Some Geometrical Isomers of the 3,4-Dimethyl-5-aryl-2,4-pentadienoic Acids. The Formation of 3-Methylene Structures

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The dehydration of the 3-hydroxy-3,4-dimethyl-5-arylpentenoic acid esters (II) gives not only the 2-*trans*- and 2-*cis*-3,4-dimethyl-5-arylpentadienoic acid isomers (IV and V, respectively) but also appreciable quantities of the nonconjugated 3-methylene-4-methyl-5-phenyl-4-*trans*-pentenoic acids (VI). The n.m.r. data for the dehydration mixture indicate that the structures are formed in the ratio of 7 IV:1 V:7 VI for the phenyl isomers; 70:15:15 for the *p*-tolyl isomers. The low yield of 2-*cis* isomer (V) is attributed to steric interaction between the phenylpropenyl and carbomethoxy groups in the hydroxy ester (VII–VIII) which favors the staggered conformation (VIII), over the skew conformation (VII), to give the 2-*trans* (IV) and 3-methylene (VI) structures preferentially.

As part of a study of the geometrical isomerism of isoprenoid-like carboxylic acids, series of methyl- and phenyl-substituted 5-phenyl-2-penten-4-ynoic[1] and 2,3-dimethyl-5-aryl-2,4-pentadienoic acids[2] have been examined. These have been extended to studies of the synthesis and nuclear magnetic resonance characteristics of some of the geometrical isomers of four 3,4-dimethyl-5-aryl-2,4-pentadienoic acids which are described in this paper.

The Reformatskiĭ reaction of 3-methyl-4-aryl-3-buten-2-one (from the appropriately substituted aldehyde and methyl ethyl ketone) and methyl bromoacetate was used to prepare an intermediate hydroxy ester (II) which was easily dehydrated with *p*-toluenesulfonic acid to give a 63–83% yield of mixtures (III) of the 2-*cis* and *trans* unsaturated esters of 3,4-dimethyl-5-aryl-2,4-pentadienoic acid (IV and V), and 3-methylene-4-methyl-5-aryl-4-pentenoic acids (VI). Alkaline saponification of the mixed esters gave the 2-*trans*-4-*trans* unsaturated acid (IV) as an insoluble, easily separable, crystalline potassium salt. The liquors from the potassium salt of the 2-*trans*-4-*trans* acid gave, in every case, a small quantity of an isomeric 3-methylene-4-methyl-5-aryl-4-*trans* pentenoic acid (VI), and in two cases (R = H, and R = CH_3) a small quantity of the isomeric 2-*cis*-4-*trans* acid V.

A 2-*trans*-4-*trans* configuration was assigned to the acids (IV) obtained by acidification of the insoluble potassium salt on the basis of their n.m.r. and ultraviolet spectral properties. N.m.r. absorption for the C-3 methyl protons of these acids occurred at 7.55–7.63 τ, and their methyl esters showed absorption at 7.60–7.68 τ. These values are well within the range previously observed for a methyl group *cis* to carboxyl or carbomethoxy[3-5] and provide unequivocal evidence for the 2-*trans* configuration. The starting ketone (I) has been shown by chemical evidence[6,7] to be *trans* at the bond adjacent to the benzene ring. The 2-*cis*-4-*trans*-6-*trans* and 2-*trans*-4-*trans*-6-*trans* isomers of methyl 3,6-dimethyl-7-phenylheptatrienoate[5] show n.m.r. absorption at 7.95–7.98 τ for a methyl group (C-6) *cis* to the benzene ring (*trans* configuration) and the dicarboxylic acid and the ketone from which these acids (or methyl esters) were prepared show absorption at 8.00–8.02 τ for a methyl group in the same magnetic environment. Thus, absorption at 7.97–8.05 τ for the C-4 methyl protons (*cis* to phenyl) of the isomeric 3,4-dimethyl-5-aryl-pentadienoic acids (IV and V) and the 3-methylene-5-aryl-4-pentenoic acids (VI) establishes the 4-*trans* configuration for these acids. Ultraviolet absorption at 291–299 mμ (methanol) for the methyl esters of the 2-*trans*-4-*trans* acids (IV) is consistent with a sterically hindered (C-4 methyl group and *ortho* hydrogens of benzene ring), but nearly linear, structure. Three of the 2-*trans*-4-*trans* acids (IVB, C, and D) show an anisotropic liquid phase upon melting. Such behavior has been observed only in linear molecules.[8,9]

The 3-methylene acids (VI) recovered from the liquors of the potassium salt of the 2-*trans*-4-*trans* acids (IV) showed saturated carbonyl absorption in the infrared at 1706–1709 and absorption at 896–902 cm.$^{-1}$ attributed to the terminal methylene group.[10] An n.m.r. spectrum showed the characteristic absorption at 4.64–4.73 and 4.85–4.93 τ of the 3-methylene group. Methyl proton absorption (C-4) at 7.98–8.04 τ indicates a 4-*trans* configuration for these acids. The similarity of ultraviolet absorption of *trans*-2-methyl-1-phenylbutadiene [$\lambda_{\max}^{CH_3OH}$ 269 mμ (ϵ 19,400)], prepared from *trans*-α-methylcinnamaldehyde,[11] with that of 3-methylene-4-methyl-5-phenyl-4-pentenoic acid [VIA, $\lambda_{\max}^{CH_3OH}$ 267 mμ (ϵ 20,600)] confirms a 4-*trans* configuration for the 3-methylene acids.

Two additional isomeric acids recovered from the liquors of the potassium salts of the 5-phenyl (IVA) and 5-*p*-tolyl (IVB) acids have n.m.r. characteristics consistent with the 2-*cis*-4-*trans* structure (V). These acids show two sets of methyl group proton absorption maxima at 7.97 and 8.02–8.05 τ attributable to C-3 and C-4 methyl protons. Definite assignment of either of these two sets to the C-3 or to the C-4 methyl groups can not be made, but both sets agree well with the value of 8.00 τ reported[4] for the C-3 methyl protons of methyl 3-methyl-5-phenyl-2-*cis*-4-*trans*-pentadienoate. Examination of a model of the 2-*cis*-4-*trans* configuration (V) shows severe steric hindrance between the 4-methyl group and the carboxyl group, resulting in a

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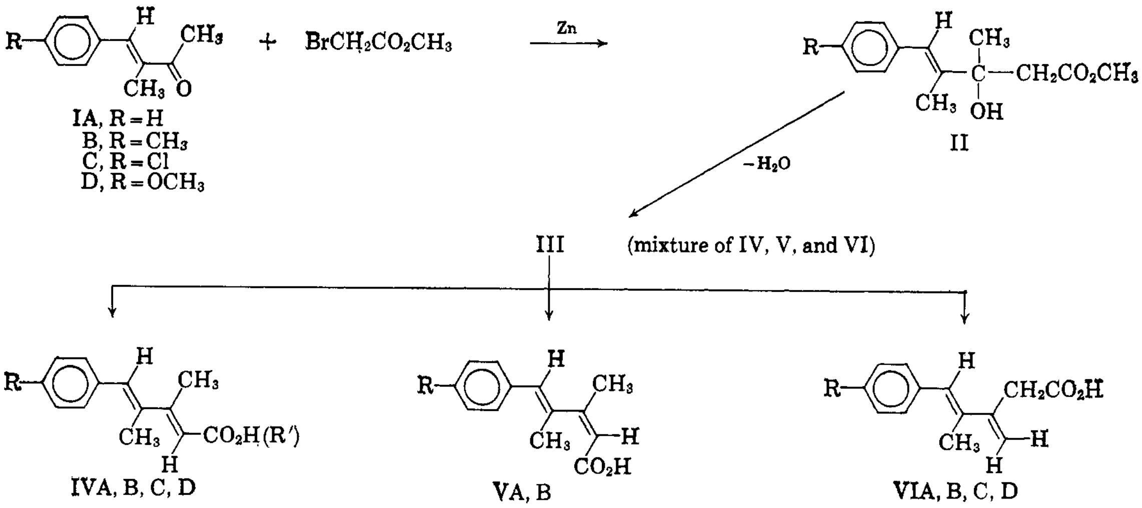
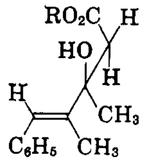
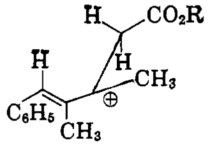
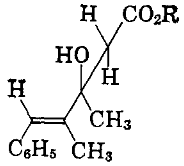




VII



IX



VIII

nonplanar structure with a *cis*-propenylbenzene unit as the effective chromophore. The ultraviolet absorption for the 3,4-dimethyl acid [VA, λ_{max} 246 mμ (ϵ 12,800)] is in good agreement with that of *cis*-propenylbenzene chromophore [λ_{max} 241 mμ (ϵ 13,800[12])] required for the hindered 2-*cis*-4-*trans* configuration.

With information available on the n.m.r. absorption characteristics of the three isomeric products formed on dehydration of the Reformatskiĭ product (III), it is possible to determine the relative yields of the competing elimination reactions. This is done conveniently by observing the relative heights of characteristic peaks, or increments of heights, for each isomer in the crude mixture of the three esters (IV, V, and VI) obtained on dehydration of II. The n.m.r. spectrum of the distilled, but not fractionated, unsaturated ester IIIA, obtained from the *p*-toluenesulfonic acid dehydration of hydroxy ester IIA showed that a mixture of the esters of IVA, VA, and VIA was present. Thus, absorption at 4.70–4.87 τ, attributable to the methylene protons (=CH₂) of the terminal methylene isomer VIA, showed that 35% of this isomer was present in the dehydration product. Absorption at 7.60 τ (C-3 methyl protons *cis* to carbomethoxy) corresponded to 35% of the 2-*trans*-4-*trans* isomer. The amount of the 2-*cis*-4-*trans* isomer is estimated to be about 5% on the basis of the added increment in the peak at 8.04 τ. To obtain this value increments appropriate to the 35% of 2-*trans*-isomer (C-4 methyl absorbs at 8.02 τ); 35% of the methylene isomer (C-4 methyl absorbs at 8.01 τ); and 25% of the starting ketone I (C-3 methyl absorbs at 8.02 τ), estimated to be present from the clearly resolved acetyl methyl absorption band at 7.70 τ, were summed. The starting ketone has been carried along into these fractions in attempts to avoid distorting the observation of relative amounts of *cis*, *trans*, and methylene isomers by fractionation. Similar evidence for the ketone-free crude fractions of ester IIIB showed that 15–20% of the terminal methylene ester or VIB was present along with 15–20% of the 2-*cis*-4-*trans* ester of VB and 70% of IVB. This spectral evidence indicates that the three isomers—terminal methylene (VI), 2-*trans*-4-*trans* (IV), and 2-*cis*-4-*trans* (V)—result directly from dehydration of hydroxy ester IIA, and are probably not artifacts from alkaline equilibration of either conjugated ester IVA or VA during the saponification reaction or during isolation. Additional data on the thermal and catalytic interconversion of the isomers is desirable for final evaluation of this point.

These data are consistent with either an E2 or E1 mechanism for the dehydration reaction. In an E2 process the formation of the 2-*cis* isomer by *trans* elimination requires the formation of the skew conformation VII; the 2-*trans* isomer requires the staggered conformation VIII; and the methylene isomer VI can be formed from either VII or VIII. The low yields of 2-*cis* isomers suggests that conformation VII with the skew phenylpropenyl and carbethoxy groups involves more steric interaction than is present in conformation VIII with these groups staggered. The conformation VIII is, therefore, presumably the more stable at equilibrium. Both D and L forms present the same conformational requirements for formation of *cis* and *trans* isomers; *i.e.*, to form the cis isomer from the D and L form, the skew conformation of phenylpropenyl and carbethoxy is required. A similar conformation in the carbonium ion (IX), required as an E1 intermediate, leads to formation of the 2-*trans* isomer and is presumably least hindered.

Experimental

All n.m.r. measurements were made with a Varian Associates HR-4302 high resolution spectrometer with a 60-Mc. oscillator with stabilizer and field homogeneity control. The calibrations were made by the side-band technique at several frequencies. Tetramethylsilane was used as an internal reference standard and the chemical shifts are reported as τ-values.[13] Samples were ex-

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(12) R. Y. Mixer, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

(13) G. V. D. Tier, *J. Phys. Chem.*, **62**, 1151 (1958).

amined in 10–15% concentration with carbon tetrachloride or deuteriochloroform as solvent. Ultraviolet absorption measurements were made with a Beckman DK-2 recording spectrometer in the solvents (Spectro Grade) stated. Infrared absorption measurements were made with a Baird double beam recording spectrometer with sodium chloride optics in chloroform (5% solutions) or as potassium bromide pellets. Melting points are uncorrected.

3-Methyl-4-phenyl-3-buten-2-one (IA).—This ketone [b.p. 87–88° (0.40 mm.), m.p. 36–36.5°] was prepared in 65% yield according to the procedure described previously by Harries and Müller.[14]

Methyl 3,4-Dimethyl-3-hydroxy-5-phenyl-4-pentenoate (IIA).—A solution of 8.0 g. (0.050 mole) of 3-methyl-4-phenyl-3-buten-2-one and 9.18 g. (0.060 mole) of methyl bromoacetate in 50 ml. of dry benzene was added to 4.00 g. (0.062 mole) of dry, acid-etched zinc at a rate sufficient to keep the benzene gently refluxing. When the addition was completed the reaction mixture was refluxed for 10 min., cooled, diluted with 50 ml. of ether, decomposed with 6 ml. of glacial acetic acid in 100 ml. of water, and washed successively with water, saturated bicarbonate solution, and water. The organic phase was dried over anhydrous magnesium sulfate, and the reaction product was distilled *in vacuo* to yield 10.2 g. (87%) of hydroxy ester, b.p. 107–111° (0.07–1.18 mm.), n^{25}D 1.5326–1.5339. Redistillation of a portion of this material gave a colorless analytical sample, b.p. 105° (0.07 mm.), n^{25}D 1.5330. An infrared spectrum showed bands at 3500 (OH), 1721 (saturated C═O), and 1171 cm.$^{-1}$ (C–O–).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.58; H, 7.71.

Methyl 3,4-Dimethyl-5-phenyl-2,4-pentadienoate (IIIA).—A solution of 15.1 g. (0.065 mole) of the hydroxy ester IIA in 125 ml. of benzene was refluxed for 30 min. with 0.50 g. of *p*-toluenesulfonic acid in a 250-ml. round-bottomed flask fitted with a water trap. When the theoretical volume of water had been collected (1.17 ml.), the reaction mixture was cooled, diluted with 50 ml. of ether, washed successively with bicarbonate solution and water, and dried over anhydrous magnesium sulfate. After the solvent was removed the residual oil was distilled *in vacuo* to yield 12.2 g. (87%) of the unsaturated ester, b.p. 85–137° (0.10–0.60 mm.), n^{24}D 1.5709–1.5770. Redistillation of a portion of this material gave a colorless analytical sample, b.p. 107–109° (0.20 mm.), n^{24}D 1.5785.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.34; H, 7.70.

3,4-Dimethyl-5-phenyl-2-*trans*-4-*trans*-pentadienoic Acid (IVA).—The unsaturated ester IIIA (10.2 g., 0.047 mole) was refluxed for 2.5 hr. with a solution of 4.00 g. (0.071 mole) of potassium hydroxide in 40 ml. of methanol. Concentration of the saponification mixture to 25 ml. precipitated a crystalline potassium salt which was collected, washed with several small volumes of ether, and air-dried to yield 4.35 g. Acidification of the potassium salt gave 3.55 g. (38%) of the acid, m.p. 126.5–128°. Recrystallization from hexane (EK-P1135) gave the analytical sample as colorless plates, m.p. 127.5–128°. An infrared spectrum (in KBr) showed significant bands at 1664 (α,β-unsaturated C═O), 1603 (phenyl group), 1267 and 1203 (C–O–), 882 (trisubstituted ethylene), 848 (unassigned), 714 (unassigned), and 753 and 695 cm.$^{-1}$ (monosubstituted phenyl group). Ultraviolet absorption: $\lambda_{\max}^{0.003\ NH+CH_3OH}$ 289 mμ (ε 22,500). N.m.r. absorption (in $CDCl_3$): 2.81 (C-5 Ar-H), 3.15 (C-5 H), 7.97 (C-4 CH_3), 7.55 (C-3 methyl protons *cis* to carboxyl), and 4.03 τ (C-2 H).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.12; H, 6.95.

Methyl 3,4-Dimethyl-5-phenyl-2-*trans*-4-*trans*-pentadienoate (IVA, R = CH_3).—The neutral ether washings from a previous saponification mixture gave a small quantity (3.0 g.) of an oily, solid ester, m.p. 41–54°. One recrystallization of this material from 50 ml. of petroleum ether (b.p. 30–60°) at −20° gave 1.85 g., m.p. 64–66°. The analytical sample was obtained after additional recrystallization as colorless needles, m.p. 66–67°. This product showed no melting point depression when mixed with the methyl ester (m.p. 66–67°) prepared by diazomethane esterification of the pure 2-*trans*-4-*trans* acid. An infrared spectrum showed bands at 1704 (α,β-unsaturated (C═O), 1610 (phenyl group), 1257 and 1167 (C–O–), and 855 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{\max}^{CH_3OH}$ 291 (ε 22,400), 224–225 mμ (ε 8,800). N.m.r. absorption (in $CDCl_3$): 2.85 (C-5 Ar-H), 3.18 (C-5 H), 8.02 (C-4 CH_3), 7.60 (C-3 methyl protons *cis* to carbomethoxy), and 4.12 τ (C-2 H).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.87; H, 7.64.

3,4-Dimethyl-5-phenyl-2-*cis*-4-*trans*-pentadienoic Acid (VA).—The methanolic filtrate from the potassium salt of the 2-*trans*-4-*trans* acid above was diluted with 250 ml. of water and extracted with ether. The aqueous phase was acidified, extracted with ether, and dried over anhydrous magnesium sulfate. Removal of solvent left 4.1 g. (45%) of yellow oil. The oil was dissolved in petroleum ether (b.p. 30–60°), treated with charcoal, filtered, and left to stand overnight. The petroleum ether was then decanted from an oil which had precipitated, and the decantate was cooled for 30 days at 0° when several clumps of thick needles, surrounded by a fine, cottony growth of crystals appeared. The thick needles (0.28 g.) were separated mechanically from the finer crystals, and were recrystallized three times from petroleum ether to give 0.15 g. (1.6%) of colorless needles, m.p. 94–95°. An infrared spectrum (in KBr) showed bands at 1661 (α,β-unsaturated C═O), 1621 (phenyl group and/or C═C), 1289 sh, 1264 (s), and 1212 (w) (C–O–), 868 (trisubstituted ethylene), and 735 and 696 cm.$^{-1}$ (monosubstituted phenyl group). Ultraviolet absorption: $\lambda_{\max}^{CH_3OH}$ 246 mμ (ε 12,800). N.m.r. absorption (in $CDCl_3$): 2.81 (C-5 Ar-H), 3.85 (C-5 H), 7.97 (C-3 methyl protons *trans* to carboxyl, or C-4 CH_3), 8.02 (C-3 methyl protons *trans* to carboxyl, or C-4 CH_3), and 4.39 τ (C-2 H).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.34; H, 6.91.

3-Methylene-4-methyl-5-phenyl-4-*trans*-pentenoic Acid (VIA).—Three recrystallizations from petroleum ether of the fine, cottony needles (0.63 g., m.p. 62–66°) obtained along with the 2-*cis*-4-*trans* acid VA gave 0.11 g. of fine colorless needles, m.p. 66.5–68°. An infrared spectrum (in CCl_4) showed bands at 1706 (saturated C═O), 1605 and 1493 (phenyl group), and 898 cm.$^{-1}$ terminal (methylene group). Ultraviolet absorption: $\lambda_{\max}^{CH_3OH}$ 267 mμ (ε 20,600). N.m.r. absorption (in $CDCl_3$): 2.83 (C-5 Ar-H), 3.45 (C-5 H), 7.99 (C-4 CH_3), 4.64 and 4.85 (C-3 terminal methylene group), and 6.59 τ (C-2 internal methylene group).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.36; H, 6.96.

3-Methyl-4-(*p*-tolyl)-3-buten-2-one (IB).—This ketone [b.p. 84–86° (0.20 mm.), m.p. 30°] was prepared in 64% yield from *p*-tolualdehyde and methyl ethyl ketone according to the procedure described previously by Harries and Müller[14] for 3-methyl-4-phenyl-3-buten-2-one. Infrared absorption (in $CHCl_3$): 1658 (α,β-unsaturated C═O), 1628 (C═C), 1613 (phenyl group), 1366, 1248, 1005 (1,4-disubstituted phenyl group), 887 (trisubstituted ethylene), and 814 cm.$^{-1}$ (1,4-disubstituted phenyl group). Ultraviolet absorption: $\lambda_{\max}^{CH_3OH}$ 287 (ε 21,100), 225 mμ (ε 8400). N.m.r. absorption (in $CDCl_3$): 2.77 (C-4H), 2.95 (C-5 Ar-H), 7.72 (*p*-CH_3 and C-3), and 8.04 τ (C-2 CH_3).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.48; H, 8.19.

The **oxime** was recrystallized from ethanol, m.p. 137.5–140.5°.

Anal. Calcd. for $C_{12}H_{15}NO$: N, 7.40. Found: N, 7.25.

The **2,4-dinitrophenylhydrazone** was recrystallized from chloroform–ethanol, m.p. 205–207.5°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.40.

Methyl 3,4-Dimethyl-5-(*p*-tolyl)-2,4-pentadienoate (IIIB).—An intermediate hydroxy ester was prepared by a Reformatskiĭ reaction of 3-methyl-4-(*p*-tolyl)-3-buten-2-one (17.7 g., 0.100 mole), methyl bromoacetate (18.7 g., 0.120 mole), and zinc (8.25 g., 0.130 mole) according to the procedure described previously. The crude hydroxy ester was dehydrated directly with *p*-toluenesulfonic acid (0.75 g.) in benzene (250 ml.), and the dehydration product was distilled *in vacuo* to give 19.4 g. (83%) of the unsaturated ester, b.p. 113–137° (0.16–0.40 mm.) n^{23}D 1.5807–1.5886. Redistillation of a portion of this product gave the analytical sample, b.p. 113–115° (0.03 mm.), n^{22}D 1.5885.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.40; H, 8.16.

3,4-Dimethyl-5-(*p*-tolyl)-2-*trans*-4-*trans*-pentadienoic Acid (IVB).—Refluxing the ester IIIB (16.1 g., 0.069 mole) for 4.0 hr. with a 1.5 mole excess of 5% methanolic potassium hydroxide followed by concentration of the saponification mixture precipitated 8.40 g. of crystalline potassium salt. Acidification of

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[14] C. Harries and G. H. Müller, *Ber.*, **37**, 966 (1902).

this salt gave 6.95 g. (46%) of the acid, m.p. 128–130° and 138–142°. Two recrystallizations from benzene–hexane (EK-P1135) gave the analytical sample as colorless needles, m.p. 144–146° and 151–153°. An infrared spectrum (in KBr) showed bands at 1667 (α,β-unsaturated C=O), 1597 (phenyl group), 1266, 1221, and 1201 (C–O–), 862 (trisubstituted ethylene), 815 (1,4-disubstituted phenyl group), and 721 cm.$^{-1}$ (unassigned). Ultraviolet absorption: $\lambda_{\mathrm{maa}}^{0.003\ \mathrm{N\ H^+ CH_3OH}}$ 296 (ϵ 23,200), 231–232 mμ (ϵ 8900). N.m.r. absorption (in $CDCl_3$): 2.89 (C-5 Ar-H), 3.13 (C-5 H), 7.97 (C-4 CH_3), 7.67 (C-3 methyl protons *cis* to carboxyl), 4.02 (C-2 H), and 7.56 τ (*p*-CH_3).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.14; H, 7.62.

Methyl 3,4-Dimethyl-5-(*p*-tolyl)-2-*trans*-4-*trans*-pentadienoate (IVB, R′ = CH_3).—The methyl ester was prepared from the 2-*trans*-4-*trans* acid IVB with diazomethane. One recrystallization from petroleum ether (b.p. 30–60°) at 0° gave colorless flakes, m.p. 40–41.5°. An infrared spectrum (in $CHCl_3$) showed bands at 1705 (α,β-unsaturated C=O), 1607 (phenyl group), 1257 and 1167 (C–O–), and 861 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 299 (ϵ 23,700), 231–233 mμ (ϵ 8800). N.m.r. absorption (in $CDCl_3$): 3.02 (C-5 Ar-H), 3.25 (C-5 H), 8.00 (C-4 CH_3), 7.68 (C-3 methyl protons *cis* to carbomethoxy), 4.15 (C-2 H), 6.40 (CO_2CH_3), and 7.60 τ (*p*-CH_3).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.16; H, 7.62.

3,4-Dimethyl-5-(*p*-tolyl)-2-*cis*-4-*trans*-pentadienoic Acid (VB).—Treatment of the methanolic filtrate from the potassium salt of the 2-*trans*-4-*trans* isomer according to the procedure described previously for 3,4-dimethyl-5-phenyl-2-*cis*-4-*trans*-pentadienoic acid gave 5.1 g. (34%) of crude, yellow-orange acid. Fractional crystallization of this crude product from hexane (EK-P1135) gave fine, colorless plates, m.p. 109–110°. An infrared spectrum (in KBr) showed bands at 1671 (α,β-unsaturated C=O), 1620 (phenyl group and/or C=C), 1305, 1269 and 1208 (C–O–), 881 and 871 (trisubstituted ethylene), and 717 cm.$^{-1}$ (unassigned). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 254–256 mμ (ϵ 14,000). N.m.r. absorption (in $CDCl_3$): 3.05 (C-5 Ar-H), 3.94 (C-5 H), 7.97 (C-4 methyl protons, or C-3 methyl protons *trans* to carboxyl), 8.05 (C-4 methyl protons, or C-3 methyl protons *trans* to carboxyl), 4.46 (C-2), and 7.70 τ (*p*-CH_3).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.75; H, 7.59.

3-Methylene-4-methyl-5-(*p*-tolyl)-4-*trans*-pentenoic Acid (VIB).—In addition to the 2-*cis*-4-*trans* acid VB, fractional crystallization of the crude acid from hexane (EK-P1135) gave a second isomeric acid as colorless rhomboidal plates, m.p. 92–93.5°. An infrared spectrum (in CCl_4) showed bands at 1709 (saturated C=O), 1605 (phenyl group), and 896 cm.$^{-1}$ (terminal methylene group). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 272 mμ (ϵ 22,900). N.m.r. absorption (in $CDCl_3$): 3.03 (C-5 Ar-H), 3.48 (C-5 H), 8.03 (C-4 CH_3), 4.72 and 4.91 (C-3 terminal methylene protons), 6.67 (C-2 internal methylene protons), and 7.71 τ (*p*-CH_3).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.87; H, 7.63.

3-Methyl-4-(*p*-chlorophenyl)-3-buten-2-one (IC).—This ketone (m.p. 48.5–50°, from petroleum ether) was prepared in 74% yield from *p*-chlorobenzaldehyde and methyl ethyl ketone according to the procedure described previously[14] for 3-methyl-4-phenyl-3-buten-2-one. Infrared absorption (in $CHCl_3$): 1656 (α,β-unsaturated C=O), 1623 (C=C), 1595 (phenyl group), 1366, 1244, 1093, 1005, 884 (trisubstituted ethylene), and 817 cm.$^{-1}$ (1,4-disubstituted phenyl group). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 282 (ϵ 22,400), 222 mμ (ϵ 9,300).

Anal. Calcd. for $C_{11}H_{11}ClO$: C, 67.87; H, 5.70. Found: C, 67.83; H, 5.76.

Methyl 3,4-Dimethyl-5-(*p*-chlorophenyl)-2,4-pentadienoate (IIIC).—An intermediate hydroxy ester was prepared by a Reformatskiĭ reaction of 3-methyl-4-(*p*-chlorophenyl)-3-buten-2-one (14.6 g., 0.075 mole), methyl bromoacetate (13.8 g., 0.090 mole), and zinc (6.05 g., 0.092 mole) according to the procedure described previously. The crude hydroxy ester was dehydrated directly with *p*-toluenesulfonic acid according to the usual procedure, and the dehydration product was distilled *in vacuo* to give 14.1 g. (75%) of the unsaturated ester, b.p. 125–147° (0.40–0.70 mm.). After standing for 3 hr. at room temperature the ester partially crystallized. Recrystallization of a portion of this material from petroleum ether (b.p. 30–60°) gave an analytical sample as colorless plates, m.p. 75–76°. Infrared absorption (in $CHCl_3$): 1706 (α,β-unsaturated C=O), 1610 (phenyl group), 1256 and 1167 (C–O–), 1092 (possibly 1,4-disubstituted benzene ring absorption), and 763 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 292 (ϵ 24,900), 225 mμ (ϵ 8200). N.m.r. absorption (in $CDCl_3$): 2.85 (C-5 Ar-H), 3.26 (C-5 H), 8.03 (C-4 CH_3), 7.62 (C-3 methyl protons *cis* to carbomethoxy), 4.14 (C-2 H), and 6.38 τ (CO_2CH_3).

Anal. Calcd. for $C_{14}H_{15}ClO_2$: C, 67.06; H, 6.03. Found: C, 67.18; H, 6.02.

3,4-Dimethyl-5-(*p*-chlorophenyl)-2-*trans*-4-*trans*-pentadienoic Acid (IVC).—Saponification of the unsaturated ester IIIC (12.9 g., 0.052 mole) with 5% methanolic potassium hydroxide in the manner described previously for 3,4-dimethyl-5-(*p*-tolyl)-2,4-pentadienoic acid gave 5.60 g. of crystalline potassium salt. Acidification of the salt precipitated 4.74 g. (39%) of the acid, m.p. 148–151° and 172–173°. One recrystallization from 2:1 cyclohexane–benzene gave a colorless analytical sample, m.p. 149–151° and 172–173°. Infrared absorption (in CCl_4): 1684 (α,β-unsaturated C=O), 1609 (phenyl group), 1265 and 1187 (C–O–), 1092 and 1016 (possibly 1,4-disubstituted benzene ring absorptions), and 866 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{\max}^{0.003\ \mathrm{N\ H^+ CH_3OH}}$ 291 mμ (ϵ 23,900), 223–224 (ϵ 7900). N.m.r. absorption (in $CDCl_3$): 2.83 (C-5 Ar-H), 3.21 (C-5 H), 7.98 (C-4 CH_3) 7.56 (C-3 methyl protons *cis* to carboxyl), and 4.07 τ (C-2 H).

Anal. Calcd. for $C_{13}H_{13}ClO_2$: C, 65.96; H, 5.54. Found: C, 65.75; H, 5.60.

Methyl 3,4-Dimethyl-5-(*p*-chlorophenyl)-2-*trans*-4-*trans*-pentadienoate (IVC, R′ = CH_3).—The methyl ester of the 2-*trans*-4-*trans* acid IVC was prepared with diazomethane. One recrystallization from warm petroleum ether (b.p. 30–60°) gave colorless plates, m.p. 75–76°. No melting point depression was observed when this material was mixed with the ester, m.p. 75–76°, recovered from the preceding dehydration reaction. N.m.r. and infrared spectra were also identical.

Anal. Calcd. for $C_{14}H_{15}ClO_2$: C, 67.06; H, 6.03. Found: C, 66.96; H, 6.02.

3-Methylene-4-methyl-5-(*p*-chlorophenyl)-4-*trans*-pentenoic Acid (VIC).—Treatment of the filtrate from the potassium salt of the 2-*trans*-4-*trans* isomer according to the procedure described previously for 3,4-dimethyl-5-phenyl-2-*cis*-4-*trans*-pentadienoic acid gave 4.0 g. (33%) of crude, yellow, oily acid. Repeated crystallization of this material from hexane (EK-P1135) gave 0.10 g. of colorless needles, m.p. 80–87°. Infrared absorption (in CCl_4): 1709 (saturated C=O), 1610 and 1495 (phenyl group), 1093, 1015, and 901 cm.$^{-1}$ (terminal methylene group). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 273.5 mμ (ϵ 23,800).

Anal. Calcd. for $C_{13}H_{13}ClO_2$: C, 65.96; H, 5.54. Found: C, 65.95; H, 5.62.

3-Methyl-4-(*p*-methoxyphenyl)-3-buten-2-one (ID).—This ketone [b.p. 99–100° (0.01 mm.), m.p. 27.5°, lit.[7] m.p. 27.5–28°] was prepared in 67% yield according to the procedure described previously by Woodruff and Conger.[15]

Methyl 3,4-Dimethyl-5-(*p*-methoxyphenyl)-2,4-pentadienoate (IIID).—An intermediate hydroxy ester was prepared by a Reformatsky reaction of 3-methyl-4-(*p*-methoxyphenyl)-3-buten-2-one (13.3 g., 0.070 mole), methyl bromoacetate (12.8 g., 0.084 mole), and zinc (5.64 g., 0.086 mole). The crude product was dehydrated directly with *p*-toluenesulfonic acid (0.50 g.) in benzene (200 ml.) and the unsaturated ester was distilled *in vacuo* to yield 10.9 g. (63%), b.p. 121–170° (0.30–0.75 mm.). After standing at room temperature for 3 hr. the ester partially crystallized. Recrystallization of a small portion of the semisolid ester from petroleum ether at 0° gave an analytical sample, m.p. 66–67°. Infrared absorption (in $CHCl_3$): 1706 (α,β-unsaturated C=O), 1603 and 1510 (phenyl group), 1253 and 1167 (C–O–), 1034 (CH_3–O–), and 861 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{\max}^{\mathrm{CH_3OH}}$ 312 (ϵ 23,700), 239 mμ (ϵ 9500). N.m.r. absorption (in $CDCl_3$): 3.13 (C-5 Ar-H), 3.24 (C-5 H), 8.02 (C-4 CH_3), 7.63 (C-3 methyl protons *cis* to carbomethoxy), 4.18 (C-2 H), 6.40 (CO_2CH_3), and 6.28 τ (*p*-CH_3O).

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.16; H, 7.52.

3,4-Dimethyl-5-(*p*-methoxyphenyl)-2-*trans*-4-*trans*-pentadienoic Acid (IVD).—Saponification of the semisolid unsaturated ester IIID (3.98 g., 0.016 mole) with 5% methanolic potassium hydroxide in the manner described previously for 3,4-dimethyl-5-

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[15] E. H. Woodruff and T. W. Conger, *J. Am. Chem. Soc.*, **60**, 465 (1938).

(p-tolyl)-2,4-pentadienoic acid gave 2.18 g. of crystalline potassium salt. Acidification precipitated 1.85 g. (49%) of the acid, m.p. 132–135° and 170–172°. Two recrystallizations from benzene–cyclohexane gave a colorless analytical sample, m.p. 134–136° and 174–175°. Infrared absorption (in CCl_4): 1683 (α,β-unsaturated C=O), 1602 and 1512 (phenyl group), 1252 and 1175 (C–O–), 1035 (O–CH_3), and 864 cm.$^{-1}$ (trisubstituted ethylene). Ultraviolet absorption: $\lambda_{\max}^{0.003\ \mathrm{N\ H^+CH_3OH}}$ 309 (ϵ 21,700), 236–237 mμ (ϵ 9900). N.m.r. absorption (in $CDCl_3$): 3.03 (C-5 Ar-H), 3.14 (C-5 H), 7.96 (C-4 CH_3), 7.57 (C-3 methyl protons *cis* to carboxyl), 4.07 (C-2 H), and 6.24 τ (p-CH_3O).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.45; H, 6.88.

Methyl 3,4-Dimethyl-5-(*p*-methoxyphenyl)-2-*trans*-4-*trans*-pentadienoate (IVD, R′ = CH_3).—The methyl ester was prepared by esterification of the 2-*trans*-4-*trans* acid with diazomethane and was recrystallized from petroleum ether at 0° to give colorless needles, m.p. 66–67°. No melting point depression was observed when the ester prepared in this manner was mixed with a sample of the ester, m.p. 66–67°, recovered from the p-toluenesulfonic acid dehydration. N.m.r. and infrared spectral data were identical.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.00; H, 7.49.

3-Methylene-4-methyl-5-(*p*-methoxyphenyl)-4-*trans*-pentenoic Acid (VID).—Treatment of the filtrate from the potassium salt of the 2-*trans*-4-*trans* isomer according to the procedure described previously for 3,4-dimethyl-5-phenyl-2-*cis*-4-*trans*-pentadienoic acid gave 0.80 g. of crude, yellow acid, m.p. 93–98°. Fractional crystallization of this material from hexane (EK-P1135) gave fine, colorless needles, m.p. 103.5–106.5°. Infrared absorption (in CCl_4): 1706 (saturated C=O), 1251 (C–O–), 1175 and 1042 (O–CH_3), and 902 cm.$^{-1}$ (terminal methylene group). Ultraviolet absorption: $\lambda_{\max}^{CH_3OH}$ 281 mμ (ϵ 23,000). N.m.r. absorption (in $CDCl_3$): 3.09 (C-5 Ar-H), 3.50 (C-5 H), 7.98 (C-4 CH_3), 4.68 and 4.89 (C-3 terminal methylene protons), 6.60 (C-2 internal methylene protons), and 6.25 τ (p-CH_3O).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.45; H, 6.97.

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Steric Effects in Radical Coupling. Arylation of 1,3-Indandiones with Dimesityliodonium Chloride[1-4]

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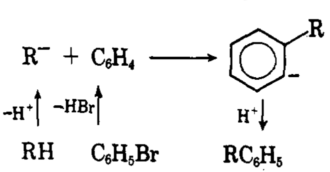
While the anion of 2-phenyl-1,3-indandione had given with diphenyliodonium chloride in t-butyl alcohol 85% of 2,2-diphenyl-1,3-indandione, it gave with dimesityliodonium chloride only 23% of the analogous 2-mesityl-2-phenyl-1,3-indandione and a small amount of 2-(o-mesitylphenyl)-1,3-indandione. 2-Mesityl-1,3-indandione, formed with related products from the anion of 1,3-indandione and dimesityliodonium chloride, was phenylated on oxygen to give the enol ether in good yield. These results are consistent with the previously proposed mechanism involving the formation and coupling of radical pairs, while the lowered yields of carbon-arylated products are believed to reflect steric hindrance to radical coupling.

In recent years two methods have been under investigation for the direct phenylation of carbanions. One is that of Leake and Levine in which the carbanion reacts with benzyne formed *in situ* by the dehydrohalogenation of bromobenzene by sodamide in liquid ammonia. This method has been used successfully with a series of dialkyl and aralkyl ketones,[6] esters,[7] and methylpyrazine.[8] The other method for the phenylation of carbanions is the reaction with diphenyliodonium salts. Phenyl derivatives of dimedone,[9] di- and tribenzoylmethane,[9] 1,3-indandiones,[3] esters,[10] and nitroparaffins[11] have been prepared by this method. The mechanism proposed[3] for these phenylations, discussed in more detail later, starts with electron transfer from carbanion (R^-) to an iodonium ion (ArI^+Ar) to give a radical pair, members of which largely combine to give ArR. Some radicals diffuse from the solvent cage and later combine to form ArR, RR, and ArAr, while some abstract hydrogen from solvent to form reduced product ArH.



Although experimental evidence[3] to date (influence of radical scavengers, dehydrogenation of solvent, formation of dimers) favors this proposed electron-transfer mechanism, the presence of a benzyne intermediate has not been definitely excluded. It was therefore of interest to use as the arylating agent dimesityliodonium chloride, from which a benzyne cannot be formed. The carbanions chosen for this study were those of 2-phenyl-1,3-indandione and 1,3-indandione, the phenylations of which previously have been reported.[3]

Reaction of 2-phenyl-1,3-indandione.—2-Phenyl-1,3 indandione (I)[3,12] reacted with sodium t-butoxide and

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(1) This article is taken from the dissertation of S. A. G. submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (chemistry).

(2) Diaryliodonium Salts. XX.

(3) Phenylation of 1,3-indandiones: F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962).

(4) For brevity the 2,4,6-trimethylphenyl radical will be called the mesityl radical and represented as mes.

(5) Eastman Kodak Co. Fellow 1961–1962; Texaco Co. Fellow 1963.

(6) W. W. Leake and R. Levine, *J. Am. Chem. Soc.*, **81**, 1169 (1959).

(7) W. W. Leake and R. Levine, *ibid.*, **81**, 1627 (1959).

(8) J. D. Behun and R. Levine, *J. Org. Chem.*, **26**, 3379 (1961).

(9) F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960). Phenylation on both carbon and oxygen was observed.

(10)(a) F. M. Beringer and P. S. Forgione, *J. Org. Chem.*, **28**, 714 (1963); (b) F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963).

(11) N. Kornblum and H. J. Taylor, *J. Org. Chem.*, **28**, 1424 (1963).

(12) W. Dieckmann, *Ber.*, **47**, 1439 (1914).