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Studies in the Terpene Series. XXX.^{1a} Thermal Reactions of 5-Ethyl- and of 4,5- and 5,6-Dimethyl-1,3-cyclohexadienes^{1b}

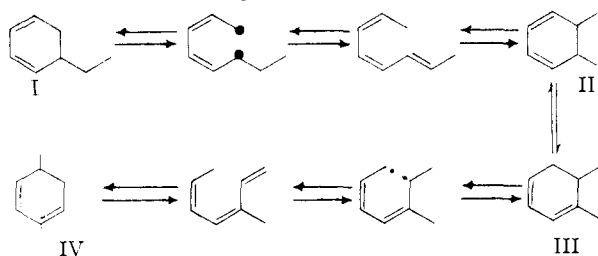
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5-Ethyl- and a mixture of 4,5- and 5,6-dimethyl-1,3-cyclohexadienes were synthesized and subjected to thermal reactions over quartz chips at 400–500° and at atmospheric pressure. The dienes underwent extensive endocyclic double bond migration at 400°. However, like the geminal dimethylcyclohexadienes they also underwent skeletal isomerization at 450–500° to form mixtures of ethyl-, 1,2- and 1,4-dimethyl-cyclohexadienes, accompanying some cracking and dehydrogenation. The 1,3-dimethyl isomers were not found in the thermal reaction mixture. Thus the previously proposed bialllyl biradical mechanism has been further substantiated.

It was shown² that *gem*-dimethyl conjugated cyclohexadienes undergo skeletal isomerization and a demethanation reaction when passed over heated quartz chips. It was thus found that 1,5,5- and 3,5,5-trimethyl-1,3-cyclohexadienes form at 500° 1,3,5-trimethyl-1,3-cyclohexadiene, mesitylene and *m*-xylene while 5,5-dimethylcyclohexadiene afforded mostly toluene, *m*-xylene and a mixture of 1,3-dimethylcyclohexadienes. At lower temperatures the shifting of double bonds was the predominant reaction. The skeletal isomerization of the geminal cyclohexadienes was explained by means of an intermediate formation of a bialllyl biradical.^{2,3}

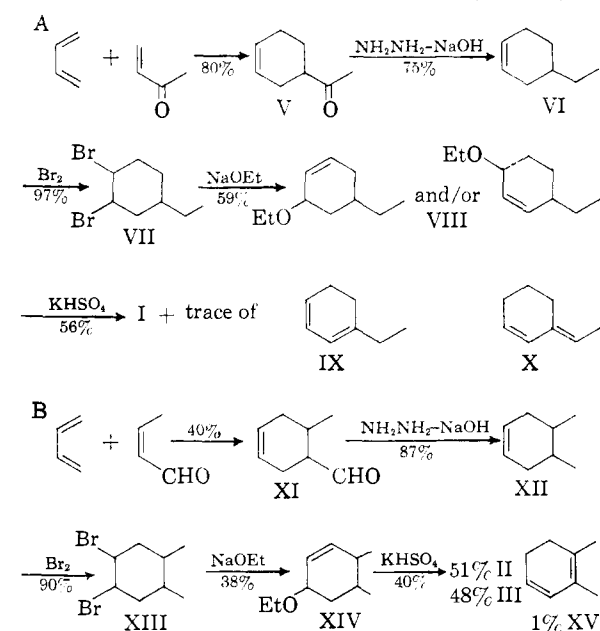
The present study was undertaken to determine whether non-geminal alkylcyclohexadienes can likewise undergo skeletal isomerization. For this purpose 5-ethyl-1,3-cyclohexadiene (I) and a mixture of 5,6- and 4,5-dimethyl-1,3-cyclohexadienes (II and III) were synthesized and subjected to a thermal reaction. It was anticipated that these compounds would form on pyrolysis a mixture composed of ethyl-, 1,2- and 1,4-dimethyl-cyclohexadienes according to the mechanism



Synthesis of the Cyclohexadienes and Analytical Procedure.—The dienes were synthesized according to the scheme V to XV.

4,5-Dimethylcyclohexene (XII) was shown to be a mixture of *cis* and *trans* isomers, since hydrogenation with a platinum oxide catalyst gave 23% *cis*- and 77% *trans*-dimethylcyclohexanes. A sample of 60% *cis*- and 40% *trans*-dimethylcyclohexane did not change its composition upon treatment with hydrogen under the same conditions. Because the formyl compound (XI) resulted from a *cis* addition,⁴ the *cis-trans* isomers of dimethylcyclohexenes

formed are probably due to the corresponding *cis-trans* mixture of crotonaldehyde used in the reaction. It is, however, not excluded that *cis-trans* isomerization might have also occurred during the Wolff-Kishner reduction of the formyl group.



The structure of the dienes was substantiated by hydrogenation to ethyl- and 1,2-dimethylcyclohexane, infrared and ultraviolet spectral analysis, and their reactions with dimethyl acetylenedicarboxylate (DMA reaction).⁵⁻⁷ The latter reaction was also used to show the type and/or amount of cyclohexadienes that were present in the thermal reaction products. The gases obtained from the DMA reaction were analyzed by vapor phase chromatography (Table IV). The liquid products from the DMA reaction were converted to phthalic anhydride derivatives and identified by infrared spectra. For this purpose 3- and 4-ethylphthalic anhydrides (XVII, XIX) were synthesized as indicated in the sequence XVI to XIX. It is interesting to note that the dehydrogenation with sulfur of XVI gave a mixture of phthalic anhydride and its 3-ethyl derivative, indicating

(1) (a) For paper XXIX of this series—see H. Pines and H. E. Eschinazi, *THIS JOURNAL*, **78**, 5930 (1956). (b) This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) H. Pines and R. H. Kozlowski, *ibid.*, **78**, 3776 (1956).

(3) H. Pines and J. Ryer, *ibid.*, **77**, 4370 (1955).

(4) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(5) K. Alder and H. F. Rickert, *Ann.*, **524**, 180 (1936).

(6) G. Dupont and R. Dulon, *Atti X congr. intern.*, **3**, 123 (1939); *C. A.*, **33**, 9312 (1939).

(7) E. D. Parker and L. A. Goldblatt, *THIS JOURNAL*, **72**, 2151 (1950).

TABLE I
 THERMAL REACTIONS OF CYCLOHEXADIENES.^a EXPERIMENTAL CONDITIONS AND RESULTS

Experiment	1	2	3	4	5
Diene, kind	I	I	I	II, III, XV	II, III, XV
Temp., °C.	400	450	500	400	450
Sample, g.	13.0	12.5	12.5	16.4	17.0
Gas product, ml.	50	340 ^b	1090 ^c	40	315 ^d
Mole, %	2	12	38	1	8
Liquid product, g.	12.6	12.1	11.4	15.9	15.6
Recovery, %	97	97	92	97	92
<i>n</i> ²⁰ _D	1.4778	1.4802	1.4858	1.4800	1.4812
λ_{\max} , m μ	261	261 ^e	232	263	263
	5000	3200	2600	4900	3900

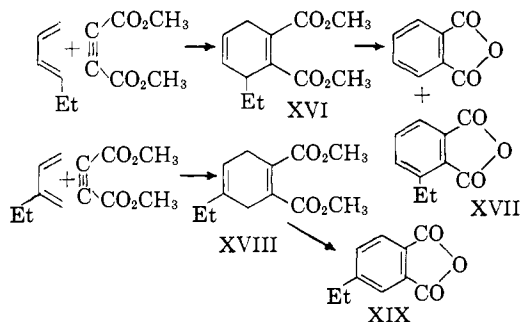
^a The cyclohexadienes were passed over quartz chips at a rate of 5.6 ml. per hour. ^b Methane 38%, ethylene 26%, ethane 36%. ^c Hydrogen 42%, methane 28%, ethylene 12%, ethane 18%. ^d Hydrogen 64%, methane 22%, ethylene 5%, ethane 8%. ^e Shoulders at 237 and 243 m μ .

 TABLE II
 SELECTIVE HYDROGENATION OF DIENES AND PYROLYSATES AND COMPOSITION OF AROMATIC HYDROCARBONS

Sample	Diene		From experiment				
	I	II, III, XV	1	2	3	4	5
Sample, g.	0.642	0.767	1.536	1.765	1.032	1.443	0.726
Platinum oxide, g.	0.016	0.047	0.051	0.055	0.043	0.044	0.032
Hydrogen absorbed, ml.	275	314	585	591	225	473	242
% Hydrogenation ^a	97	86	82	72	44	70	71
Product							
<i>n</i> ²⁰ _D	1.4338	1.4360	1.4410	1.4470	1.4624	1.4485	1.4520
λ_{\max} , m μ	262	263	262	262	262	263	263
ϵ	5	41	33	48	128	62	90
Saturated	97 ^b	89 ^c	88	77	43	84	68
Aromatics	2	11	12	23	57	16	32
Composition of aromatics, wt. %							
Benzene							4
Toluene					3		10
Ethylbenzene	100		100	100	80		3
<i>o</i> -Xylene		100			10	100	80
<i>p</i> -Xylene					7		3

^a Assuming molecular weight of alkylcyclohexadienes to be 108; based on 2 moles of hydrogen absorbed per mole of hydrocarbons. ^b Ethylcyclohexane. ^c 1,2-Dimethylcyclohexane.

the comparable probability of ethyl and hydrogen elimination. The isomeric XVIII, on the other hand, gave only 4-ethylphthalic anhydride.



Hydrogenation (Table II) and subsequent dehydrogenation (Table III) were employed to show the skeletons and amounts of components having that skeleton in the thermal reaction products. No attempt was made to determine the amounts of individual dienes since the dienes underwent 2-15% of disproportionation on hydrogenation with a platinum oxide catalyst. The extent of disproportionation was even greater with a palladium catalyst.

The infrared absorption band at 14.52 μ for *m*-xylene was used to exclude its presence in the aro-

matics ultimately obtained in the experiments with 1,2-dimethylcyclohexadiene, because its strongest characteristic band at 13.02 μ is disturbed by a close band of ethylbenzene. The presence of up to 1% of *m*-xylene in a synthetic mixture could be detected by a shoulder at 14.52 μ . In the experiments with ethylcyclohexadienes the concentration of ethylbenzene was so high that no conclusion could be drawn from infrared spectra concerning *m*-xylene. It was assumed, by analogy with 1,2-dimethylcyclohexadiene, that *m*-xylene was also absent.

Results of the Thermal Reactions. 5-Ethyl-1,3-cyclohexadiene (I).—Table I summarizes the pyrolysis experiments. This hydrocarbon underwent only endocyclic double bond migration at 400°. Hydrogenation of the reaction product gave 12% of ethylbenzene and 88% of ethylcyclohexane. The latter separated by chromatography gave only ethylbenzene upon dehydrogenation. The DMA reaction (Table IV) of the thermal reaction product gave a mixture of gases consisting of 90% of ethylene (corresponding to IX and XX, Table V) and 10% of 1-butene (corresponding to I).

At 450° skeletal isomerization was indeed observed. Hydrogenation of the product gave 77% of saturated compounds and 23% of ethylbenzene. Dehydrogenation of the saturated fraction gave

TABLE III

COMPOSITION OF ALKYL-CYCLOHEXANES OBTAINED FROM SELECTIVE HYDROGENATION OF PYROLYSATE (TABLE II), AS DETERMINED BY MEANS OF DEHYDROGENATION TO THE CORRESPONDING AROMATIC HYDROCARBONS

From experiment	1	2	3	4	5
Sample, g.	3.7	2.6	2.0	3.7	3.5
n_D^{20}	1.4329	1.4339	1.4371	1.4313	1.4323
Gas evolved, ml.	2080	1400	1190	2090	1900
Dehydrogenation, %	87	84	80	87	85
Liquid product, g.	3.2	2.1	1.6	2.7	2.9
n_D^{20}	1.4858	1.4840	1.4811	1.4972	1.4863
Composition of aromatics, wt. %					
Benzene			8		
Toluene		2	17		2
Ethylbenzene	100	90	51		2
<i>o</i> -Xylene		8	15	100	88
<i>p</i> -Xylene			9		8

TABLE IV

STRUCTURE OF ALKYL-CYCLOHEXADIENES AS DETERMINED BY REACTION WITH DIMETHYL ACETYLENEDICARBOXYLATE

Sample	Diene		From experiment				
	I	II, III, XV	1	2	3	4	5
Sample, g.	2.4	4.0	5.0	5.1	4.7	2.0	2.1
DMA, ^b g.	3.3	5.7	7.0	7.1	6.4	3.1	3.2
Gas produced, ml.	465	735	1000	800	425	460	345
Yield, ^a %	80	80	86	68	39	99	71
Composition of gas, ^c vol. %							
Ethylene		1	90	84	78	72	66
Propene		53		2	16	28	34
1-Butene	100		10	14	6		
<i>cis</i> -2-Butene		8					
<i>trans</i> -2-Butene		38					

^a Assuming molecular weight of 108. ^b Dimethyl acetylenedicarboxylate. ^c For relation between composition of gases and structure of alkylcyclohexadienes see Table V.

TABLE V

CLASSIFICATION OF ALKYL-CYCLOHEXADIENES FROM THE COMPOSITION OF GASES OBTAINED FROM THE REACTION WITH DIMETHYL ACETYLENEDICARBOXYLATE

Group	Gas produced	1,3-Cyclohexadiene
1	1-Butene	5-Ethyl- (I)
2	2-Butene	5,6-Dimethyl- (II)
3	Propene	4,5-Dimethyl- (III)
		2,5-Dimethyl- (IV)
4	Ethylene	4-Ethyl- (IX)
		1,2-Dimethyl- (XV)
		2-Ethyl- (XX)
		2,3-Dimethyl- (XXI)
		1,4-Dimethyl- (XXII)
		1-Methyl-
		2-Methyl-
		1,3-Cyclohexadiene
5	None	3-Ethylidenecyclohexene (X)

2% of toluene, 90% of ethylbenzene and 8% of *o*-xylene. The DMA reaction gave 84% of ethylene (corresponding to Group 4, Table V), 2% of propene (corresponding to Group 3) and 14% of 1-butene (corresponding to I).

At 500° skeletal isomerization and cracking occurred to a greater extent than at 450°, and dehydrogenation was also observed. Hydrogenation gave 43% of saturated compounds and 57% of aromatics consisting of 3% of toluene, 80% of ethylbenzene, 10% of *o*-xylene and 7% of *p*-xylene. Dehydrogenation of the saturated compounds gave 8% of benzene, 17% of toluene, 51% of ethyl-

benzene, 15% of *o*-xylene and 9% of *p*-xylene. The DMA reaction gave 78% of ethylene (corresponding to Group 4), 16% of propene (corresponding to Group 3) and 6% of 1-butene (corresponding to I).

The liquid products from the DMA reaction of the thermal reaction products at all temperatures studied gave mixtures of phthalic anhydride and its 3- and 4-ethyl derivatives.

The production of more *o*-xylene (corresponding to 1,2-dimethylcyclohexadienes) than *p*-xylene (corresponding to the 1,4-isomers) is reasonable inasmuch as the former is the necessary intermediate for the production of the latter according to the proposed mechanism.

Dimethylcyclohexadienes.—A mixture consisting of 8% of *cis*- and 38% of *trans*-5,6-dimethyl-, 53% of 4,5-dimethyl- and 1% of 1,2-dimethyl-1,3-cyclohexadienes (II, III, XV) was used for thermal reaction. At 400° only endocyclic double bond migration occurred as in the case of the 5-ethyl isomer. Hydrogenation gave 16% of *o*-xylene and 84% of 1,2-dimethylcyclohexane. Dehydrogenation of the saturated fraction gave *o*-xylene. The DMA reaction gave 72% of ethylene (corresponding to XV and XXI) and 28% of propene (corresponding to III).

At 450°, however, skeletal isomerization, dehydrogenation and cracking were observed. Hydrogenation gave 68% of saturated compounds and 32% of aromatics consisting of 3% ethylbenzene, 80% of *o*-xylene and 3% of *p*-xylene. The

saturated fraction gave upon dehydrogenation 2% each of toluene and ethylbenzene, 88% of *o*-xylene and 8% of *p*-xylene. The DMA reaction gave 66% of ethylene (corresponding to Group 4) and 34% of propene (corresponding to Group 3).

The production of more *p*-xylene than ethylbenzene perhaps reflects the greater stability of the 1,4-dimethylcyclohexadienes than the ethyl isomers. This assumption is reasonable in view of the greater stability of 1,4-dimethyl- than ethylcyclohexane on the one hand and of *p*-xylene than ethylbenzene on the other.⁸ It is seen from the favored production of ethylene over the others in all DMA reactions that cyclohexadienes more substituted at the double bonds are the more stable.

Conclusion.—The results described above indicate that even non-geminal alkylcyclohexadienes can undergo skeletal isomerization at elevated temperatures. The validity of the proposed biallyl biradical mechanism has therefore been further substantiated. It should be noted that the mechanism predicted no formation of 1,3-dimethylcyclohexadienes, the absence of which was also confirmed by the present study.

Experimental

A. Synthesis of Materials. 1. **5-Ethyl-1,3-cyclohexadiene (I).** a. 4-Acetylcyclohexene (V) was prepared from butadiene and methyl vinyl ketone according to Petrov⁹ in 80% yield. The ketone distilled at 185–186°, n_D^{20} 1.4694; its semicarbazone melted at 165–166°, and its *p*-nitrophenylhydrazone at 142–143° (lit.⁹ 165–166° and 142–143°, respectively).

b. 4-Ethylcyclohexene (VI) was prepared from ketone V by the Huang-Minlon modification¹⁰ of Wolff-Kishner reduction in 75% yield. The olefin distilled at 133°, n_D^{20} 1.4475 (lit.¹¹ 133° and 1.449, respectively); infrared spectrum (in μ) taken in a 0.041-mm. NaCl cell: 3.35s, 3.50s, 3.81w, 6.06s, 6.17w, 6.85s, 6.97s, 7.26s, 7.49m, 7.65w, 7.77w, 8.01m, 8.21w, 8.37m, 8.74s, 8.89w, 9.24w, 9.54w, 9.65m, 9.89w, 10.43m, 10.72m, 10.95s, 11.03s, 11.32w, 11.51s, 11.72w, 12.35m, 12.98s, 13.80s, 15.32s. The symbols signify: s, strong; m, medium; and w, weak absorption.

c. 1,2-Dibromo-4-ethylcyclohexane (VII) was prepared by bromination of 4-ethylcyclohexene in 97% yield. A procedure of Hofmann and Damm¹² was adopted for this bromination and the subsequent reactions with sodium ethoxide and with potassium bisulfate leading to dienes. The new dibromide distilled at 109–110.5° (5.5 mm.), n_D^{20} 1.5332, d_4^{20} 1.5837.

Anal. Calcd. for $C_8H_{14}Br_2$: C, 35.59; H, 5.23. Found: C, 35.80; H, 5.19.

d. Ethylcyclohexenyl ethyl ether (VIII) was prepared in 50% yield by reaction of dibromide VII with sodium ethoxide. The new ether distilled at 81–84° (17 mm.), n_D^{20} 1.4520–1.4525, d_4^{20} 0.9134.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.76; H, 11.36.

A 16% yield of 5-ethyl-1,3-cyclohexadiene was also obtained.

e. 5-Ethyl-1,3-cyclohexadiene (I) was prepared by the reaction of ether VIII with potassium bisulfate in 42% yield. Vapor phase chromatography of the product indicated that it contained a trace of probably 1-ethyl-1,3-cyclohexadiene (IX) and 3-ethylidenecyclohexene (X). The latter was revealed by a shoulder at 232 μ (calcd. λ_{max} 232 μ) in the ultraviolet spectrum. The pure I

was obtained by chromatography of the crude product on silica gel. The new diene distilled at 128–129°, n_D^{20} 1.4676, d_4^{20} 0.8354, $M_R D$ 36.03 (calcd. 36.01), λ_{max} 259 μ (in 2,2,4-trimethylpentane), ϵ 4,300; infrared spectrum (in μ) taken in a 0.041-mm. NaCl cell: 3.34s, 3.50s, 5.26w, 5.86m, 6.14m, 6.33m, 6.83s, 7.00m, 7.10m, 7.25s, 7.57w, 7.69w, 7.75w, 7.85w, 8.02w, 8.29m, 8.60m, 8.90w, 9.01w, 9.15w, 9.40m, 9.60m, 10.08s, 10.49s, 10.71m, 10.97s, 11.58m, 12.43s, 12.70s, 13.23s, 14.80s.

Anal. Calcd. for C_8H_{12} : C, 88.82; H, 11.14. Found: C, 88.95; H, 10.80.

2. **5,6- and 4,5-Dimethyl-1,3-cyclohexadiene (II and III).** a. 4-Methyl-5-formylcyclohexene (XI) was prepared from butadiene and crotonaldehyde in 40% yield according to Diels and Alder.¹³ The aldehyde distilled at 175–176° (744 mm.), n_D^{20} 1.4680, and its semicarbazone melted at 168° (lit.¹³ 168°).

b. 4,5-Dimethylcyclohexene (XII) was prepared by Huang-Minlon modification¹⁰ of Wolff-Kishner reduction of aldehyde XI in 87% yield. The new olefin distilled at 126°, n_D^{20} 1.4441, d_4^{20} 0.8073, $M_R D$ 36.19 (calcd. 36.48).

Anal. Calcd. for C_8H_{14} : C, 87.20; H, 12.80. Found: C, 87.25; H, 12.21.

Hydrogenation of the olefin with a platinum oxide catalyst at room temperature and atmospheric pressure gave 23 and 77%, respectively, of *cis*- and *trans*-1,2-dimethylcyclohexanes.

c. 1,2-Dibromo-4,5-dimethylcyclohexane (XIII) was prepared by bromination of olefin XII in 90% yield. The new dibromide distilled at 117–119° (6.5 mm.), n_D^{20} 1.5317–1.5321, d_4^{20} 1.5792.

Anal. Calcd. for $C_8H_{14}Br_2$: C, 35.59; H, 5.23. Found: C, 36.21; H, 5.49.

d. 3-Ethoxy-5,6-dimethylcyclohexene (XIV) was prepared by reaction of dibromide XIII with sodium ethoxide in 38% yield. The new ether distilled at 100–102° (50 mm.), n_D^{20} 1.4500, d_4^{20} 0.8738.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.95; H, 11.71.

A 20% yield of dimethylcyclohexadienes was also obtained.

e. Dimethylcyclohexadienes were prepared in 40% yield by reaction of ether XIV with potassium bisulfate. Chromatography on silica gel of the crude product gave as the first fraction (10%) a mixture of *cis*- and *trans*-5,6-dimethyl-1,3-cyclohexadienes, distilling at 117–119°, n_D^{20} 1.4614, d_4^{20} 0.8228, $M_R D$ 36.08 (calcd. 36.01), λ_{max} 260 μ (in 2,2,4-trimethylpentane), ϵ 4300.

Anal. Calcd. for C_8H_{12} : C, 88.82; H, 11.14. Found: C, 88.95; H, 10.77.

The second fraction (90%) from the chromatography distilled at 117–130°, n_D^{20} 1.4648–1.4770, d_4^{20} 0.8297, λ_{max} 261 μ , ϵ 5370. This was used for the thermal reaction.

3. **3-Ethylphthalic Anhydride (XVII).** a. 1,3-Hexadiene was prepared by dehydrating 1-hexene-3-ol with potassium bisulfate according to Alder and Schumacher.¹⁴ The diene boiled at 73–76°, λ_{max} 225 μ , ϵ 36,000.

b. Dimethyl 3,6-dihydro-3-ethylphthalate (XVI).—A mixture of 6.7 g. of 1,3-hexadiene, 14.7 g. of dimethyl acetylenedicarboxylate, 0.1 g. of hydroquinone and 25 ml. of toluene was held at 145° in an autoclave for 12 hr. The toluene was distilled off leaving 20.8 g. of residue. This residue was distilled twice to give 9.9 g. (54% yield) of the adduct, b.p. 119–121° (2 mm.), n_D^{20} 1.4885, d_4^{20} 1.1138 (new compound).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.32; H, 6.94.

c. **Dehydrogenation of the Adduct XVI.**—A mixture of 3.9 g. of the adduct above and 0.58 g. of sulfur was heated up to 250° giving 275 ml. of gas in 30 min. The reaction mixture was refluxed with 2.1 g. of potassium hydroxide in 25 ml. of 80% ethanol for an hour. The hydrolysis mixture was evaporated, the residue diluted with water, and extracted with ether. The water solution was acidified with concd. hydrochloric acid and extracted with ether. The ether solution was evaporated and the residue refluxed with 25 ml. of thionyl chloride for an hour. The reaction mixture was evaporated and the residue sublimed at 190° (2

(8) J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947).

(9) A. A. Petrov, *J. Gen. Chem., U. S. S. R.*, **11**, 309 (1941).

(10) Huang-Minlon, *This Journal*, **68**, 2487 (1946).

(11) "Selected Values of Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Table 19a, October 31, 1950.

(12) F. Hofmann and P. Damm, *Mitt. Kohlenforschungsmit. Breslau*, **2**, 113, 127 (1925); *C. A.*, **22**, 1249 (1928).

(13) O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

(14) K. Alder and M. Schumacher, *ibid.*, **571**, 150 (1951).

mm.). The sublimate weighing 1.6 g. (53% yield) was recrystallized from ether-hexane twice to give 0.5 g. of phthalic anhydride, m.p. and mixed m.p. 127°. Its identity was further confirmed by infrared spectra.

Anal. Calcd. for $C_8H_4O_3$: C, 65.01; H, 2.72. Found: C, 65.21; H, 2.66.

The mother liquid from the above recrystallization was evaporated and the residue recrystallized twice from ether-hexane to give 0.4 g. of 3-ethylphthalic anhydride, m.p. 97–98° (lit.¹⁴ 98°). The infrared absorption band at 14.0 μ characteristic of phthalic anhydride was very faint in its infrared spectrum.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58. Found: C, 68.64; H, 4.41.

4. 4-Ethylphthalic Anhydride (XIX). a. 2-Ethylbutadiene was prepared by pyrolysis of 2-ethyl-3-acetoxy-1-butene according to Marvel and Williams.¹⁵ The diene boiled at 66–68.5°, n_D^{20} 1.4325 (lit.¹⁵ 65–66°, 1.4325).

b. Dimethyl 3,6-dihydro-4-ethylphthalate (XVIII) was prepared from 2-ethylbutadiene as in 3-b in 45% yield. The adduct had b.p. 135–136° (3 mm.), n_D^{20} 1.4928, d_4^{20} 1.1138 (new compound).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.60; H, 7.20.

c. Dehydrogenation of the adduct XVIII was performed as in 3-c, and 4-ethylphthalic anhydride was obtained in 68% yield (new compound), m.p. 76–77°; mixed m.p. with the 3-ethyl isomer, 66–69°. Infrared spectrum showed the absence of phthalic anhydride.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58. Found: C, 68.49; H, 4.46.

B. Apparatus and Procedure. Apparatus.—The apparatus consisted of a Pyrex reaction tube having a reaction

(15) C. S. Marvel and J. L. R. Williams, *THIS JOURNAL*, **70**, 3842 (1948).

zone of 2.0 cm. outside diameter heated by a thermostatically controlled vertical furnace. The dienes were introduced into the tube, packed with 32 ml. of about 1/8 inch quartz chips in the reaction zone, by means of a motor driven syringe at a rate of 5.6 ml./hr. The lower end of the reaction zone was attached to a liquid receiver, which in turn was attached through Dry Ice-acetone cooled trap to a gas collecting bottle.

Infrared spectra were taken on a Baird double beam recording infrared spectrophotometer having rock salt optics.¹⁶

Ultraviolet spectra were taken on a Cary model 11 recording quartz spectrophotometer.¹⁷

Hydrogenations were carried out with a micro-hydrogenation set-up using a platinum oxide catalyst at room temperature and atmospheric pressure.

Vapor phase chromatographic analysis was made on a Podbielniak chromacon.¹⁸ A 6-ft. column packed with 44% of fluorene-picric acid (1:1) on 35–60 mesh fire-brick (density 59 g./100 ml.) was used for analysis of aromatics at 80°. A 12-ft. column packed with 30% of tricresyl phosphate on 35–60 mesh fire-brick (density 59 g./100 ml.) was used for gas analysis. A 6-ft. column of the same kind was used for general purposes. Helium was used as the carrier gas.

Dehydrogenation¹⁹ was done by passing saturated samples over 10 ml. of a platinum-alumina catalyst at 290°.

Reaction with dimethyl acetylenedicarboxylate was done according to Parker and Goldblatt.⁷ The gaseous products were analyzed by vapor phase chromatography. The liquid products were converted into phthalic anhydrides and identified by infrared spectra.

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(17) Allied Physics Corporation, Pasadena, Calif.

(18) Chromacon, Series 9175, Podbielniak, Inc., Chicago, Ill.

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The Absolute Configuration of Plant Growth Substances—Partially Hydrogenated 1-Naphthoic Acids¹

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It was shown in the previous papers that (–)-1,2,3,4-tetrahydro-1-naphthoic acid (I), (+)-1,4-dihydro-1-naphthoic acid (II) and (+)-1,2-dihydro-1-naphthoic acid (III), having greater plant growth activities than their respective antipodes, possess the same configuration around the asymmetric carbon atom. Recently Westman established the absolute configurations of I and α -phenylglutaric acid (V). The authors have confirmed this by another method: (+)-V has been correlated through (+)-2-phenylpentane (IX) to (+)- α -phenylvaleric acid (X) of known absolute configuration, and (+)-V to (+)-III; (–)-I, (+)-II and (+)-III have been shown to possess the same configuration as the physiologically more active enantiomers of the other plant growth substances. The absolute configurations of the intermediates of the transformations have also been determined.

Optically active α -(3-indole)-propionic acid,² reported by Kögl in 1937, provided the first example of a synthetic plant growth substance having an asymmetric carbon atom whose antipodes showed different plant growth activities. Since about 1950 a number of studies on the relationship between plant growth activities of optical antipodes and their configurations have been carried out. It has been found that α -aryloxyalkylcarboxylic acids,^{3–5}

α -arylalkylcarboxylic acids^{5–7} and 1-indancarboxylic acid⁸ also show differences between their antipodes, and the physiologically more active enantiomers of these acids possess the same configuration,^{8–11} the same arrangement of four substituents around the central asymmetric carbon atom: aromatic ring system, carboxyl group, alkyl chain and hydrogen atom. This arrangement is shown by the projection formula¹²

(1) Abstracted partly from the Master Thesis submitted by K. Kawazu, March, 1957, partly reported in *Kagaku-no-Ryoiki (J. Japan. Chem.)*, **12**, 2 (1958), and presented in the monthly meeting of Kansai Branch of the Agricultural Chemical Society of Japan, Kyoto, April 19, 1958.

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(3) M. S. Smith and R. L. Wain, *Proc. Roy. Soc. (London)*, **B139**, 118 (1951).

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(12) This configuration was assigned to the D-series by Fredga.¹¹ whether R = O-aryl or aryl. According to the rules proposed by