terial was almost identical to that of anthraquinone, but a mixture of the two melted at 255–260°.

Anal. Calcd. for $C_{14}H_8O_2$ or $C_{28}H_{16}O_4$: C, 80.71; H, 3.65. Found: C, 80.76; H, 3.87.

Compound III when heated in a test tube gave a brownish gum from which a yellow solid sublimed. The yellow solid melted at 276–278° and did not depress the melting point of authentic anthraquinone. When anthraquinone was heated similarly no brownish gum resulted from decomposition.

Anthraquinone when ignited burned with a typical smoky flame while III burned with a spitting sparkling flame typical of a peroxide.

Sodium iodide in acetic anhydride as well as potassium iodide in acetone gave no iodine test. After sodium thiosulfate crystals were added to the acetic anhydride solution a yellowish white solid precipitated slowly and melted at 241°. It was unchanged by acetic anhydride in pyridine and showed a carbonyl and a hydroxyl group in its infrared spectrum and a strong band at 748 cm.$^{-1}$ suggestive of a 9,10-dihydroanthracene. The compound was not investigated further.

When anthrone was heated in dioxane with ethylene and without base the same sort of mixture containing thermochromic compounds was obtained.

When compound I was heated with boiling aqueous alkali or ethanolic sodium ethoxide or even 9% potassium hydroxide in ethanol for as long as 40 hr. only a slight decomposition was noticed and I was recovered almost quantitatively.

π-Complexes. The few crystals of the compounds to be tested were placed on a spot plate and a drop of chloroform containing tetracyanoethylene was added. The colors were observed visually and usually appeared immediately although some complexes were observed only around the edge of the drop as the solvent evaporated.

BOULDER, COLO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

The Geometrical Isomers of 3-Methyl-7-phenyl-2,4,6-heptatrienoic Acid

RICHARD H. WILEY, PIERRE F. G. NAU, AND T. H. CRAWFORD

Received April 21, 1961

The configurations of 3-methyl-7-phenyl-2-*cis*-4-*trans*-6-*trans*-heptatrienoic acid (I), m.p. 194°, methyl ester, m.p. 46.5°, and its all *trans* isomer (II), m.p. 203°, methyl ester, m.p. 64°, have been established by analogy with related structural systems and by their NMR characteristics. The 3-methyl group in the 2-*trans* structure is deshielded (τ = 7.72) by *cis* carboxyl group whereas that in the 2-*cis* structure is not (τ = 8.03). The product, m.p. 169°, formerly thought to be a third isomer is apparently a mixture of the other two. The 4-carboxy derivative (III, m.p. 228° dec.) has properties consistent with the 2-*cis*-4-*cis* structure and is isomerized to the 2-*cis*-4-*trans* structure on decarboxylation. Both acids are altered by diffuse daylight without isomerization at the 2-double bond.

There are eight possible geometrical isomers of 3-methyl-7-phenyl-2,4,6-heptatrienoic acid. Three materials having this composition with melting points of 203°, 169°, and 192° have been reported[1–3] and attempts to assign *cis-trans* structures to these materials have been partially successful. The Reformatsky reaction of 6-phenyl-3,5-hexadien-2-one with methyl bromoacetate has given[1] two solids m.p. 203° and 169°. The latter was not reproducibly obtainable. A third solid, m.p. 192°, has been obtained[2] by the Reformatsky reaction of methyl γ-bromosenecioate with cinnamaldehyde and by decarboxylation[3,4] of 4-carboxy-3-methyl-7-phenyl-2,4,6-heptatrienoic acid obtained from the condensation of cinnamaldehyde with diethyl β-methylglutaconate. This last reaction has been reported to give two dicarboxy acids: 1) m.p. 199–200° dec.[5] (dibutylamine salt, m.p. 141° dec., readily converted to an anhydride, m.p. 180°) and 2) m.p. 187.5° dec. (dibutylamine salt not given). The anhydride, m.p. 180°, on hydrolysis is reported[4] to give a diacid, m.p. 183–185° dec. (dibutylamine salt, m.p. 119–123°). A previous analysis[4] of these data, and some additional data, has resulted in a tentative assignment of the 2-*trans*-4-*trans* structure (I) to the solid, m.p. 203°; the 2-*cis*-4-*trans* structure (II) to the solid, m.p. 169°; and the 2-*trans*-4-*cis* structure to the solid, m.p. 192°. The diacid, m.p. 187°, has been assigned the 2-*trans*-4-*cis* structure, with reservations, and the diacid, m.p. 199°, presumably has the 2-*cis*-4-*cis* structure (III).[4] No data have been presented indicating any structure other than *trans* for the 6–7 double bond. Because of the known instability of *cis*-cinnamic types, there seems to be no reason to question the validity of this assumption. Analysis of a somewhat similar situation presented by the 3-methyl-5-phenylpentadienoic acids[6] has established that these reactions (Reformatsky and decarboxylation) give, in fact, only two isomers, *2-cis*-4-*trans* and 2-*trans*-4-*trans*, and that a third supposed isomer is a molecular complex or mixture of the two. We have now re-examined the heptatrienoic acids and established similar conclusions which have been corroborated by NMR characteristics.[7]

---

(1) R. Kuhn and M. Hoffer, *Ber.*, **65**, 651 (1932).

(2) K. Ziegler, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 120 (1942).

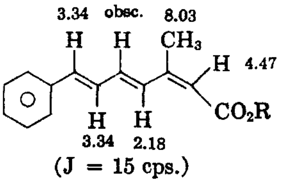
(3) J. D. Cawley and D. R. Nelan, *J. Am. Chem. Soc.*, **77**, 4130 (1955).

(4) J. D. Cawley, *J. Am. Chem. Soc.*, **77**, 4125 (1955).

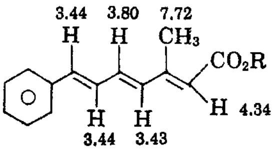
(5) V. Petrow and O. Stephenson, *J. Chem. Soc.*, 1310 (1950).

(6) R. H. Wiley, *J. Chem. Soc.*, 3831 (1958).

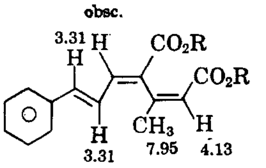
(7) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960); *Proc. Chem. Soc.*, 196 (1958).



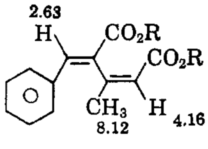
I



II



III



IV

The Reformatsky reaction of methyl bromoacetate with 6-phenyl-3,5-hexadien-2-one gives a crude product which dehydrates too easily to permit isolation of the β-hydroxy ester. If the crude ester is dehydrated over *p*-toluenesulfonic acid, an overall 58% yield of the crude methyl ester is obtained. Saponification with aqueous methanolic (80:20 methanol:water) potassium hydroxide gives a precipitate of the potassium salt of the acid, m.p. 203°, in beautiful flakes. Diazomethane with the acid gives the methyl ester, m.p. 64°; *p*-bromophenacyl ester, m.p. 171°. Acidification of the mother liquors from the saponification gives an isomeric acid, m.p. 194°, after recrystallization from alcohol; methyl ester, m.p. 46.5° and *p*-bromophenacyl ester, m.p. 138°. A mixture of the two acids, which melts at 167–184°, could not be separated into components. It was also not possible to separate the *cis* acid from the reaction mixture by recrystallization unless the potassium salt had been first precipitated.

The NMR absorption characteristics from the two esters are summarized in Table I. These data establish: 1) that each is a pure compound by the absence in each of C-methyl absorption at field strengths characteristic of the other; 2) that the 3-methyl group in the ester derived from the 203° acid is deshielded (τ = 7.72) a characteristic amount (0.31 p.p.m.) with respect to that in the isomeric (194° acid) ester (τ = 8.03); 3) that the deshielded C-4 proton of the 194° acid-ester appears as a low field (τ = 2.18) doublet with a coupling constant of 15 c.p.s. characteristic of a trans-relationship between the C-4–C-5 protons; and 4) that the C-6–C-7 protons appear as a rather strong peak at τ = 3.34 (2-*cis* isomer) of 3.44 (2-*trans* isomer) characteristic of the *trans* structure in similar phenyl- substituted olefins—*e.g.*, *trans*-1-phenyl-propene[8] and 2-*trans*-4-*trans*(not 4-*cis*)-3-methyl-5-phenyl-2,4-pentadienoic acid.[9] The acids in pyridine show similar methyl proton absorption patterns.[9]

TABLE I

NMR ABSORPTION DATA[a]

	I	II	III	IV
H-2	4.47	4.34	4.13	4.16
H(CH$_3$)	8.03	7.72	7.95	8.12
H-4	2.18 (J = 15 c.p.s.)	3.43[b]	—	—
H-5	(obscured)	3.80[b]	(obscured)	2.63
H-6	3.34	3.44	3.31	—
H-7	3.34	3.44	3.31	—

[a] For description of instrumentation, techniques, and conventions, see the experimental section. All absorption maxima, except the broad aromatic proton absorption at τ = 2.9–3.0 and the methoxyl proton absorption at τ = 6.4, of significant intensity are listed. [b] These doublets are not well defined and assignments based on these would be unreliable.

In addition to providing consistent support for these assignments, the data also are inconsistent with the NMR absorption characteristics to be expected of some of the alternative structures. Thus, the ester of the 203°-acid shows no absorption in the low field (τ *ca.* 2.2) region where that for the *cis* (to carboxyl) olefinic C$_4$ proton absorbs in such structures. The *cis* C-6–C-7 olefinic proton structure is probably eliminated in both isomers by the appearance of strong peaks at τ = 3.34–3.44 in their respective spectra. Because the spectrum is very complex in this region and several other lines appear as a result of the A_2BX or of an approximated A_2B coupling interaction, the assignment is not conclusive. The configuration at the C-4–C-5 double bond of II (R=H) cannot be conclusively established from the available analyses of the NMR data. There is no evidence in the NMR characteristics of these compounds for a third isomer and current studies with the complete series of pentadienoic analogs indicate that there would very likely be if such an isomer were present even to the extent of as little as 5%. These facts and analyses are in accord with the previous assignment of the all *trans* structure (II) to the acid, m.p. 203°, but the 2-*cis*-4-*trans*-6-*trans* structure must now be assigned to the acid, m.p. 194°.

The transformations undergone by these two acids, m.p. 194° and 203°, on exposure to sunlight has been followed by changes in their NMR characteristics. The 2-*cis* acid, m.p. 194°, which has been converted to the all *trans* isomer on irradiation with ultraviolet in the presence of iodine,[3] is converted by daylight into a white powder, m.p. 153–197°. This product shows no absorption at τ = 7.72 characteristic of the methyl protons in the all trans isomer. Similarly, the all *trans* isomer is converted to a more yellow substance, m.p. 167–194°, which shows no methyl proton absorption at τ = 8.03 characteristic of the methyl protons in the 2-*cis* structure. If the transformations taking place under these conditions involve *cis-trans* isomerizations, they apparently do not concern the 2-3

---

[8] R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, 30, 944 (1959).

[9] Richard H. Wiley and T. H. Crawford, unpublished observations.

TABLE II

ULTRAVIOLET ABSORPTION DATA[a]

Compounds	mμ		mμ		Solvent
I (R = H)	336	44,000	245	9,200	100% Ethanol
	337.1	47,000	246	10,470	96% Ethanol
	336	45,800	245	10,800	100% Ethanol[c]
II (R = H)	334	51,700	243	7,880	100% Ethanol
	335.3	51,600	243.5	8,200	96% Ethanol
	333	52,300	242.5	6,500	100% Ethanol[c]
I (R = CH_3)	337	48,000	246	10,900	Methanol
II (R = CH_3)	336.5	62,300	243	9,250	Methanol
III (R = H)	316.5	36,000			100% Ethanol
	322	[b]			Cyclohexane
III (R = CH_3)	319.6	48,500			Methanol
IV (R = CH_3)	279.5	18,600			Methanol

[a] For description of instrumentation and details of techniques see the experimental section. [b] Too insoluble to give a meaningful absorption coefficient. [c] Ref. 3.

double bonds to an extent great enough to be detected (*ca.* 5%). It is, of course, probable that oxidation reactions are involved.

The dicarboxylic acid obtained in the condensation of dimethyl β-methylglutaconate with cinnamaldehyde does not have an easily reproducible capillary melting point. It decarboxylates, as does also its dibutylamine salt, at or near its melting point and the melting points as observed in different laboratories are of little or no comparative significance. We have observed that the recrystallized diacid, which has been reported to melt at 199–200°[5] and 187–187.5°,[4] melts as high as 228° on a hot metal surface and at 207° (capillary); our melting point for the dibutylamine salt is 148° (hot surface) or 139–141° (capillary). The dimethyl ester, readily prepared with diazomethane, melts without decomposition sharply at 95.5–96° and is, therefore, a good derivative for characterization purposes. Furthermore, the diester prepared from the crude diacid and that from the most carefully recrystallized diacid, both obtained in substantially quantitative conversions, showed no differences in the NMR absorption. This indicates the absence of an isomer in the crude acid which was removed on recrystallization. We have no evidence, at present, that more than one isomer is available from the cinnamaldehyde condensation.

The previous assignments of the 2-*cis*-4-*cis* configuration to both this diacid and its ester (III) and the analogous 4-carboxy-3-methyl-5-phenylpentadienoic acid and its ester (IV) are reconfirmed by the data now available. The 2-*cis*-4-*cis* configurations were previously assigned[4,6] with some assurance on the basis of the ultraviolet absorption characteristics of the diacids. The 4-*cis* configuration, but not the 4-*trans*, requires nonplanarity of the —C(CH_3) = $CHCO_2H$ grouping and the residual grouping to leave as the effective chromophore only the *trans*-cinnamic acid (λ_{max} 273, ϵ 21,000) structure in the pentadienoic acid and only the 5-phenylpentadienoic acid (λ_{max} 307, ϵ 36,700) structure in the heptadienoic acid. Both of these are at much lower wave lengths than those for either of the known decarboxylated pentadienoic or heptatrienoic acid structures. (λ_{max} 308–307, ϵ 27,700–33,800; λ_{max} 336–334; ϵ 44,000–51,700).

The NMR data for the esters of these two diacids (III, IV) confirm the 2-*cis*-4-*cis* structural assignments. The data are summarized in Table I. For the pentadienoate (IV) the methyl proton absorption (τ = 8.12) and the C-2 proton absorption (τ = 4.16) are characteristic for the *trans* (to carboxyl) methyl and C-2 olefinic proton for which previously recorded[7] values are τ = 7.96–8.27 (*trans*) *vs.* 7.71–8.03 (*cis*) for the methyl group and 3.90–4.47 for the C-2 proton. The values are τ = 8.04 and 4.27 for dimethyl *cis*-β-methylglutaconate itself.[7] An absorption band at τ = 2.63 is assigned to the C-5 proton deshielded by the C-4 carbomethoxy. These two assignments (H-2 = 4.16 and H-5 = 2.63) cannot be reversed without assigning an absorption to an olefinic proton alpha to a benzene ring well above the highest (τ = 3.68) value previously observed.

The NMR data for the heptatrienoate (III) show a methyl absorption at τ = 7.95 ambiguously in the middle of the range for *cis* (to carboxyl) methyl and at the lower limit of the *trans* (to carboxyl) range. The 2-*cis* structure is confirmed, however, by the absorption at τ = 4.13 assignable to the normal C-2 olefinic proton. The alternative 2-*trans* structure would place this proton within the deshielding (τ *ca.* 0.80) range of the 4-carboxyl to give an estimated[7] τ = 3.3, a region in which there is no observed absorption. Absence of absorption in this region likewise establishes that H-5 is *cis* to the 4-carbomethoxy and is shifted to a lower field (τ *ca.* 2.9) where it is obscured by the aromatic proton absorption. No low field doublet (τ *ca.* 1.5) required for the C-6 proton in the 4-*trans* structure is observed. There is a large singlet at τ = 3.31, the position assigned to the H-4–H-5 in methyl 3-methyl-5-phenyl-2-*trans*-4-*trans*-pentadienoate[9], which is here assigned to the *trans* H-6–H-7 structure. Apparently the H-4 and H-5 and H-6–H-7 protons are so nearly

TABLE III

INFRARED ABSORPTION DATA[a]

I ($R = CH_3$) (2-*cis*-4-*trans*)	II ($R = CH_3$) (2-*trans*-4-*trans*)	III ($R = CH_3$) (2-*cis*-4-*cis*)	IV ($R = CH_3$) (2-*cis*-4-*cis*)
2941w	2940w	2940w	3145w
1692m	1701s	1706s	1709s
1608s/1580w	1603s/1575w	1647w/1626m/1600w	1647m/1618w
1495w	1495w	1491w	1495w
1451m, 1435m	1439m	1441m	1445m
1379w	1408w/1395w	1377w	1374w
1256s	1276w/1244s	1277s/1239s	1259s
1160s	1186w/1164s/1157s[b]	1156m/1134m	1140s
1073w	1070w	1055w	1079w/1058w
1046w	1039w	1044w	1042m
994s	988s	972m	—
851w/826w	883m/860m	866m	863m
687w	687w	687w	689w

[a] For description of instrumentation and techniques see the experimental section. Values given in cm.$^{-1}$; s = strong, m = medium, w = weak. [b] This apparent splitting of this C—O stretching band is so weakly defined that it is not regarded as characteristic.

alike in structures of this type that no coupling occurs. If *cis*, they would probably be observed as an unsymmetrical doublet, with $J = 9–12$, instead of as a singlet. These data not only confirm the 2-*cis*-4-*cis*-6-*trans* structure but are also inconsistent with any of the seven alternative structures.

The ultraviolet and infrared absorption characteristics of the compounds are given in Tables II and III. The ultraviolet data show some solvent shifts of interest and the infrared data present characteristic patterns which distinguish the 2-*cis* and 2-*trans* structures. The most obvious differences in the infrared are the splitting of the single band (CH deformation in C—CH_3; aromatic C=C stretching) at 1439 cm.$^{-1}$ in the 2-*trans* to a doublet (1451, 1435 cm.$^{-1}$) in the 2-*cis*: the shift of the strong band (C—O stretching) from 1244 cm.$^{-1}$ in the 2-*trans* to 1256 cm.$^{-1}$ in the 2-*cis*; the shift of the carbonyl stretching vibration from 1701 cm.$^{-1}$ in the 2-*trans* to 1692 cm.$^{-1}$, which although very low is comparable to that in methyl 3-methyl-5-phenylpentadienoate, in the 2-*cis*; and the shift of the strong band (C—H out of plane deformation in *trans* CH=CH; absent in IV) at 988 cm.$^{-1}$ in the 2-*cis* to 994 cm.$^{-1}$ in the 2-*trans*. Differences of a somewhat similar character have been observed previously[6,10] with other related geometrical isomers. Additional confirmation of these tentative assignments are needed to establish their ultimate value in structural correlations.

EXPERIMENTAL[11]

Reformatsky reaction. 6-Phenyl-3,5-hexadiene-2-one, m.p. 68°, was prepared from cinnamaldehyde and acetone.[12] The ketone, 8.6 g., with 4 g. of zinc and 9.2 g. of methyl bromoacetate (added slowly) in 80 ml. of dry benzene, gave a vigorous reaction and a deep red complex product. The mixture was decomposed with acetic acid, diluted with ether, and washed with water. Dehydration with 0.5 g. of *p*-toluenesulfonic acid in 250 ml. of benzene was complete in 30 min. Distillation gave three fractions: 1) 140°/0.04 mm., 0.35 g.; 2) 140–150°/0.04 mm., 4.60 g.; and 3) 150–155°/0.04 mm., 1.65 g. The first two were 40:60 and the third a 35:65 *cis/trans* mixture based on relative intensity of NMR absorption at $\tau = 7.72$ and 8.03. Saponification of 5.4 g. of the mixed esters with 5 g. of potassium hydroxide in 20 ml. of water and 80 ml. of methanol (warmed to solution, 24 hr. at 25°, 24 hr. at 0°) resulted in the precipitation of 2.65 g. of white plates of the potassium salt. Acidification of this salt gave 2.15 g. of the acid (II. $R = H$), m.p. 199–200°. After two recrystallizations from aqueous ethanol there was obtained 1.95 g. (22% from the starting ketone), m.p. 202–203°, of the pure acid.

Anal. Calcd. for $C_{14}H_{14}O_2$: Neut. equiv. 214.3. Found: Neut. equiv. 214.5.

The *p*-bromophenacyl ester was recrystallized from ethanol, m.p. 170.5–171°.

Anal. Calcd. for $C_{22}H_{19}O_3Br$: Br, 19.47. Found: Br, 19.76.

The methyl ester (II. $R = CH_3$) was prepared by adding diazomethane in ether to an ether solution of the acid and recrystallized from petroleum ether (b.p. 40–60°), m.p. 64°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.88; H, 6.93.

The mother liquor from the precipitated potassium salt was diluted with water, evaporated under reduced pressure to remove methanol, washed to remove neutral material, and acidified to precipitate the crude acid. Four recrystallizations from ethanol gave 1.3 g. (15% over-all) of pale yellow crystals, m.p. 193.5–194°, of the acid (I. $R = H$).

Anal. Calcd. for $C_{14}H_{14}O_2$: Neut. equiv. 214.3. Found: Neut. equiv. 216.

The *p*-bromophenacyl ester was recrystallized from aqueous ethanol, m.p. 138–138.5°.

Anal. Calcd. for $C_{22}H_{19}O_3Br$: Br, 19.47. Found: Br, 19.75.

The methyl ester (I. $R = CH_3$) prepared as above and recrystallized from aqueous ethanol, m.p. 46°5.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.93; H, 7.06.

The mixed melting point of the two esters is below room temperature; of the two acids, 167–184°, with some evidence of individual crystals, m.p. 167°. The mixture can be separated by fractional precipitation of the potassium salt but not, at least readily, by fractional recrystallization.

---

(10) Richard H. Wiley and H. G. Ellert, *J. Am. Chem. Soc.*, **79**, 2266 (1957).

(11) Except as otherwise noted melting points are made in capillary tubes and are not corrected. Analyses by Micro Tech Laboratories.

(12) R. Cornubert and H. G. Eggert, *Bull. soc. chim. France*, 532 (1954).

Condensation of cinnamaldehyde with β-methylglutaconate. The directions given previously[4] gave yellow crystals, m.p. 205° dec. (on a heated metal surface). Several recrystallizations from aqueous methanol gave yellow needles, m.p. 207° dec. (capillary); m.p. 228° dec. (metal surface) of 4-carboxy-3-methyl-7-phenyl-2,4,6-heptatrienoic acid (III. R = H).

Anal. Calcd. for $C_{15}H_{14}O_4$: Neut. equiv. 258.3. Found: Neut. equiv. 261.

The di(*n*-butylamine) salt was prepared as described previously[5] as white crystals, m.p. 139–141° (cap.), 148° dec. (metal). The dimethyl ester (III, R = CH_3) was prepared as above from diazomethane, m.p. 95.5–96°, from cyclohexane.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.46; H, 6.31.

Decarboxylation. The dicarboxylic acid refluxed in lutidine with copper acetate[3] evolved the theoretical amount of carbon dioxide. The product was isolated and recrystallized from benzene-cyclohexane to give a 41% yield of the acid, m.p. 191–193°; mixed melting point with acid from the Reformatsky reaction, 192–194°. Same infrared absorption characteristics.

Methyl 4-carbomethoxy-3-methyl-5-phenyl-2-cis-4-cis-pentadienoate (IV. R = CH_3). The crude acid obtained from benzaldehyde and β-methylglutaconic ester prepared as described previously[6] was esterified with diazomethane in ether solution and fractionated to give the product, b.p. 125°/0.3 mm.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.10, H, 6.11.

The ultraviolet absorption measurements were made with a Beckman DK-3 recording spectrometer in the solvents (spectrograde) stated. The infrared absorption measurements were made with a Baird double beam recording spectrometer with sodium chloride optics and in chloroform (0.04 g./ml.) or as potassium bromide pellets. The NMR measurements were made with a Varian High Resolution (Model HR-4302) spectrometer with 60 megacycle oscillator with superstabilizer and field homogeneity control. The calibrations were made by the side band technique at several frequencies. Tetramethylsilane was used as an internal reference standard. Data for the acids were obtained in pyridine solutions, data for the esters in the carbon tetrachloride at about 15% concentration. Values are given in τ units.[13] Microanalyses by Micro Tech Laboratories, Skokie, Ill.

Acknowledgment. The authors gratefully acknowledge partial support of this research under Grant NSF G-11108 from the National Science Foundation. One of us (T. H. Crawford) is grateful for a National Science Foundation Cooperative Graduate Fellowship (1959–1961) and another (P. F. G. Nau) is grateful for a Fulbright Travel Grant in support of a postdoctoral appointment. The authors also acknowledge grants from the Atomic Energy Commission AT-(40-1)-229 and AT-(40-1)-2055; National Institutes of Health H-4952; from the Lilly Co.; and from the Mead Johnson and Co. which made possible purchase of the NMR spectrometer used in this study.

LOUISVILLE 8, KY.

---

[13] G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

Synthesis of Some 2,2-Disubstituted Dihydrodicyclopentadienes

CHICITA F. CULBERSON AND PELHAM WILDER, JR.

Received May 1, 1961

Alkylation and cyclization of the ditosylate of *endo-cis*-2,3-bis(hydroxymethyl)norbornene with sodio diethyl malonate or sodio phenylacetonitrile yields 2,2-disubstituted 1,2-dihydro-*endo*-dicyclopentadienes. Attempted reactions with several other anions failed. Sodio diethyl malonate and the ditosylate of *exo-cis*-2,3-bis(hydroxymethyl)norbornene yield diethyl 1,2-dihydro-*exo*-dicyclopentadiene-2,2-dicarboxylate. These dihydrodicyclopentadienes represent the first of established ring geometry substituted exclusively in the 2-position. Other derivatives and a synthesis of the new hydrocarbons 2,2-dimethyl-1,2-dihydro-*endo*-dicyclopentadiene and 2,2-dimethyl-1,2-dihydro-*exo*-dicyclopentadiene are described.

In 1956, Cope and Anderson[1] described a new synthetic method leading to bicyclic products, illustrated by the preparation of 3,6-epoxycycloheptane derivatives (II) upon condensation of *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran ditosylate (I) with either sodio diethyl malonate or sodio ethyl cyanoacetate. Later, Cope and Fournier[2] obtained substituted epoxycyclooctane derivatives IV by treating ditosylate III with sodio diethyl malonate. We have now used this condensation-cyclization to synthesize 2,2- disubstituted dihydrodicyclopentadienes from the known ditosylates of *endo-cis-* and *exo-cis*-bicyclo[2.2.1]-5-heptene-2,3-dimethylol (V and XIV). Preparative routes leading to 2-substituted dicyclopentadienes are of especial interest at the present time since recent studies have emphasized the proximity of the 9,10-double bond and the 2-position in *endo*-dicyclopentadiene type molecules, and the effects of this geometry on reactions of related compounds.[3,4]

Diethyl malonate reacted with both *endo-cis-* and *exo-cis*-ditosylates V and XIV, yielding 59% and 83% respectively of 2,2-diethyl esters, VIII and XV. Sodio phenylacetonitrile and *endo-cis*-ditosylate V yielded 89% of an isomeric mixture of

---

[1] A. C. Cope and B. C. Anderson, *J. Am. Chem. Soc.*, 78, 149 (1956).

[2] A. C. Cope and A. Fournier, Jr., *J. Am. Chem. Soc.*, 79, 3896 (1957).

[3] R. B. Woodward and T. J. Katz, *Tetrahedron*, 5, 70 (1959).

[4] P. Wilder, Jr., and Chicita F. Culberson, *J. Am. Chem. Soc.*, 81, 2027 (1959); Chicita F. Culberson and P. Wilder, Jr., *J. Am. Chem. Soc.*, 82, 4939 (1960).