III. Animal Fat Concentrate No. A-21

Collaborator No.	Method No. A-21 Conjugated Diene	Conjugated Triene	Conjugated Tetraene	Linoleic Acid	Linolenic Acid	Arachidonic Acid	Pentaenoic Acids
	%	%	%	%	%	%	%
1	2.08	0.04[a]	0.00	4.6[a]	7.9[a]	21.2	2.0
2	2.12	0.03[a]	0.00[c]	6.4[a, b]	8.4[a, b]	22.2	2.3
3	2.17[b]	0.05[a]	0.00[a, b]	7.3[a, b]	3.3[a, b, d]	26.2[b]	2.5[b]
4	2.31	0.01[a]	0.00[b]	5.1[a]	4.0[a]	25.6	2.5
5	2.32	0.50[a, b, e]	0.00[c]	4.6[a]	11.8[a]	23.5	2.2
6	......	......	......	6.7[a,b]	4.4[a, b]	25.3[b]	2.6
7	1.95[b]	0.03[a, b, d]	0.00[b, d]	8.9[a, b, d]	16.2[a, b, d]	14.9[d]	1.3[d]
8	2.06	0.04	0.00	7.1	9.0	21.1	1.5
Avg.	2.14	0.03	0.00	6.3	8.1	22.5	2.1

[a] Indicates that one or more of the slit widths involved in measurements from which these values were calculated were not within the range 0.8 to 0.9 mm. required by Tentative Method Cd 7-48 for measurements in the triene region.

[b] Indicates that one or more of the absorbancies involved in this calculation were not within the range of 0.2 to 0.8 required by Tentative Method Cd 7-48.

[c] Value calculated by chairman.

[d] Value recalculated by chairman.

[e] Not included in average.

ples known to contain no arachidonic acid, *i.e.*, most vegetable and drying oils, by elimination of all values in the tetraene region, about 300 mμ. Can a further simplification of similar nature be made for oils known to contain no linolenic acid, *i.e.*, cottonseed, sesame, peanut oil, etc., by elimination of all values in the triene region, about 268 mμ?

In your opinion has this collaborative work satisfactorily demonstrated that such a simplification should be recommended and included in Method Cd 7-48?

Objective: Certain laboratories dealing primarily with animal fats, fish oils, etc., prefer to work with 21% alkali for determinations of arachidonic acid, pentaenoic acids, etc. Other laboratories, working primarily with vegetable and drying oils, consider the 6.6% alkali more convenient. Can Tentative Method Cd 7-48 provide 21% and 6.6% alkali as alternate methods for all samples, thus eliminating the requirement for some groups to work with both concentrations?

In your opinion does the collaborative work on Linseed Oil, reported here, justify this alternate method?

Objective: A method involving 21% alkali is proposed as superior for determination of arachidonic acid and essential for determinations of acids more unsaturated than arachidonic acid.

In your opinion should the 21% alkali be introduced into Tentative Method Cd 7-48 for all polyunsaturated acids more unsaturated than arachidonic?

Should determination of arachidonic acid be recommended with 6.6%, 21% alkali, or optional use of either?

IV. Tung Oil Methods No. T-1 and T-2

Collaborator No.	Method T-1 Conjugated Diene	Conjugated Triene α-Eleostearic Acid	β-Eleostearic Acid	Linoleic Acid	Method T-2 Linoleic Acid
	%	%	%	%	%
1	0.12	80.6	0.0[a]	6.4	7.0
2[b]	0.00	81.0	0.0	5.8	7.0
3[b]	1.22	77.0	2.4	4.2	6.4
4	0.00	81.2	10.4	4.0	4.4
5	......	......	......	......	......
6[b]	0.08	74.8	5.5	4.5	5.2
7[c]	2.32	41.1	35.7	2.2	3.0
8	0.16	79.3	0.0	6.2	7.4
Avg.	0.26	79.0	3.0	5.2	6.2

[a] Actually reported as a negative value.

[b] Indicates that one or more absorbancies used in the calculations were not obtained on a Beckman DU with maximum sensitivity.

[c] Not included in averages.

Objective: At the present time no official method exists for the determination of non-conjugated acids in the presence of large quantities of conjugated constituents. The linoleic acid content of tung oil studied is one example. Should Tentative Method Cd 7-48 be extended to include the method studied here? If so, should the simplified calculation of Method T-2 be used or is the more rigorous Method T-1 desirable?

Properties of the Methylene Group in 1,4-Dienes. I. Catalytic Polymerization of 1,4-Pentadiene[1]

OLIVER GRUMMITT and C. C. CHUDD,[2] Western Reserve University, Cleveland, Ohio

THE METHYLENE GROUP in the 1,4-diene system of linoleic and linolenic acids is a key structural feature in the chemical behavior of non-conjugated drying oils. The simplest compound containing this structure is 1,4-pentadiene. While this is not an exact model of the fatty acids, because of the terminal double bonds in 1,4-pentadiene, its chemical behavior should be closely analogous. The purpose of this work was to study catalytic isomerization and polymerization reactions of 1,4-pentadiene in relation to those reactions of drying oils.

According to the current theory of thermal polymerization (heat bodying), non-conjugated oils, such as linseed and soybean, initially isomerize on heating so that a fraction of the ethylenic groups are conjugated. Polymerization then proceeds by Diels-Alder addition between a 1,3-diene group in one acid radical and a double bond in another.

While many substances accelerate the thickening of fatty oils, the important catalysts, *i.e.* substances which do not permanently combine with the oil, are sulfur dioxide, quinones, and nickel. These compounds are also isomerization catalysts because they accelerate the conversion of 1,4-diene groups to conjugated structures. Among other isomerization catalysts, alkali metal hydroxides are best known. Typical catalysts of these types have now been investigated for their quantitative effects on 1,4-pentadiene.

Polymerization of 1,4-Pentadiene

Thermal and boron fluoride-catalyzed polymerizations of 1,4-pentadiene have been reported by Ahmad and Farmer (1), who showed that 1,4-pentadiene

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[1] Presented before the Organic Chemistry Division, American Chemical Society, Atlantic City, September, 1952.

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without catalyst was stable up to 200°. At 250° the dimer portion of the polymer consisted in part of 1-methyl-2-allylcyclohexene-5. The formation of this product was interpreted as a Diels-Alder condensation of a molecule of 1,3-pentadiene, formed by isomerization, with 1,4-pentadiene as the dienophile. Thus the conjugation and addition paralleled the reactions which occur in the thermal polymerization of non-conjugated oils.

1,4-Pentadiene is not commercially available. Therefore the Boord synthesis (5, 6, 18) was developed to give consistent yields. In this synthesis *alpha*-chloroethyl ethyl ether, made from paraldehyde, ethanol, and hydrogen chloride, is brominated to *alpha, beta*-dibromoethyl ethyl ether, which is alkylated with allylmagnesium bromide to *alpha*-allyl-*beta*-bromoethyl ethyl ether. Reaction with zinc removes bromine and ethoxyl to give 1,4-pentadiene. No 1,3-pentadiene is formed. The purity of the intermediates was checked by quantitative halogen analyses, and the over-all yield of purified 1,4-pentadiene was 35–37%.

The isomeric 1,3-pentadiene (piperylene) was obtained in 48% yield by the alumina catalyzed dehydration of 3-penten-2-ol, which was made from crotonaldehyde and methylmagnesium bromide (8).

To detect the formation of 1,3-pentadiene, ultraviolet absorption spectra were determined on mixtures of 10–90% of 1,3 and 1,4-pentadienes. The average deviation of this method was ± 1.4%, and the maximum was ± 2.4%. A more sensitive test is the orange-red color given by the coupling of 1,3-pentadiene with p-nitrobenzenediazonium chloride to form an azo derivative (9). 1,4-Pentadiene is negative in this test, and 1% of 1,3-pentadiene in 1,4 is easily detected.

The isomerization and polymerization experiments were run in a 250-ml. stainless steel bomb, electrically heated and magnetically stirred. The products were separated by fractional distillation into C_5, dimer, and polymer fractions. With 20 g. (30 ml.) of pentadiene in the bomb and no catalyst, heating at 250° for 36 hours gave no reaction. The addition of 2.5% of anthraquinone had no effect. These results contradicted the earlier work (1), where the uncatalyzed reaction at 250° (in a copper bomb) gave 15% of polymer. That copper had no catalytic effect was shown by adding copper wool in one of our experiments.

A possible explanation for this discrepancy was that all of the 1,4-pentadiene was in the gas phase as a consequence of heating above the critical temperature. If this were the case, then the relative volumes of liquid and bomb would determine the concentration of 1,4-pentadiene. Critical data for 1,4-pentadiene do not appear to have been published. An approximate determination of the critical temperature gave 200°, which showed that only gaseous pentadiene was present in these 250° experiments. Next, experiments were run with increasing charge in the bomb so as to increase concentration in the gas phase. With 65 g. (100 ml.) of pentadiene at 250° the initial pressure was 900 p.s.i., and, after 36 hrs., the yield of polymer was 8.2% (Exp. 1).

Neither the initial pressure of 900 p.s.i. nor the final pressure of about 700 p.s.i. (Exp. 1) is critical. For example, with the charge adjusted to an initial pressure of 760 p.s.i. at 250°, the final pressure was 650 p.s.i. and the yield of polymer was only slightly less than that of Exp. 1.

As soon as polymer forms, the reaction becomes heterogeneous because 1,4-pentadiene is distributed between the liquid polymer and the gas phase.

Table I summarizes experiments run at various temperatures and times, with and without catalysts. The catalysts, compared under identical conditions, were anthraquinone (I), anthraquinone-β-carboxylic acid (II), β-chloroanthraquinone (III), sulfur dioxide (IV), and aqueous sodium hydroxide (V). The catalyst concentration was 0.8% by weight with respect to 1,4-pentadiene. In no case was 1,3-pentadiene found in the reaction products, either by ultraviolet absorption or the color test. After recovery of unreacted 1,4-pentadiene, a fraction distilling at 168-182° was shown to be $C_{10}H_{16}$ or dimerized pentadiene. The boiling range and refractive index (n_D^{20}) of 1.4786 (1.4672–1.4733 if catalysts are used) were close to the values reported earlier (1): 176° and *ca.* 1.4808. Thus at least part of the reacted 1,4-pentadiene had presumably isomerized and condensed to dimeric products. The varying values of the refractive index indicate that isomeric dimers are present.

With sulfur dioxide as a catalyst, no 1,3-pentadiene sulfone or polysulfone was found. The sulfone decomposes at about 100° (4), but under pressure this temperature is undoubtedly higher.

The strong catalytic action of sulfur dioxide was demonstrated in experiments run under conditions where 1,4-pentadiene is recovered unchanged. With a bomb charge of only 20 g. plus 2.5% of sulfur dioxide, a reaction at 250° for 36 hrs. had an initial pressure of 365 p.s.i. The total polymer yield was 10.5%, the dimer yield was 2.0% (19% of the polymer).

TABLE I
Polymerization of 1,4-Pentadiene

Experiment	Catalyst 0.5 g. (0.8%)	Temperature ±3°C.	Pressure[a] (psi.)	Time (hours)	Total polymer yield,		Dimer,		High boiling polymer,		% Dimer[c]
					g.	(%)[b]	g.	(%)[b]	g.	(%)[b]	
1	None	250	850–790	36	5.5	(8.5)	1.0	(1.5)	4.5	(6.9)	18.2
2	Anthraquinone (I)	195	450	36	0.6	(0.9)	....		....		......
3	Anthraquinone (I)	225	725–700	36	3.5	(5.4)	0.3	(0.5)	3.2	(4.9)	8.6
4	Anthraquinone (I)	250	900[a]	12	5.2	(8.0)	0.6	(0.9)	10.7	(16.5)	11.5
5	Anthraquinone (I)	250	900–720[a]	24	10.6	(16.3)	1.3	(2.0)	10.7	(16.5)	12.3
6	Anthraquinone (I)	250	900–750	36	12.7	(19.5)	1.8	(2.8)	10.9	(16.8)	14.2
7	Anthraquinone—β-carboxylic acid (II)	250	900–700	36	16.4	(25.2)	1.9	(2.9)	14.5	(22.3)	11.4
8	β-chloroanthraquinone (III)	250	900–700	36	16.0	(24.6)	2.3	(3.5)	13.7	(21.1)	14.4
9	Sulfur dioxide (IV)	250	900–550	36	26.7	(41.0)	4.0	(6.2)	22.7	(34.9)	15.0
10	Sodium hydroxide (V)	250	900–400	36	36.8	(56.5)	11.9	(18.3)	24.9	(38.3)	32.4

[a] Observed initial and final pressures. The other minimum pressures listed were taken at about the 28th hour; these reactions were stopped during the night at 36 hrs. by an automatic timer.

[b] Based on initial charge, 65 g. (100 ml.), of 1,4-pentadiene.

[c] Based on total yield of polymer.

The catalysts not only increased the total yield of polymer and lowered the reaction temperatures but in some cases changed the dimer/polymer ratio. This ratio was 18.2% with no catalyst (Exp. 1). The quinones and sulfur dioxide decreased the ratio slightly, sodium hydroxide almost doubled it.

Under the conditions of these experiments there is no dissociation or decomposition of polymer to form 1,4-pentadiene. This was demonstrated in an experiment with anthraquinone as the catalyst (Exp. 6) by removing the monomer, reheating the polymer and catalyst for 21 hours at 250°. There was no pressure increase, and no C_5 products were obtained.

Reactions of 1,3 and 1,4-Pentadienes

Reactions of mixtures of 1,3 and 1,4-pentadienes represent the second step in the isomerization-polymerization of 1,4-pentadiene and of non-conjugated oils. The effect of the catalysts on the interaction of equimolar mixtures of 1,3 and 1,4-pentadienes was determined under conditions where 1,4-pentadiene does not appreciably react (Table II). Hence it was assumed that the products formed either by condensation of 1,3-pentadiene with 1,4 or by polymerization of 1,3-pentadiene.

TABLE II

Reactions of 1,3-Pentadiene and 1,4-Pentadiene[a]

Experiment	Catalyst 0.5 g. (2.5%)	Total polymer yield,		Dimer,		High boiling polymer,		Dimer[c]
		g.	(%)[b]	g.	(%)[b]	g.	(%)[b]	
11	None	10.2	(51.0)	4.7	(23.5)	5.5	(27.5)	46
12	I	11.3	(56.5)	4.2	(21.0)	7.1	(35.5)	37
13	IV	11.9	(59.5)	3.8	(19.0)	8.1	(40.5)	32
14	V	17.9	(89.5)	10.4	(52.0)	7.5	(37.5)	58

[a] Charge: 20 g., 10 g. of each hydrocarbon; temp. 250°; initial press., 350 p.s.i.; time, 36 hrs.

[b] Based on 20 g. charge of dienes.

[c] Based on total yield of polymer.

With no catalyst at 250° and an initial pressure of 350 p.s.i. (Exp. 11) the mixture gave about 50% polymer, almost one-half of which was dimer. No 1,3-pentadiene was recovered from this or subsequent experiments. Anthraquinone (I) and sulfur dioxide (IV) catalyze the formation of total polymers by 11–17% and decrease the proportion of dimer. Sodium hydroxide (V) almost doubled the yield of polymer and increased the relative amount of dimer by 25%. All of the catalysts gave about the same yield of polymer exclusive of dimer. Because Diels-Alder additions are rarely catalyzed (13), it appears that alkali promotes condensation reactions other than diene addition. From the standpoint of catalyzed oil polymerization, it may be noted that anthraquinone and sulfur dioxide catalyze considerably the isomerization-polymerization of 1,4-pentadiene (Table I), but the coreaction of 1,4 and 1,3-pentadienes is only slightly catalyzed.

Experimental

1,4-Pentadiene.[3] A mixture of 200 g. (201 ml., 4.54 moles) of paraldehyde (redistilled, b.p. 121–122.5°) and 200 g. (254 ml., 4.34 moles) of absolute ethanol in a 2-l., three-necked flask fitted with a mechanical stirrer and gas inlet tube reaching to the bottom of the flask is cooled to —5° in dry ice-acetone. Dry hydrogen chloride (cylinder gas dried with sulfuric acid and calcium chloride) is passed into the stirred reaction mixture maintained at —5° until 200 g. (5.48 moles) have been absorbed. This requires about 2 hrs. The reaction mixture separates into two layers, the upper layer of α-chloroethyl ethyl ether is removed, and dissolved hydrogen chloride is displaced by bubbling in *dry* nitrogen gas. After drying with 25 g. of anhydrous calcium sulfate overnight, the yield of ether is 411-432 g. (87-92% based on ethanol). This ether is a lachrymator, hydrolyzes rapidly in air, and resinifies readily above 0°. Therefore it is not distilled but is stored in a dry ice chest during drying and until the next step.

Then 425 g. (3.92 moles) of α-chloroethyl ethyl ether are placed in a 1-l., three-necked flask fitted with a dropping funnel, stirrer, and gas outlet tube. With the flask cooled in ice, 625 g. (200 ml., 3.92 moles) of bromine are added portionwise so that the mixture becomes almost colorless after each addition. At the end of this step, which requires 5–6 hrs., dry nitrogen is slowly bubbled through to remove hydrogen chloride; otherwise decomposition of the dibromoether is accelerated. The product, dried overnight with 25 g. of anhydrous calcium sulfate, is distilled at 70–75°/27 mm. to remove aldehyde, alcohol, and water before the Grignard step. The yield of colorless α,β-dibromoethyl ethyl ether is 599–663 g. (66–73% based on the α-chloroethyl ethyl ether taken); n_D^{20} 1.5097–1.5102. This ether is also a lachrymator.

Then 195 g. (8 g. atoms) of dry magnesium turnings and 2,400 ml. of absolute ether are placed in a 5-l., three-necked flask fitted with a mercury sealed stirrer, reflux condenser and drying tube, dropping funnel, and nitrogen inlet tube. The flask is cooled in ice, a small crystal of iodine is added, and then 400.5 g. (287 ml., 3.31 moles) of allyl bromide (redistilled, b.p. 69–71°), dissolved in an equal volume of absolute ether, are added dropwise in about 17 hrs. while a slow stream of dry, oxygen-free nitrogen is passed through the flask. After the addition the reaction mixture is stirred for one-half hour, and the reagent is ready for the next step. However, in finding optimal conditions, the Grignard yield was measured in several runs by decanting the ether solution into a dry, graduated storage bottle, rinsing the flask with 150–200 ml. of dry ether, and titrating the combined solutions (11). The yield of allylmagnesium bromide is 2.62–2.95 moles (79–89%).

Allyl chloride (6) may replace the bromide, but in our experience it gave lower yields of Grignard reagent and the volume of solution is inconveniently large.

The flask containing allylmagnesium bromide is immersed in ice, and a solution of 579.5 g. (2.5 moles) of α,β-dibromoethyl ethyl ether, dissolved in an equal volume of dry ether, is added slowly with stirring in 3–4 hrs. The excess of Grignard reagent (*ca.* 10%) increases the yield. After standing overnight, the mixture is hydrolyzed with 75 ml. of 20% acetic acid in water, followed by 500 ml. of water. The ether layer is washed four times with 100-ml. portions of 10% sodium bicarbonate solution and four times with 100-ml. portions of water. After drying with 100 g. of anhydrous calcium sulfate overnight and distillation at 72–75°/21 mm., the yield of colorless α-allyl-

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[3] The assistance of E. P. Budewitz in developing this synthesis is acknowledged.

β-bromoethyl ethyl ether is 370–396 g. (77–82% based on the α,β-dibromoethyl ethyl ether taken); n$_D^{20}$ 1.4606.

Next, 380 g. (1.97 moles) of α-allyl-β-bromoethyl ethyl ether are dissolved in 550 ml. of n-butyl alcohol in a 2-l., three-necked flask fitted with a stirrer and a reflux condenser, 28 cm. long, at the top of which is a 2.5 x 35 cm. Vigreux fractionating column. The take-off of the column is attached to an efficient water condenser set for distillation. Water at 35–40° is pumped through the reflux condenser and ice water through the distillation condenser. The receiver is cooled in ice, and its outlet is connected to a dry-ice cooled trap. To the solution in the flask are added 550 g. (8.4 g. atoms) of zinc dust and 2 g. of anhydrous zinc chloride (catalyst). The reaction mixture is stirred vigorously and heated gradually (caution) so that the distillation rate is about one drop/two seconds. The reflux condenser and column return most of the n-butyl alcohol to the flask. The reaction takes 5-6 hrs. for completion. The distillate is washed with five 100-ml. portions of ice water (to remove alcohol), then dried overnight with 15 g. of calcium chloride. The dried product is distilled through the Vigreux column to give 97–102 g. (72–76%) of colorless 1,4-pentadiene; b.p. 25.5–26.0°, n$_D^{20}$ 1.3887. The over-all yield from the four steps is 35–37%.

1,3-Pentadiene. 3-Penten-2-ol, b.p., 72–79°/141 mm.; n$_D^{25}$ 1.4257, was made from crotonaldehyde and methylmagnesium bromide (8) in 76% yield. Dehydration by heating with 10–15% of aniline hydrobromide gave lower yields than vapor phase dehydration over alumina. The 100 g. (1.16 moles) of 3-penten-2-ol were placed in a 500-ml. distilling flask fitted with a capillary ebullition tube. The flask was connected to a slightly tilted 2.5 x 77 cm. combustion tube, filled with activated alumina (8–15 mesh, Aluminum Ore Co.) and electrically heated to 460°. The outlet of the tube was connected to a vertical spiral air condenser, an ice-cooled trap, and a cold-finger condenser filled with dry ice-acetone. The side arm of the receiver attached to this condenser was connected to a manometer, manostat, and vacuum pump. The system was evacuated to 20 mm., the alcohol was distilled through the heated tube in about 2 hrs. Water and unreacted alcohol (20 g.) in the trap were separated, and the alcohol was recycled. The total crude piperylene obtained was 66.7 g. (84%). This was purified in the same way as for 1,4-pentadiene to give 49.0 g. (62%), b.p. 41.5–42.3°, n$_D^{20}$ 1.4309. The over-all yield based on crotonaldehyde was 48%.

Ultraviolet Analysis of Mixtures of 1,4 and 1,3-Pentadiene. The low boiling points of these hydrocarbons necessitate careful handling in quantitative work. Samples were weighed in tared glass ampoules cooled in dry ice and then sealed. The solvent was ice-cold isooctane (Phillips Petroleum Spectrograde), and the spectra were measured with a Beckman Model DU spectrophotometer. The standard solutions of 1,4 and 1,3-pentadiene each contained 0.022 g./l. and these solutions were used to make known binary mixtures at concentrations of 0.0022 g./l. Nine mixtures varying in steps of 10% over the range of 10–90% were used.

The maximum for 1,3-pentadiene is a flat portion in the curve at 2230–2235 Å, specific extinction (k) 369. The previously reported maximum was 2235 Å (3). 1,4-Pentadiene is very low in absorption, and there is practically a straight line at 2180–2300 Å. The absorption by mixtures, which is almost linear, is slightly higher at 2230 Å than at 2235 Å. The specific extinction for 1,4-pentadiene at 2230 Å was 29.6. Therefore, assuming linearity,

$$\% \text{ 1,3-pentadiene} = \frac{k_{2230} - 29.6}{369 - 29.6} \times 100.$$

The composition of our 1,3-pentadiene as *cis* and *trans* isomers was not determined. The absorption of the isomers differs (14).

Critical Temperature of 1,4-Pentadiene. Samples were sealed into tubes 3 mm. in diameter and 1.0 cm. long. A tube attached to a thermometer was heated in an oil bath as in the determination of a melting point. A magnifying glass and spot lamp allowed observation of the liquid-to-vapor transition. With liquid filling ⅓ or more of the tube, bubbles formed at 173° and the meniscus gradually disappeared at about 200–202°.

Thermal Polymerization. The bomb (Autoclave Engineers Co., Erie, Pa.) was swept out with dry, oxygen-free nitrogen at room temperature while cooling in ice. A 67.0 g. (100 ml.) charge of 1,4-pentadiene, freshly distilled from sodium, b.p. 25.3–26.0°, n$_D^{20}$ 1.3888, was poured into the bomb, which was then sealed as quickly as possible. The temperature was raised rapidly to the desired point. With a constant voltage source, variable transformer, and shielding of the bomb, the temperature control was ± 3°.

At the end of the reaction period the bomb was allowed to cool to room temperature, volatile material was distilled through the exhaust valve and copper tubing connected to a cold-finger type condenser and a 150-ml. round bottom flask with a sidearm stopcock. This was connected to a trap, which in turn was connected to the vacuum line. The condenser, receiver, and trap were cooled with dry ice-acetone.

The stopcock on the receiver was used to control the distillation rate at room temperature while the pressure was reduced to 150 mm. Then the bomb was slowly heated to 70°. The distillate, 61.0 g. (Exp. 1), was redistilled through the Vigreux column to give 59.9 g. of 1,4-pentadiene, b.p. 25.5–26.5°, n$_D^{20}$ 1.3888. The color test for conjugation was weakly positive (9). A sample of distillate, 0.2233 g., diluted with isooctane to 0.0022 g./l., contained 1.3% piperylene by UV analysis, a value below the limit of accuracy of the method (± 2.4%).

The polymer in the bomb was removed with benzene, and this solution was distilled through a micro concentric tube column (Metro Industries, Long Island City, N. Y.), 13 cm. long, with the larger tube 9 mm. in diameter and the smaller, 5 mm. Distillation gave 1.0 g. of colorless dimer, b.p. 165–180°, n$_D^{20}$ 1.4786; a residue of 4.5 g. The total was 5.5 g., 8.5% of the 1,4-pentadiene taken, and the dimer yield was 18.2% of the total polymer. The dimer was analyzed: calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8; mol. wt. 136. Found: C, 88.5; H, 11.6; mol. wt. 136.

Catalyzed Polymerizations. The quinone catalysts were purified by crystallization: I, m.p. 283–5°; II, 284–6°; III, 205–6°. The catalyst, 0.5 g. (0.8%), was put in the bomb first, then the 65.5 g. of 1,4-pentadiene were charged as described above. Volatile products were isolated and analyzed in the usual way. The residue in the bomb was extracted with petroleum ether (Skellysolve B), which is a good solvent for the polymer but not for the quinones. The catalyst was removed by filtration, recrystallized from toluene, and dried. For example, 0.3–0.4 g. of anthraquinone was recovered (Exp. 6), m.p. 282–284°. It gave no depression in a mixed melting point with authentic anthraquinone.

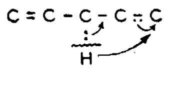
The sodium hydroxide catalyst (40% aqueous solution, carbonate-free) was handled like the quinones, but the procedure was modified for sulfur dioxide. A 25 x 200 mm. side-arm test tube, with a drying tube on the side arm, was fitted with a stopper and a 7-mm. gas inlet tube, which reached almost to the bottom. The tube was sealed by rubber tubing and a pinch clamp, then cooled in dry ice-acetone, weighed rapidly, returned to the cooling mixture, and connected to a tank of sulfur dioxide. Gas was passed in until approximately 0.5 g. had liquefied, the tube was resealed, quickly reweighed, and returned to the dry ice. A 20–25-ml. portion of previously weighed, cold 1,4-pentadiene was added to the test tube, and the mixture was quickly poured into the bomb, which was already cooled in dry ice. The remainder of the 1,4-pentadiene was added to the bomb.

The distillation system was changed to include a gas washing bottle containing 20% sodium hydroxide solution connected to the bomb exhaust valve. The gas from this passed through calcium chloride and then to the condenser and receiver previously described. The gain in weight of the sodium hydroxide solution about equalled the sulfur dioxide taken. A qualitative sodium fusion test for sulfur on the high boiling polymer showed only a trace of sulfur.

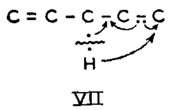
The reactions of 1,4 with 1,3-pentadiene (Table II) were run by the same general procedure. The C_5 material distilled was 1,4-pentadiene; no 1,3-pentadiene was recovered. The residue in the bomb was worked up according to the catalyst used. The polymer was distilled at atmospheric pressure to collect a dimer fraction, b.p. 165–180°. The refractive indices for the four dimer fractions were: uncatalyzed, n_D^{20} 1.4676; anthraquinone, n_D^{20} 1.4674; sulfur dioxide, n_D^{20} 1.4672; sodium hydroxide, n_D^{20} 1.4686.

Mechanisms

The 1,4 to 1,3-isomerization of dienes, a three-carbon prototropic change (12), may occur by either a polar or a free radical mechanism. A hydrogen of the active methylene group shifts as a proton if the cleavage of the C-H bond is heterolytic (VI) and as a hydrogen atom if it is homolytic (VII). The hydrogen shift is 1,3 (allylic) as the π electrons of the double bond rearrange. The driving force for this reaction is the greater stability through resonance of the conjugated structure.

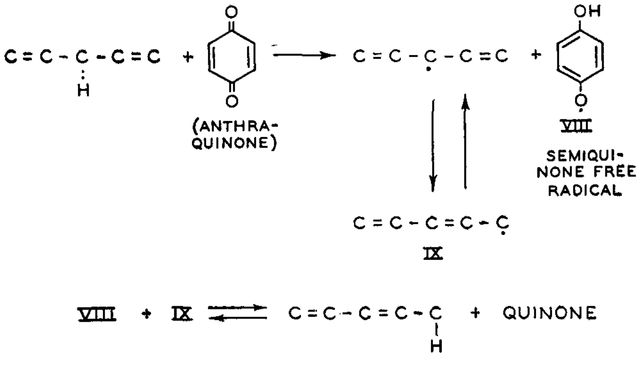


VI



VII

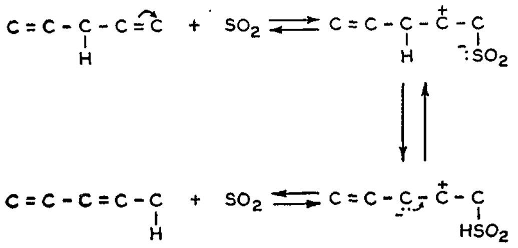
For the quinone catalyzed reactions a free radical mechanism appears most logical. A hydrogen atom from the active methylene group adds to an oxygen of the quinone to give an intermediate semiquinone free radical (VIII) which is resonance stabilized (15). This may be hydrogen-bonded to the pentadiene group (14, 15). Rearrangement of the pentadienyl radical to a 1,3-diene radical (IX) is followed by transfer of hydrogen from the semiquinone radical.



The greater catalytic activity of *beta*-chloro- and *beta*-carboxyanthraquinones compared to anthraquinone is probably due to the increased resonance stabilization of the intermediate semiquinone free radicals as a result of participation of unshared electrons from the substituent. The oxidizing power of naphthoquinones, which is a measure of catalytic activity (7, 17), is also increased by *beta* substitution of groups such as halogens and carboxyl (10).

When quinones are used with oils, conjugated isomers can be obtained (7, 17). In this work 1,3-pentadiene could not be isolated from catalyzed or non-catalyzed reactions. Therefore the conjugated hydrocarbon must be more reactive than the conjugated linoleate and linolenate in addition and other polymerization reactions.

For sulfur dioxide a polar mechanism seemed more probable than the free radical process proposed earlier (2) because a) sulfur dioxide is electrophilic; b) free radical conditions, light and peroxides, are absent; and c) when sulfur dioxide adds to an olefinic double bond by free radical addition, polysulfones are formed (16).



The highly polar nature of aqueous sodium hydroxide undoubtedly catalyzes a polar isomerization through the nucleophilic activity of the hydroxide ion.[4]

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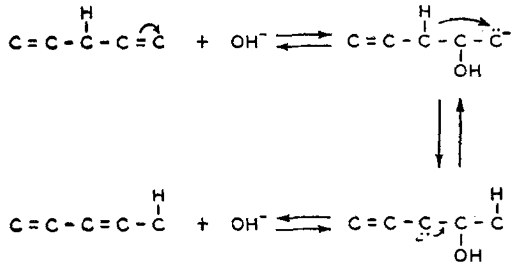
[4] The mode of addition shown for both sulfur dioxide and sodium hydroxide is the normal or Markownikoff addition. It is recognized however that the other vinyl group is electron-attracting, as shown by the zero dipole moment of styrene and the acid strengthening effect found in acids such as $CH_2{=}CH{-}CH_2{-}COOH$; and therefore reversed addition is a possibility.



Summary

Attempts to obtain 1,3-pentadiene from the uncatalyzed or catalyzed isomerization of 1,4-pentadiene at 200–250° were not successful. Dimers and higher polymers were formed, presumably by conjugation and addition reactions. The activity of several catalysts was measured by the yields of polymer. Sodium hydroxide was most effective, followed by sulfur dioxide, *beta*-chloroanthraquinone, anthraquinone-*beta*-carboxylic acid, and anthraquinone in order of decreasing activity. In 1,4 and 1,3-pentadiene mixtures, anthraquinone and sulfur dioxide catalyze slightly the formation of high polymers, but sodium hydroxide catalyzes both total polymer and dimer. The quinones are believed to function in 1,4 to 1,3-diene isomerization by a free radical mechanism, sulfur dioxide and sodium hydroxide by polar mechanisms. These results are related to the polymerization of non-conjugated drying oils.

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Dilatometric Investigations of Fatty Acid Methyl Esters[1]

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DILATOMETRY or the measurement of volume change with temperature is a means of studying physical changes in solid and liquid states in which adequate time may be allowed for attaining equilibrium. The melting dilations and coefficients of expansion of liquid and solid states have been reported for a number of glycerides (3, 5, 10, 11) and fatty acids (8, 9, 13).

A linear volume-temperature relationship has been found for the liquid state of all fatty acids and glycerides. However the same relation does not appear to be valid for the solid state of the same materials. Bailey and Singleton (3) used the temperature interval from —38°C. to —20°C. to calculate the coefficient of expansion of the solid state of a number of saturated glycerides. The validity of this temperature interval for the solid state was corroborated by calorimetric data and the coefficients varied in magnitude from 0.00019 to 0.00030 ml. per gram per degree. A number of unsaturated fatty acids were found to have coefficients greater than 0.00030 ml. per gram per degree in the temperature region above —38.87°C. On the basis of calorimetric data (where temperatures below the melting point of mercury could be used) and the large observed coefficients of expansion, these materials were not in a completely solid state even at —38°C., and an arbitrary coefficient of 0.00030 ml. per gram per degree was used to calculate the melting dilation.

An examination of existing dilatometric data on fatty acids and glycerides shows that there is a curvilinear relation between volume and temperature within a few degrees of the melting point. The relation between volume and temperature in the temperature interval from that of the completely solid state to the melting temperature has not been thoroughly investigated. Vaeck (12) reported an inflection point in the solidus line for cocoa butter at around —20°C. and a linear relation for volume-temperature from —20°C. to 14°C. Craig, Lundberg, and Geddes (5) reported two coefficients of expansion for the solid state of a number of saturated glycerides and indicated that the "break-point" might be related to the melting point of the particular glyceride.

The present work on methyl esters of fatty acids was undertaken to provide additional data on melting dilations and the coefficients of expansion of solid and liquid states. The methyl esters appeared to be especially appropriate for this type of study since they may be obtained easily in a state of high purity. Particular attention was directed to a study of the volume-temperature relation in the solid state.

Experimental

Methyl palmitate, methyl stearate, methyl arachidate, methyl behenate, and methyl oleate were purified by fractional distillation and fractional crystallization and their properties have been described elsewhere (4). The esters were thoroughly degassed under vacuum by agitation during repeated melting and solidification, and the saturated methyl esters were formed under vacuum into solid rods of 4 mm. diameter.

The gravimetric dilatometer described by Bailey and Kraemer (2) was modified for use in this study.

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