxy-3-cyclohexenecarboxylate at 435° produced a mixture of methyl 2,4-cyclohexadienecarboxylate, methyl 1,3-cyclohexadienecarboxylate and methyl 1,5-cyclohexadienecarboxylate. It was shown that each of these three compounds gave this same mixture when passed through the pyrolysis tube under these indentical conditions. Reduction of this mixture of cyclohexadienecarboxylates gave 4-methylene-2-cyclohexenyl acetate, which, on pyrolysis at 450°, produced a mixture containing toluene, 3-methylenecyclohexene, and bibenzyl. The formation of the bibenzyl indicated the formation of free radicals as a competing reaction during the pyrolysis of the acetate.

As the pyrolysis of esters had been successfully employed to produce a series of isomers of aromatic compounds, such as 4,5-dimethylenecyclohexene,[5] isomeric with *o*-xylene, and 3,6-dimethylenecyclohexene,[6] isomeric with *p*-xylene, an attempt was made to extend this method of synthesis to other unusual isomers of aromatic compounds. In all the cases studied previously the shift of two hydrogen atoms is required for the aromatization of the compounds. In addition to this hydrocarbon series, many cases are described in the literature of iso-

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(1) Previous paper in this series, *J. Org. Chem.*, **26**, 3193 (1962).

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(3) Office of Naval Research Fellow, 1954–1955; Celanese Corp. Fellow, 1955–1956.

(4) Office of Naval Research Fellow, 1955–1957; Goodyear Tire and Rubber Co. Fellow, 1957–1958.

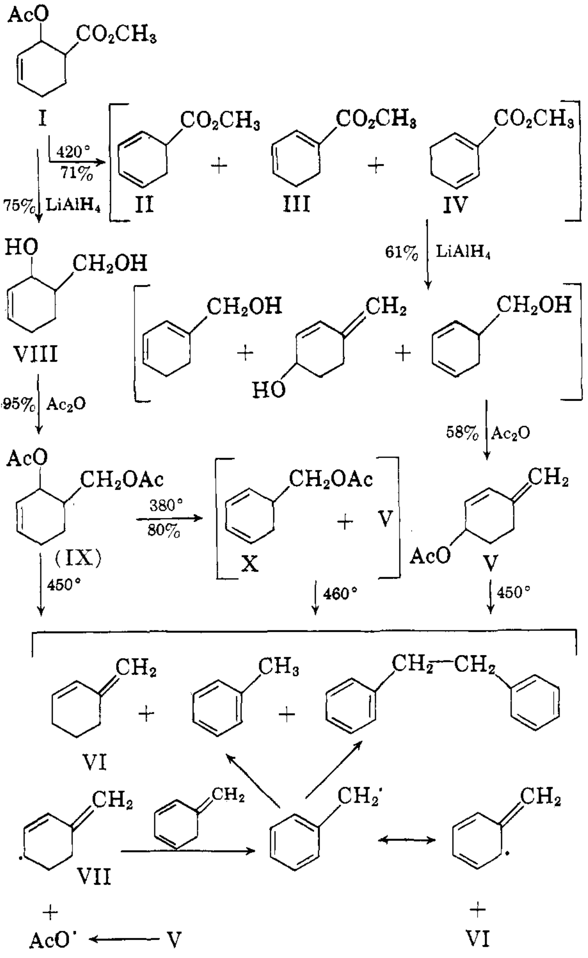
(5) W. J. Bailey and J. Rosenberg *J. Am. Chem. Soc.*, **77**, 73 (1955).

(6) W. J. Bailey and R. Barclay, Jr., *J. Am. Chem. Soc.* **81**, 5393 (1959).

mers of aromatic compounds, such as the Diels-Alder adducts of quinone,[7] isopropylidenecyclohexenone,[8] and 1-isopropenyl-1,4-cyclohexadiene,[9] which also require the shift of two hydrogen atoms to produce the aromatic derivative. It was of interest, therefore, to attempt the synthesis of an isomer of an aromatic compound in which the shift of only one hydrogen atom was required for aromatization. The simplest compound meeting this requirement is 5-methylene-1,3-cyclohexadiene.

In a previous publication[10] a convenient synthesis was reported for methyl *cis*-2-acetoxy-3-cyclohexenecarboxylate (I). This cyclohexenyl acetate I appeared to be a convenient starting material for the preparation of the methylenecyclohexadiene. For this reason, the ester I was pyrolyzed at 435° over glass helices with the liberation of 73% of the theoretical amount of acetic acid and the isolation of a 50% yield of a mixture of methyl cyclohexadienecarboxylates. Vapor phase chromatography indicated that the mixture consisted of methyl 2,4-cyclohexadienecarboxylate (II), methyl 1,3-cyclohexadienecarboxylate (III) and methyl 1,5-cyclohexadienecarboxylate (IV) in the approximate ratio of 1:6:2. The structures of these three compounds were indicated by the collection of the material corresponding to each peak, for which were obtained an analysis and an ultraviolet absorption spectrum. In addition, Diels-Alder adducts were obtained from both compounds II and III. It would appear at first glance that the elimination of acetic acid from compound I to produce the conjugated cyclohexadiene III involves a *trans* elimination. In order to determine whether a *trans* elimination or a rearrangement of the initial product of the reaction is involved, each of the isomeric cyclohexadienecarboxylates, II, III, and IV, was passed through a micropyrolysis apparatus under conditions identical with those which produced the mixture from compound I. In each case, equilibration took place and a mixture of all three of the isomeric cyclohexadienecarboxylates resulted. Thus, it appears that the three isomers are equilibrated under relatively mild conditions.

As it did not appear to make any difference whether the initial methyl 2-acetoxy-3-cyclohexene-1-carboxylate (I) was a pure isomer, a mixture of the *cis* and *trans* isomers of compound I was pyrolyzed at 420° to give a 71% yield of a mixture of the methyl cyclohexadienecarboxylates. This mixture was then reduced with lithium aluminum hydride to obtain a 61% yield of a mixture of dihydrobenzyl alcohols. As these alcohols were very difficult to separate, they were converted directly to the corresponding acetates by treatment with acetic anhydride.



From the mixture of diene acetates was isolated a 58% yield of 4-methylene-2-cyclohexenyl acetate (V), the structure of which was indicated by analysis and ultraviolet and infrared spectra. When the acetate V was dropped through the pyrolysis tube at 450°, 61% of the theoretical amount of acetic acid was liberated. From the pyrolysate was obtained a 19% yield of low-boiling hydrocarbons which was shown by ultraviolet and infrared studies to contain toluene and 3-methylenecyclohexene[11] (VI). From the high boiling residue was obtained a 16% yield of bibenzyl. In none of the fractions was there any evidence of the presence of the 5-methylene-1,3-cyclohexadiene.

The presence of the bibenzyl was rationalized by the assumption that benzyl free radicals were formed in the reaction. A possible explanation for the formation of the benzyl free radicals is that the unsaturated acetate V did indeed decompose to a large extent to the desired 5-methylene-1,3-cyclohexadiene. However, at the same time compound V dissociated at least partially into two free

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(8) A. J. Birch, *J. Proc. Roy. Soc. N.S. Wales*, **83**, 245 (1949).

(9) A. A. Petrov and N. P. Sopov, *Doklady Akad. Nauk SSSR*, **79**, 811 (1950).

(10) W. J. Bailey and R. A. Baylouny, *J. Am. Chem. Soc.*, **81**, 2126 (1959).

(11) W. J. Bailey and J. C. Goossens, *J. Am. Chem. Soc.*, **78**, 2804 (1956).

radicals—one the acetoxy free radical and the other the methylenecyclohexenyl radical (VII). The radical VII could react with the methylenecyclohexadiene to produce a resonance form of the benzyl free radical plus the 3-methylenecyclohexene (VI). The benzyl free radical could then dimerize to form the bibenzyl or abstract a hydrogen from the triene to produce the toluene.

In an effort to minimize the free radical reactions, an effort was made to find an alternative route from the methyl 2-acetoxy-3-cyclohexenecarboxylate (I) which would produce an unsaturated acetate in which the ester group was not as highly activated as the acetate group was in compound V. For this reason, compound I was reduced with lithium aluminum hydride to give a 75% yield of 2-hydroxy-3-cyclohexene-1-methanol (VIII), which was acetylated with acetic anhydride to give a 95% yield of the corresponding 2-acetoxy-3-cyclohexene-1-methyl acetate (IX). The structure of the diacetate IX was proved by dehydrogenation to a known 2-acetoxycyclohexanemethyl acetate.[11] When the diacetate IX was pyrolyzed at 450° under such conditions that one and one-half molar equivalents of acetic acid were eliminated, the products of pyrolysis were again toluene, bibenzyl, and 3-methylenecyclohexene (VI). When the diacetate IX was pyrolyzed at 380° under conditions such that only 55% of one molar equivalent of acetic acid was liberated, the yield of a mixture of diene acetates was 80%. The infrared spectrum of this mixture indicated the presence of V and 5-acetoxymethyl-1-3-cyclohexadiene (X). Pyrolysis of this mixture of diene acetates at 460° again produced the same disproportionation products.

It became evident from these pyrolytic studies that the presence of diene acetate in which the ester group was highly activated, such as in compound V, would probably always produce some free radicals and make the isolation of any methylenecyclohexadiene very difficult. The present work further emphasizes that free radicals can be produced by the pyrolysis of esters under ordinary pyrolytic conditions if the radical possesses a high degree of stability. One must therefore design esters so as to eliminate this competing reaction, in order to produce highly sensitive compounds. The use of this technique for the successful synthesis of 5-methylenecyclohexadiene is reported in a subsequent paper.[12]

EXPERIMENTAL[13]

Pyrolysis of methyl cis-2-acetoxy-3-cyclohexene-1-carboxylate (I). At the rate of fifteen drops per minute, 18.0 g. (0.09 mole) of molten methyl *cis*-2-acetoxy-3-cyclohexenecarboxylate (I), m.p. 44.2–44.6°, was dropped through a helix-packed Vycor tube at 435°. The pyrolysate was dissolved in ether and this solution was extracted with 250 ml. of distilled water. (Titration of an aliquot portion indicated the liberation of 73% of the theoretical amount of acetic acid.) Distillation of the dried pyrolysate yielded 6 g. (50%) of a mixture of methyl cyclohexadienecarboxylates, b.p. 78° (10 mm.), n_D^{25} 1.5028. The Perkin-Elmer Model 154 vapor Fractometer with the "A" column (di-*n*-decyl phthalate on Celite) heated at 148° and a helium pressure of 20 lb./sq. inch indicated the presence of three peaks with the retention times of 24.7, 39.5 and 43.0 min., corresponding to methyl 2,4-cyclohexadienecarboxylate (II), methyl 1,3-cyclohexadienecarboxylate (III), and methyl 1,5-cyclohexadienecarboxylate (IV). Their relative ratios were 1:6:2.

By use of a gas-phase chromatographic column containing ethylene glycol succinate polyester on Chromosorb a sample of methyl 2,4-cyclohexadiene-1-carboxylate (II) representing the first peak was collected.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.52; H, 7.29. Found: C, 69.49; H, 7.55.

A solution of II in isooctane (1.68 × 10^{-4} mole/l.) had an ϵ_{max} of 4650 at 256–257 mμ.

A mixture of 40 mg. of compound II, 27 mg. of maleic anhydride, and 10 ml. of dry benzene was heated under reflux for 4 hr. After the benzene was removed by distillation, the residue was recrystallized from ethyl acetate to yield 11 mg. (16%) of 7-carbomethoxy-5-bicyclo[2.2.2]octene-2,3-dicarboxylic anhydride, m.p. 118–122°.

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 60.98; H, 5.22.

Collection of the material corresponding to the second peak gave a sample of methyl 1,3-cyclohexadiene-1-carboxylate (III).

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.52; H, 7.29. Found: C, 69.28; H, 7.08.

A solution of III in isooctane (4.95 × 10^{-3} mole/l.) had an ϵ_{max} of 12,000 at 287–288 mμ.

A mixture of 210 mg. of III and 135 mg. of maleic anhydride was allowed to react in the same manner described for compound II to yield 51 mg. (15%) of a 1-carbomethoxy-5-bicyclo[2.2.2]octene-2,3-dicarboxylic anhydride, m.p. 124–125°.

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.28; H, 5.16.

A mixture of 0.3 g. (0.002 mole) of III and 0.3 g. of potassium hydroxide in 5 ml. of water was heated on a steam bath for about 1 hr. The cooled solution was neutralized with a 10% solution of sulfuric acid and the resulting mixture was extracted with ether. After evaporation of the ether from the combined extracts, the residue was dissolved in chloroform. To this chloroform solution was added dropwise a solution of bromine in chloroform until a permanent color appeared. Evaporation of the chloroform produced a semisolid which was recrystallized from dilute ethanol to yield 0.16 g. (28%) of a dibromide of 1,3-cyclohexadiene-1-carboxylic acid, m.p. 167–169° (reported[14] m.p. 166–167°).

Collection of the material corresponding to the third peak gave methyl 1,5-cyclohexadiene-1-carboxylate (IV).

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.52; H, 7.29. Found: C, 69.37; H, 7.31.

A solution of IV in isooctane (1.37 × 10^{-4} mole/l.) had an ϵ_{max} of 2780 at 274–279 mμ.

Isomerization of methyl cyclohexadienecarboxylates. Each of the pure methyl cyclohexadienecarboxylates, II, III, and IV, was isomerized by passage through a helix-packed micropyrolysis tube at 420°. This isomerization took place when

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[12] W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, in press.

[13] The authors are grateful to Dr. Mary H. Aldridge, Mrs. Kathryn Baylouny, Mrs. Jane Ratka, and Dr. Franz Kasler for the microanalyses and to Dr. Ellis R. Lippincott and Dr. Joseph Wenograd for their assistance in the interpretation of the infrared spectra. The infrared spectra were determined with a Beckman IR-4 infrared spectrometer on the pure liquids. The ultraviolet absorption spectra were determined on a Beckman DK-1 spectrophotometer.

[14] W. Langenbeck, O. Godde, L. Weschky, and R. Schaller, *Ber.*, **75B**, 232 (1942).

the packing in the pyrolysis tube was acid-washed glass helices, Vycor chips, quartz chips, or Nichrome (gauge 28) helices. These different materials produced small variations in the ratios of the isomers but the over-all results were qualitatively the same. To show that this isomerization occurs also with the pyrolysis of methyl *cis*-2-acetoxy-3-cyclohexene-1-carboxylate, this compound was pyrolyzed in the micropyrolysis tube at 420°. The ratio of the areas of the peaks obtained in this way was similar to that obtained by a large scale pyrolysis.

Methyl cyclohexadiene-1-carboxylates. Through the pyrolysis tube at 420° was dropped 210 g. (1.06 moles) of a mixture of methyl *cis*- and *trans*-2-acetoxy-3-cyclohexenecarboxylates over a period of 4.25 hr. A solution of the pyrolysate in 300 ml. of ether was extracted with a solution of 70 g. of potassium carbonate in 250 ml. of water and then with water. After the combined aqueous layers were extracted once with ether, this second ether extract was washed once with water and then added to the original ether solution. The resulting solution, to which had been added a small amount of *N*-phenyl-2-naphthylamine, was dried over magnesium sulfate. After the ether was removed by distillation through a 16-in., helix-packed column at atmospheric pressure, the residue was fractionally distilled through the same column to yield 104 g. (71%) of a mixture of methyl cyclohexadiene-1-carboxylates, b.p. 52.5–53° (2.5 mm.), n^{25}_{D} 1.5048.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 70.20; H, 7.23.

The ultraviolet spectrum of this mixture of dienes was determined in cyclohexane solution (0.0151 g./l.), ϵ_{max} 6310 at 287 mμ, with end absorption, ϵ 2280 at 215 mμ.

4-Methylene-2-cyclohexenyl acetate (V). In a 1-l., three-necked flask, equipped with a stirrer, a condenser, and a dropping funnel, were placed 11 g. (0.30 mole) of lithium aluminum hydride and 150 ml. of anhydrous ether. To this solution, heated under reflux, was added, over a period of 2 hr., a solution of 56 g. (0.41 mole) of a mixture of methyl cyclohexadienecarboxylates in 150 ml. of ether. After the solution had been heated under reflux for an additional 50 min., the excess lithium aluminum hydride was destroyed by the cautious addition of 100 ml. of water. When a solution of 30 g. of sodium hydroxide flakes in 1.6 l. of water was then added, most of the aluminum hydroxide remained undissolved. The aqueous solution was filtered and the filtrate was extracted with two 250-ml. portions of ether. The combined organic layers were dried over magnesium sulfate, and 0.25 g. of *N*-phenyl-2-naphthylamine was added. After the ether was removed by distillation through a 6-in., helix-packed column at atmospheric pressure, the residue was fractionally distilled through the same column to yield 27.1 g. (61%) of an impure mixture of dihydrobenzyl alcohols, b.p. 59–75° (2.5–3.0 mm.), n^{25}_{D} 1.5141.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.32; H, 9.05.

The ultraviolet spectrum of the analyzed sample showed an ϵ_{max} 4910 at 262 mμ (0.0204 g./l. in cyclohexane). A fraction of lower boiling point [62–65° (2.5–2.9 mm.)] showed a second maximum near 227.5 mμ.

In a 1-l. flask equipped with a reflux condenser were placed 134 g. (1.22 moles) of the mixture of dihydrobenzyl alcohols, 249 g. (2.4 moles) of acetic anhydride and 10 ml. of acetic acid. After the solution had been heated under reflux for 12 hr., the acetic acid and acetic anhydride were removed by distillation through a 12-in. Vigreux column under reduced pressure, and the residue was fractionally distilled through the same column to yield, in three fractions, 133 g. (72%) of a mixture of acetates, b.p. 55–78° (2.9 mm.). The middle fraction (107 g., 58%) was shown to be 4-methylene-2-cyclohexenyl acetate (V), b.p. 65–66° (3.9 mm.), n^{25}_{D} 1.4840.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.30; H, 7.89.

The ultraviolet spectrum of 4-methylene-2-cyclohexenyl acetate (V) was determined in cyclohexane solution (0.0163 g./l.): ϵ_{max} 11,400 at 230 mμ.

The infrared spectrum, determined in carbon disulfide solution, showed strong bands at 2844, 1360, 1232, 1031, and 891 cm.$^{-1}$; medium bands at 1177, 981, and 947 cm.$^{-1}$; and weak bands at 1717, 1138, 1080, 962, 920, 859, 795, and 777 cm.$^{-1}$

Pyrolysis of 4-methylene-2-cyclohexenyl acetate (V). Through the pyrolysis tube heated at 450–455° was dropped 28.7 g. (0.189 mole) of 4-methylene-2-cyclohexenyl acetate (V) over a period of 49 min. The pyrolysate was dissolved in ether, and the solution was washed several times with water. (Titration of aliquots of the aqueous extracts showed that 61% of the theoretical amount of acetic acid had been liberated.) After the solution had been dried over magnesium sulfate, the ether was removed by distillation through a 6-in., helix-packed column at atmospheric pressure. The residue was fractionally distilled through the same column to yield the following fractions: (1) 3.3 g. (19%) of low-boiling hydrocarbons, b.p. 42.5–45° (69 mm.), n^{25}_{D} 1.4857; (2) 5.1 g. (18%) of acetates, b.p. 51–61° (1.0–1.2 mm.), n^{25}_{D} 1.4914; and (3) 3.4 g. (20%) of high-boiling hydrocarbons, b.p. 92.5–93.5° (1.1 mm.), n^{25}_{D} 1.5511.

The ultraviolet spectrum of the low-boiling fraction, determined in cyclohexane solution, showed the following maxima: ϵ_{max} 505–586 at 268.5 mμ; ϵ_{max} 533–615 at 265 mμ; ϵ_{max} 592–716 at 262 mμ; ϵ_{max} 4970–6390 at 232.5 mμ. These bands would be expected in a mixture of toluene[15] and 3-methylenecyclohexene (VI).[11]

The infrared spectrum, determined in carbon disulfide solution, gave strong bands at 878, 728, and 693 cm.$^{-1}$ and weak bands at 1237, 1173, 1076, 1028, 989, 976, 959, 946, 908, and 768 cm.$^{-1}$. With two exceptions (1237 and 946 cm.$^{-1}$) all of these bands are present in the reported spectrum of toluene[16] or of 3-methylenecyclohexene.[11]

On the basis of the ultraviolet absorption data, the content of 3-methylenecyclohexene was estimated to be 25 to 30%. The toluene content was higher but could not be estimated accurately because of the strong background absorption. Several attempts to prepare adducts with maleic anhydride were unsuccessful.

The ultraviolet spectrum of the acetate fraction determined in cyclohexane solution (0.160 g./l.) showed several bands of low intensity: ϵ_{max} 263 (inflection) at 267.5 mμ; ϵ_{max} 388 at 263.5 mμ; ϵ_{max} 551 at 257 mμ; ϵ_{max} 646 at 251 mμ. No specific absorption was observed in the 230 mμ region.

The high boiling fraction solidified when it has cooled to 5°. Two recrystallizations of the solid from petroleum ether (b.p. 30–60°) yielded pure bibenzyl, m.p. 52–53° (reported[17] m.p. 52.5–53°), which was not depressed by admixture with an authentic sample. The infrared spectrum of the original fraction (in carbon disulfide solution) was essentially identical to that of bibenzyl, except that foreign bands were observed at 1717, 1685, and 1216 cm.$^{-1}$ (The bands at 1717 and 1216 cm.$^{-1}$ were very probably due to the presence of acetates in this fraction.) The intensity of absorption at 1943 and 1868 cm.$^{-1}$ indicated that the bibenzyl content was about 80%.

2-Hydroxy-3-cyclohexene-1-methanol (VIII). In a 5-l., three-necked flask, equipped with a stirrer, a condenser and a dropping funnel, were placed 57 g. (1.5 moles) of lithium aluminum hydride and 1500 ml. of anhydrous ether. To the solution, heated under reflux, was added, over a period of 11 hr., a solution of 198 g. (1.00 mole) of methyl 2-acetoxy-3-cyclohexenecarboxylate (I) in 500 ml. of ether. After the solution had been heated under reflux for an additional 10 hr., the excess lithium aluminum hydride was destroyed by the dropwise addition of 100 ml. of water, and the complexes were decomposed by the addition of 220 ml. of a saturated

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(15) T. W. Campbell, S. Linden, S. Godshalk, and W. G. Young, *J. Am. Chem. Soc.*, **69**, 880 (1947).

(16) J. Turkevich, H. A. McKenzie, L. Friedman, and R. Spurr, *J. Am. Chem. Soc.*, **71**, 4045 (1949).

(17) H. A. Smith, D. M. Alderman, Jr., C. D. Shacklett, and C. M. Welch, *J. Am. Chem. Soc.*, **71**, 3772 (1949).

aqueous solution of potassium sodium tartrate. The slurry was stirred for 2.25 hr., and the precipitate was removed by filtration and washed several times with ether. After the combined ether solutions were dried over magnesium sulfate, the ether and by-product alcohols were removed by distillation through a 12-in. Vigreux column. The residue was fractionally distilled through the same column to yield 96.3 g. (75%) of 2-hydroxy-3-cyclohexene-1-methanol (VIII), b.p. 117° (2.6 mm.), n^{25}_{D} 1.5081.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.32; H, 9.34.

2-Acetoxy-3-cyclohexene-1-methyl acetate (IX). To a 2-l., three-necked flask, fitted with a dropping funnel and a condenser and containing 605 ml. (6.4 moles) of hot acetic anhydride, was added a solution of 204 g. (1.59 moles) of 2-hydroxy-3-cyclohexene-1-methanol (VIII) in 92 ml. (1.6 moles) of glacial acetic acid over a period of 1 hr. After the solution had been heated under reflux for 16 hr., the acetic acid and acetic anhydride were removed by distillation through a 12-in., helix-packed column under reduced pressure. The residue was fractionally distilled through the same column to yield 321 g. (95%) of 2-acetoxy-3-cyclohexene-1-methyl acetate (IX), b.p. 124° (3.4–3.5 mm.), n^{25}_{D} 1.4612.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.59. Found: C, 62.46; H, 7.48.

Pyrolysis of 2-acetoxy-3-cyclohexene-1-methyl acetate (IX). Preliminary pyrolysis of 2-acetoxy-3-cyclohexene-1-methyl acetate (IX) at 450° indicated that 1.5 molar equivalents of acetic acid had been eliminated and the pyrolysate contained a mixture of toluene, 3-methylenecyclohexene (VI) and bibenzyl. For this reason, 149 g. (0.702 mole) of IX was dropped through the pyrolysis tube at 378–383° over a period of 5.5 hr. and a solution of the pyrolysate in 350 ml. of ether was washed with a solution of 35 g. of sodium carbonate monohydrate in 175 ml. of water. (In a parallel run, when the pyrolysate solution was extracted exhaustively with water, titration of aliquots of the aqueous washings showed that 55% of one molar equivalent of acetic acid had been liberated.) After the ether extracts were dried over magnesium sulfate, the solvent was removed at atmospheric pressure through a 12-in. Vigreux column. The residue was fractionally distilled through the same column to yield 46.0 g. (43%) of a mixture of diene acetates, b.p. 72–74° (5.6–4.2 mm.), n^{25}_{D} 1.4809, and 68.7 g. (46% recovery) of unsaturated diacetates, b.p. 118–124° (4.0 mm.), n^{25}_{D} 1.4641. The yield of diene acetates, based on unrecovered starting material, was therefore 80%.

Refractionation of the mixture of diene acetates through an 18-in., Podbielniak-type column afforded only a partial separation. As the index of refraction of the fractions passed through a minimum, at least three components were present. Elemental analysis showed the presence of a nonisomeric impurity. The ultraviolet spectra of all fractions showed absorption in the vicinity of 260 mμ; a second maximum near 230 mμ appeared only in the lower boiling fractions. A fraction, b.p. 64.5° (3.6–3.7 mm.), n^{25}_{D} 1.4790; ϵ_{max} 4260 at 257.5 mμ; ϵ_{max} 4720 at 232.5 mμ, was subjected to infrared analysis. The spectrum was qualitatively similar to that of 4-methylene-2-cyclohexenyl acetate (V), but the intensity of the band at 891 cm.$^{-1}$ was substantially diminished.

Further pyrolysis of this mixture of diene acetates at 460–465° yielded toluene, 3-methylenecyclohexene (VI), and bibenzyl.

In a small Erlenmeyer flask fitted with a reflux condenser were placed 1.23 g. (0.0125 mole) of maleic anhydride, 2.04 g. (0.0134 mole) of the mixture of diene acetates described above, 6 ml. of dry benzene, and a small amount of hydroquinone. After the solution was heated on a steam bath for 13.5 hr., the solvent was removed by evaporation in a current of air, and the residue was dissolved in a mixture of toluene and petroleum ether. The solution was chilled in a Dry Ice–Methyl Cellosolve bath, and the very viscous material which separated was discarded. The supernatant liquid was decanted and was freed of solvents by evaporation. The resulting residue was dissolved in ether and chilled in the Dry Ice–Methyl Cellosolve bath to yield, after recrystallization from a mixture of ether and acetone, 0.22 g. (7%) of a crystalline adduct, m.p. 122.5–124°.

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.58; H, 5.71.

The infrared spectrum (in carbon disulfide) included strong bands at 1780, 1739, 1218, 946, and 909 cm.$^{-1}$ and weak bands at 1080 and 786 cm.$^{-1}$.

Vulgarin, a Sesquiterpene Lactone from *Artemisia vulgaris* L.

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Vulgarin, a sesquiterpenoid lactone from *Artemisia vulgaris* L., has been shown to have the structure III.

In the course of the examination of various genera of the Compositae for alkaloids, a crystalline compound was isolated from an Australian specimen of *Artemisia vulgaris* L.[1] This substance, now called vulgarin, was nonnitrogenous and gave an intense purple coloration in the hydroxamic acid test. This behavior, coupled with its composition, expressed in the formula $C_{15}H_{20}O_4$, suggested that it was a sesquiterpenoid lactone and a new member of the group of these substances in which the genus *Artemisia* abounds. The recent description[2] of a compound called tauremisin-A, from *Artemisia taurica*, leads us to believe that vulgarin and tauremisin-A are the same compound (m.p., rotation, spectral properties), but Rybalko *et al.* have not recorded sufficient additional information to confirm this identity.

Vulgarin, obtained from the dry plant in 0.15% yield, has m.p. 174–175°, $[\alpha]^{27}_{5461}$ + 48.7°, and strong infrared absorption at 3520 (hydroxyl), 1775 (γ-lactone), and 1665 cm.$^{-1}$ The ultraviolet

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(1) The compound was first obtained as a crystalline material by Dr. C. C. J. Culvenor, C.S.I.R.O., Melbourne, to whom we are grateful for calling it to our attention and for providing additional plant material for our study.

(2) K. S. Rybalko, A. I. Ban'kovskii, and M. E. Perel'son, *Med. Prom. U.S.S.R.*, **14**, No. 10, 21 (1960).