solution was acidified and extracted with ether. The ethereal solution was dried over magnesium sulfate and concentrated to leave 12.3 g. of crude angelic acid, m.p. 38–43°, which was recrystallized to separate 10.4 g. (35%) of angelic acid as white prisms, m.p. 40–43° (lit.[9] m.p. 45.0–45.5°), with infrared absorption[17] at 2950 cm.$^{-1}$ (broad, assoc. O—H), at 1685 cm.$^{-1}$ (conj. carboxyl C═O) and at 1640 cm.$^{-1}$ (conj. C═C) and an ultraviolet maximum[15] at 213 mμ (ϵ 7,400). A 5.0-g. (0.05 mole) sample of this acid, after esterification with diazomethane in the usual manner, yielded 4.48 g. (79%) of ester *10*, b.p. 45° (26–28 mm.), $n^{25.5}_{D}$ 1.4292 (lit.[9] b.p. 127.6–128°, n^{25}_{D} 1.4321) which contained[21] more than 98% of methyl angelate.[23] The ester *10* has infrared bands[17] at 1715 cm.$^{-1}$ (conj. ester C═O) and at 1645 cm.$^{-1}$ (conj. C═C) with an ultraviolet maximum at 216 mμ (ϵ 9,200).

Reaction of the phosphorane 3 with acetaldehyde. To a solution of 30.0 g. (0.086 mole) of the ylid *3* in 100 ml. of methylene chloride was added, dropwise under a nitrogen atmosphere, 7.8 g. (0.18 mole) of acetaldehyde. The resulting solution was allowed to stand overnight and then concentrated, diluted with 200 ml. of petroleum ether and filtered to remove the precipitated triphenylphosphine oxide. Distillation of the filtrate separated 8.84 g. (90%) of a product mixture, b.p. 68–69° (62–65 mm.), n^{25}_{D} 1.4274, containing[21] 93.5% methyl tiglate and 3.2% methyl angelate corresponding to an ester mixture containing 96.5% methyl tiglate and 3.5% methyl angelate. Fractional distillation of this mixture separated a sample of pure methyl tiglate, $n^{25.5}_{D}$ 1.4337, which had infrared absorption identical with that of the authentic sample.

To establish that methyl angelate would be stable under the conditions of this preparation, a solution of 3.94 g. (0.0345 mole) of methyl angelate, 9.6 g. (0.0345 mole) of triphenylphosphine oxide and 3 mg. of the ylid *3* in 25 ml. of methylene chloride was refluxed for 4 hr. and then worked up as previously described. The recovered methyl angelate, 2.15 g. (55%), b.p. 43.5–44.5° (26 mm.), n^{25}_{D} 1.4281, contained[18] less than 1% of methyl tiglate.

Reaction of the phosphorane 15 with methyl pyruvate (18). Reaction of 39 g. (0.15 mole) of triphenylphosphine with 22 g. (0.20 mole) of ethyl bromide in 50 ml. of benzene at 135° in an autoclave for 20 hr. followed by recrystallization of the precipitated phosphonium salt from water and subsequent drying afforded 49.5 g. (89%) of ethyltriphenylphosphonium bromide as white prisms, m.p. 209–210.5° (lit.[24] m.p. 203–204°).

An ethereal solution (90 ml.) containing 0.105 mole of phenyllithium was added, with stirring in a nitrogen atmosphere, to a suspension of 40.0 g. (0.108 mole) of the phosphonium salt in 200 ml. of ether. After the addition was complete, the resulting red solution was stirred for 1 hr. at which time the mixture gave a negative Gilman color test for phenyllithium. The ethereal solution of the ylid was added, dropwise and with stirring in a nitrogen atmosphere, to a solution of 9.0 g. (0.088 mole) of methyl pyruvate in 10 ml. of ether until the red color of the mixture persisted in the reaction mixture. At this point the reaction mixture was heated to reflux, the remainder of the ylid solution was added, and the resulting mixture was refluxed overnight with stirring. The bulk of the ether was distilled from the pasty reaction mixture and 400 ml. of tetrahydrofuran was added. The resulting mixture was refluxed for 36 hr. under a nitrogen atmosphere and again concentrated to about 75 ml. by distillation of the tetrahydrofuran through a 30-cm. Vigreux column. The reaction mixture was diluted with ether and the ethereal solution was separated from an insoluble semisolid and distilled. The ester mixture obtained, b.p. 34–36° (25 mm.), $n^{24.5}_{D}$ 1.4396–1.4405, amounted to 2.10 g. (21%) and contained[19] 68% methyl tiglate and 32% methyl angelate. Samples collected from the chromatograph[19] were identified by comparison of their spectra with the spectra of authentic samples.

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[23] The substantial contamination with methyl tiglate noted in the previous preparation [A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **76**, 1902 (1954)] of angelic acid by this procedure was almost certainly due to the use of impure bromo olefin as the starting material (see ref. 22).

[24] G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Diels-Alder Reactions of 9-Substituted Anthracenes. V. Adducts of Ethylene[1]

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The condensation of ethylene with 9- and 9,10-disubstituted anthracenes at 170–200° under pressure is a convenient way of preparing bridgehead compounds. A variety of anthracenes are readily available and undergo this reaction.

Some time ago we announced a convenient synthesis of bridgehead compounds by the condensation of a 9-substituted anthracene with ethylene.[2] This method has been used since then in two different studies by others.[3,4]

The ready availability of a variety of 9-substituted anthracenes, together with satisfactory yields, makes this method a general one for obtaining 9-substituted 9,10-dihydro-9,10-ethanoanthracenes.

Ethylene, the simplest possible dienophile, was first used in a Diels-Alder reaction by Joshel and Butz in 1941.[5] They condensed it with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and cyclopentadiene at temperatures of almost 200°.

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[1] Supported in part by the National Science Foundation.

[2] Presented in part at the 123rd meeting of the American Chemical Society, Los Angeles, Calif., March 1953.

[3] M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40**, 2129 (1957).

[4] T. W. Campbell, E. V. McCoy, J. C. Kauer, and V. S. Foldi, *J. Org. Chem.*, **26**, 1422 (1961).

[5] L. M. Joshel and L. W. Butz, *J. Am. Chem. Soc.*, **63**, 3350 (1941).

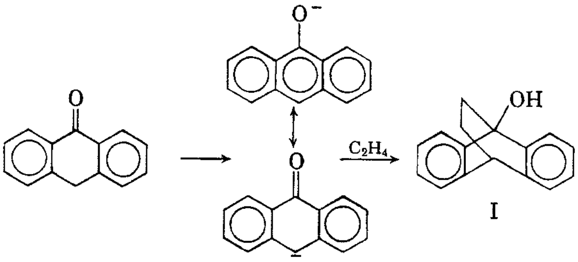
Furan and ethylene also undergo the Diels-Alder reaction.[6] In 1946 a patent by Thomas disclosed the condensation of anthracene with ethylene.[7] His only modification was to use a solvent with the high melting anthracene and he made no claim of condensing any substituted anthracene.

Using essentially the same conditions as previous workers, it has now been found that 9-anthraldehyde, its methyl acetal, 9-aceto-, 9-acetoxy-, 9-cyano-, 9-nitro-, 9-methoxy, 9-chloro- and 9-bromoanthracene can be condensed with ethylene in satisfactory yields. While this is not surprising in view of previous work, it should be pointed out that terminal substitution of a diene can lower its reactivity due to steric and electronic effects. Bachmann and Kloetzel report that 9-phenylanthracene reacts much more slowly than does anthracene with maleic anhydride in boiling benzene and they noted further that 9,10-diphenylanthracene and maleic anhydride are slow to react even in boiling xylene.[8]

9,10-Disubstituted anthracenes were also found to condense with ethylene; 9,10-dichloro-, 9,10-dibromo-, and 9,10-diacetoxyanthracene have been condensed thus. Recently 9,10-dinitro- and 9,10-bisformamidoanthracene have been converted into ethanoanthracenes.[4]

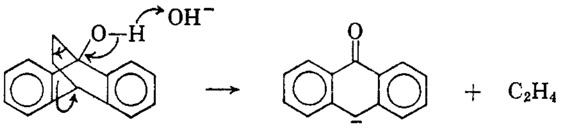
The only 9-substituted anthracenes that so far have failed to react with ethylene are 9-bromomethylanthracene and 9,9′-bianthryl. The bromine atom is allylic in nature in the first compound and it decomposes at 142° which is lower than the temperature necessary for the condensation with ethylene. 9,9′-Bianthryl is reported to be inert to maleic anhydride[9,10] and no Diels-Alder reaction is yet known for this compound. Ethylene is a smaller dienophile than maleic anhydride but no trace of an adduct could be obtained with either ethylene or *N*-*p*-maleimidobenzoic acid. A Catalin model of 9,9′-bianthryl shows that free rotation of the 9,9′-bond is prohibited and the two anthracene systems are perpendicular to each other so that one blocks the addition of a dienophile to the other. The diethylene adduct likewise should have restricted rotation and would consist of a *meso* compound and *dl* pair depending upon how the bicyclic ring systems are locked together.

Since 9-anthrol isomerizes to the more stable anthrone, the condensation of ethylene with anthrone was tried in the presence of base with aqueous dioxane as the solvent, and 9-hydroxy-9,10-dihydro-9,10-ethanoanthracene (I) was produced. At that time[11] there was no report of a salt ever having been used in a Diels-Alder reaction, but since then sodium acrylate has been condensed with sodium 9-anthracenecarboxylate and with sodium 2,4-pentadienoate.[12]



I

Since the formation of the bridgehead alcohol (I) was promoted by base, it was thought that possibly the reverse reaction would be facilitated by the loss of a proton to regenerate ethylene and the sodium salt of anthrone as follows:



However, no such reverse reaction was detected by heating I with either aqueous or ethanolic sodium hydroxide. Since the sodium salt of anthrone is a bright yellow, the formation of even a trace of it would have been easily detected.

When anthrone was heated with ethylene in neutral dioxane or toluene, highly colored high melting products were obtained from which bianthrone was isolated. When dioxane and base were used a yield of I as high as 60% could be obtained, but the alcohol had some biathrone and anthrone present. When pyridine was used as the solvent a 60% yield was obtained, and 40% of the starting anthrone was recovered. There were no highly colored products so that better material was obtained. Collidine also appears to be a satisfactory solvent.[13]

The bianthrone (II) on melting turned green and it was further identified by melting point and spectral comparisons with material obtained by Tieman from the reduction of anthraquinone.[14] An attempt to make a diacetate of II with acetic anhydride and sodium acetate lead to a compound which melted at 281° and had an analysis consistent with anthraquinone. However, anthraquinone depressed the melting point of the substance. On heating the compound it decomposed to a red gum under conditions not affecting anthraquinone. On burning, the compound gave a flame which sputtered in a fashion typical of peroxides and has been assigned tentatively structure III. The compound did not

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(6) W. Nudenberg and L. W. Butz, *J. Am. Chem. Soc.*, **66**, 307 (1944).

(7) C. L. Thomas, U. S. Patent 2,406,645 (1946).

(8) W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **60**, 481 (1938).

(9) C. Dufraisse, L. Velluz, and L. Velluz, *Bull. soc. chim. France*, [5] **5**, 600 (1938).

(10) E. de B. Barnett, J. W. Cook, and M. A. Matthews, *J. Chem. Soc.*, **123**, 1994 (1923).

(11) V. C. Godefroi, Master's thesis, University of Colorado, 1950.

(12) K. Alder and K. Heimbach, *Ber.*, **86**, 1312 (1953).

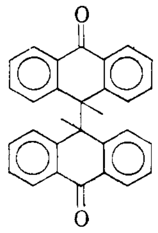
(13) C. Bouboulis, University of Colorado, unpublished work.

(14) C. Tieman, Ph.D. thesis, University of Colorado, 1953.

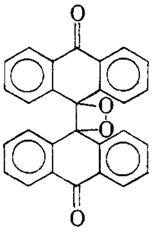
TABLE I

Substituents in 9- Position of Adduct	Crude Yield, %[a]	M.P.	M.P. of Anal. Sample[b]	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
—Cl	35	97–108	108.5–109	$C_{16}H_{13}Cl$	79.83	5.44	77.79	5.34
—Br	72	132–135		$C_{16}H_{13}Br$	67.38	4.59	67.56	4.69
—NO_2	67	139.5–140		$C_{16}H_{13}NO_2$	76.47	5.21	76.51	5.22
—CN	72	107–109		$C_{17}H_{13}N$	88.28	5.66	88.25	5.65
—$OCOOH_3$	61	92–95	93–93.5	$C_{18}H_{16}O_2$	81.79	6.10	81.75	6.05
—OH	78	164–166		$C_{16}H_{14}O$	86.45	6.35	86.55	6.37
—CHO	45	107–109	108.5–109	$C_{17}H_{14}O$	87.15	6.02	87.04	6.09
—$COCH_3$	58	132–132.5		$C_{18}H_{16}O$	87.06	6.50	86.88	6.68
—COC_6H_5	40	167–168		$C_{23}H_{18}O$	89.00	5.84	89.20	5.76
—$CH(OCH_3)_2$	37	164–165		$C_{19}H_{20}O_2$	81.39	7.19	81.39	6.95
—OCH_3	63	148–153	155.5–156	$C_{17}H_{16}O$	86.40	6.83	86.27	6.63
Substituents in 9,10- Position								
—Cl	53	106–116	125–127	$C_{16}H_{12}Cl_2$	69.83	4.40	69.66	4.51
—Br	90	111–113	113–114	$C_{16}H_{12}Br_2$	52.78	3.32	52.55	3.40
—$OCOCH_3$	34	186–203	207–208	$C_{20}H_{18}O_2$	74.53	5.63	74.66	5.70

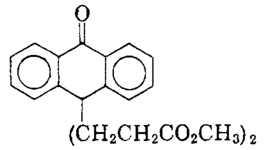
[a] Yields are sometimes for amounts obtained after one crystallization from alcohol. [b] Many samples were purified by sublimation.



II



III



IV

liberate iodine from a sodium iodide acetic anhydride solution but did oxidize sodium thiosulfate.

Attempts to condense ethylene with 10-nitroanthrone, 10-bromoanthrone and oxanthrone led to highly colored materials from which only anthraquinone was isolated. An attempt to condense methyl acrylate with anthrone in methanol containing some sodium methoxide gave a conjugate addition rather than a Diels-Alder reaction and IV was obtained.

The spectra of over fifty 9,10-dihydro-9,10-ethanoanthracenes with substituents located at only 9, 10, 11 or 12 positions have been examined. All of them have a distinct peak between 754–760 cm.$^{-1}$ All seem to be missing the usual peak near 1600 cm.$^{-1}$ attributed to benzene rings and condensed systems save when functional groups such as a double bond or tosylate give a peak in this region. 9,10-Dihydroanthracenes give peaks around 750 ± 10 cm.$^{-1}$, and a peak in this region suggests an *ortho*-disubstituted benzene. However, the examination of the spectra of systems known to be rearranged from a dibenzbicyclo[2.2.2]octadiene system (9,10-dihydro-9,10-ethanoanthracene) to a dibenzbicyclo[3.2.1]octadiene system showed the appearence of a band near 1600 cm.$^{-1}$ and the loss of the 754–760-cm.$^{-1}$ band.[15] If the condensation of ethylene had occurred at the 1,4-positions of anthracene, one would expect to find a strong peak between 800–830 cm.$^{-1}$ and a medium peak between 830–855 cm.$^{-1}$ characteristic of a β-naphthalene as well as an isolated double bond peak around 1600–1650 cm.$^{-1}$

It was hoped that tetracyanoethylene[16] might yield a simple spot test to distinguish between an ethanoanthracene and the rearranged 3.2.1-system but these systems seemed to give similar yellow π-complexes. Ethanoanthracene gave a typical yellow color while ethenoanthracene gave a red complex. Many of the anthracenes gave a greenish complex although 9,10-diacetoxyanthracene gave a blue one. 9,9′-Bianthryl gave a faint greenish color typical of other anthracenes and its internal hindrance to Diels-Alder reactions does not seem to inhibit complex formation nor did the bridge in the ethanoanthracenes appear to inhibit complexing.

EXPERIMENTAL

9-Substituted anthracenes. 9-Chloroanthracene was prepared by chlorinating anthracene in carbon disulfide,[17] and melted at 102–105°.

9-Bromoanthracene was prepared by the method of Perkin[17] and an attempt to duplicate the procedure and yield of Mikhaĭlov and Promyslov[18] using anthracene and phosphorus pentabromide gave only a 16% yield of 9-bromoanthracene, m.p. 96–98°.

9-Acetylanthracene was prepared from acetyl chloride and anthracene[19] and benzoic anhydride was used similarly in

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[15] The spectra of rearranged compounds were kindly furnished by Professor S. J. Cristol and his students at the University of Colorado.

[16] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[17] W. H. Perkin, *Chem. News*, **34**, 145 (1876).

[18] B. M. Mikhaĭlov and M. S. Promyslov, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 338 (1950).

[19] C. Merritt, Jr., and C. E. Braun, *Org. Syntheses*, Coll. Vol. **I**, 1 (1950).

carbon disulfide with aluminum chloride to obtain 9 benzoylanthracene.[20]

9-Acetoxyanthracene was prepared by the method of Liebermann in which 9-anthrone was heated with acetic anhydride.[21] A 13% yield was obtained but the use of pyridine[22] as a solvent gave better results and the product melted at 133–135°.

9-Anthraldehyde was prepared by the formylation of anthracene with *N*-methylformanilide.[23] When anthracene was heated with dimethylformamide for 3 hr. at 130–140° in the presence of phosphorus oxychloride an 11% yield of 9-anthraldehyde was obtained. Recrystallization from acidified methanol gave the methyl acetal[24] melting at 145–146°. 9-Anthraldehyde (1.8 g.) was placed in a Soxhlet extractor over 0.4 g. of lithium aluminum hydride in ether. The extractor was run overnight and then the ether solution was decomposed first with some ethyl acetate and then with hydrochloric acid. The organic layer was decanted and evaporation with cooling gave 1.6 g. of 9-anthrylcarbinol (88%) melting at 160–162°, lit. m.p. 154–155°.[25] When 3.3 g. of the 9-anthrylcarbinol was treated with 1 ml. of phosphorus tribromide in 15 ml. of carbon tetrachloride for 30 min. at 50–60°, the light yellow alcohol changed to a canary yellow compound. Evaporation of some of the solvent in a stream of dry air led to solidification. Methanol was added to destroy excess phosphorus tribromide and after filtering and washing with methanol 2.7 g. (70%) of solid was obtained, melting at 137.5–142.5° dec. The compound appeared to decompose on standing in the dry state for 2 months. In a second experiment another yellow compound melting at 221–226° was isolated but was not investigated further.

Anal. Calcd. for $C_{15}H_{11}Br$: C, 66.44; H, 4.09. Found: C, 66.54; H, 4.00.

9-Cyanoanthracene was prepared from 9-bromoanthracene and copper (I) cyanide[26] as well as by converting the aldehyde to the oximes and dehydrating these derivatives.[27]

9-Anthrone[28] was converted into 9-methoxyanthracene by the use of sodium hydroxide and methyl sulfate.[29]

9-Nitroanthracene was readily obtainable and melted at 145–146°.[30]

9,10-Disubstituted anthracenes 9,10-Dichloroanthracene was prepared from anthrone and phosphorus pentachloride[10] and melted at 212–214°.

9,10-Dibromoanthracene was obtained from W. Barasch.[31]

9,10-Diacetoxyanthracene[32] melting at 271–273° was obtained by reducing anthraquinone with zinc dust in the presence of acetic anhydride and pyridine.

Preparation of ethanoanthracenes. In most cases 2–5 g. of the substituted anthracene was placed in a Parr high pressure hydrogenation bomb, around 100 ml. of toluene was added along with a pinch of an inhibitor such as 4-*t*-butylcatechol. Ethylene was admitted under pressure and the reaction mixture shaken for a few minutes to dissolve ethylene before the bomb valve was closed. Starting pressures ranged from 400 to 1200 lb. maximum if a new tank of ethylene was on hand. After heating to around 180–200° the pressure would rise to 1500 to 3500 p.s.i. After 1 or 2 days of heating the bomb was opened, the solvent was evaporated and the material was crystallized from alcohol.

10-Bromoanthrone was prepared by brominating anthrone in carbon disulfide, and hydrolysis in aqueous acetone gave oxanthrone.[33] The 10-nitroanthrone was prepared by nitrating anthrone.[34]

When pyridine solutions of these compounds were heated with ethylene and a trace of inhibitor, only dark colored materials were obtained. The 9-nitroanthrone gave rise to anthraquinone apparently by self oxidation. When anthrone and acrylic acid were refluxed in pyridine for 36 hr., only crude anthrone was deposited on cooling.

One-half gram of sodium was dissolved in 50 ml. of methanol, and then 5 g. of anthrone and 2.6 g. of methyl acrylate were added to the boiling solution. The mixture was heated under a reflux condenser for 1 day. Evaporation to 25 ml. caused the precipitation of 1.5 g. of yellow crystals, m.p. 109–113°. Methanolic acetone was used to recrystallize the solid, and about 0.4 g. of anthraquinone was separated. Concentration of the filtrate gave 0.6 g. of white plates, m.p. 106–111°. These were recrystallized from a chloroform-hexane mixture and the analytical sample melted at 114–115.5°.

Anal. Calcd. for $C_{22}H_{22}O_5$: C, 72.12; H, 6.05. Found: C, 71.96; H, 6.11.

The infrared spectrum showed a ketonic carbonyl group and that of an ester and the compound was assigned structure IV.

Preparations of 9,10-dihydro-9,10-ethano-9-anthrol. Forty grams of anthrone, 180 ml. of dioxane and 40 ml. of 50% sodium hydroxide were heated with ethylene for 21 hr. at about 195° and 1750 p.s.i. After cooling, solid was noted between the two layers and was filtered. This fraction weighed 26.3 g. and was almost pure bridgehead alcohol, m.p. 168–169°. Acidification of the filtrate with hydrochloric acid gave 14 g. of material which was separated into an additional 4 g. of alcohol, 7 g. of condensed anthrone and 3 g. of anthrone.

Thirty grams of anthrone was dissolved in 200 ml. of pyridine and gave a homogeneous yellow solution. It was heated at 204–235° for 33 hr. at an ethylene pressure of 1500 p.s.i. The pyridine was removed with steam and the product was crystallized from petroleum ether (b.p. 60–68°) plus a trace of benzene which was added to dissolve the last bit of product. Cooling and evaporation gave a total of 24.3 g. of product (78%), and no side products were noted.

Twenty grams of anthrone in 200 ml. of toluene was heated at 180° for 24 hr. with ethylene at 1950 p.s.i. The toluene was evaporated. The dark residue was heated in 400 ml. of ethanol with charcoal and filtered. The red filtrate on cooling gave some crystals. From this 3.8 g. of compound I was obtained. The portion sparingly soluble in alcohol was triturated with acetone and gave 1.5 g. of a white solid which turned green on melting at 270–275°. Bianthrone is reported to melt at 275°,[35] and bianthrone obtained by Tieman[14] from the reduction of anthroquinone melted at 271–275° and turned green on melting. The infrared spectra of both materials were identical.

From the acetone filtrate 6.2 g. of brownish crystals melting near 250° was obtained, and upon heating with sodium acetate and acetic anhydride for 5 hr. gave reddish yellow crystals, m.p. 277.5–280°. The infrared spectrum of the ma-

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(20) J. W. Cook, *J. Chem. Soc.*, **129**, 1282 (1926).

(21) C. Liebermann, *Ann.*, **212**, 1 (1892).

(22) E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, 2631 (1923).

(23) L. F. Fieser, J. L. Hartwell, and J. E. Jones, *Org. Syntheses*, Coll. Vol. III, 98 (1951).

(24) J. S. Meek and J. R. Dann, *J. Org. Chem.*, **21**, 968 (1956).

(25) F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **77**, 3852 (1955).

(26) W. E. Bachmann and M. C. Kloetzel, *J. Org. Chem.*, **3**, 55 (1938).

(27) J. S. Meek and J. R. Dann, *J. Am. Chem. Soc.*, **77**, 6677 (1955).

(28) K. H. Meyer, *Org. Syntheses*, Coll. Vol. I, 60 (1941).

(29) K. H. Meyer and H. Schlosser, *Ann.*, **420**, 126 (1920).

(30) C. E. Braun, C. D. Cook, C. Merritt, Jr., and J. E. Rousseau, *Org. Syntheses*, **31**, 77 (1951).

(31) W. Barasch, Ph.D. thesis, University of Colorado, 1952.

(32) E. de B. Barnett, N. F. Goodway, A. G. Higgens, and C. A. Lawrence, *J. Chem. Soc.*, 1224 (1934).

(33) K. H. Meyer, *Ann.*, **379**, 62 (1911).

(34) K. H. Meyer, *Org. Syntheses*, Coll. Vol. I, 390 (1941).

(35) E. de B. Barnett and M. A. Mathews, *J. Chem. Soc.*, 387 (1923).

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.

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

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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]

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