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Study of the Terpene Series. XXVIII.¹ Thermal Reactions of *gem*-Dimethyl Type Conjugated Cyclohexadienes²

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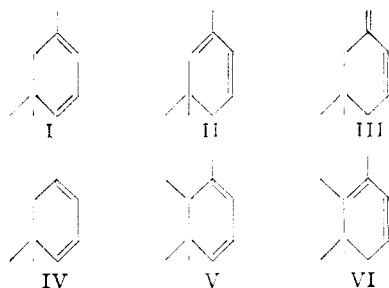
The thermal reactions of 1,5,5- and 3,5,5-trimethyl-1,3-cyclohexadiene, 5,5-dimethyl-3-methylenecyclohexene and 5,5-dimethyl-1,3-cyclohexadiene over quartz chips at 300–500° and atmospheric pressure were studied. It was found that at 300–400°, 1,5,5- and 3,5,5-trimethyl-1,3-cyclohexadienes reversibly isomerize. At 500° a mixture of the latter dienes yielded mostly *m*-xylene, mesitylene and 1,3,5-trimethyl-1,3-cyclohexadiene. 5,5-Dimethyl-3-methylenecyclohexene was found to be stable at 400°, whereas at 500° it gave only 5–10% reaction, the products of which were *endo*-cyclohexadiene isomers and their thermal reaction products as given above. 5,5-Dimethyl-1,3-cyclohexadiene at 500° afforded mostly toluene, *m*-xylene and conjugated 1,3-dimethylcyclohexadienes. A bialllyl biradical mechanism is proposed to explain the various products of the reactions.

The presence and structures of α - and β -pyronene, obtained by the pyrolysis of α -pinene, have been elucidated by Dupont and Dulou.⁴ It was shown by Goldblatt and Palkin⁵ that the pyrenes are formed by the recyclization of alloöcimene, one of the principal products obtained in α -pinene pyrolysis. The presence of other hydrocarbons in the alloöcimene pyrolysate was noted and identified.⁶

Recently, a mixture consisting of the pyrenes and 1,5-dimethyl-5-ethyl-1,3-cyclohexadiene, obtained from alloöcimene isomerization, was pyrolyzed and a biradical mechanism was suggested to explain the skeletal isomerization.⁷

In order to test the validity of such a mechanism, a study of the thermal reactions of C₉H₁₄ and C₈H₁₂ *gem*-dimethyl type conjugated cyclohexadienes has been undertaken. It was judged expedient to prepare compounds similar to α - and β -pyronene (V and VI, respectively) but with fewer carbon atoms in order to make identification of the thermal reaction product mixture simpler.

Synthesis of the Cyclohexadienes.—The following *gem*-dimethyl type conjugated cyclohexadienes were synthesized: 1,5,5- and 3,5,5-trimethyl-1,3-cyclohexadiene (I and II, respectively), 5,5-dimethyl-3-methylenecyclohexene (III) and 5,5-dimethyl-1,3-cyclohexadiene (IV).



(1) For paper XXVII of this series see H. Pines and H. E. Eschinazi, *THIS JOURNAL*, **78**, 1178 (1956).

(2) Taken in part from the dissertation submitted by R. H. Kozlowski to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree in November, 1955.

(3) Universal Oil Products Company Predoctoral Fellow, 1953–1955.

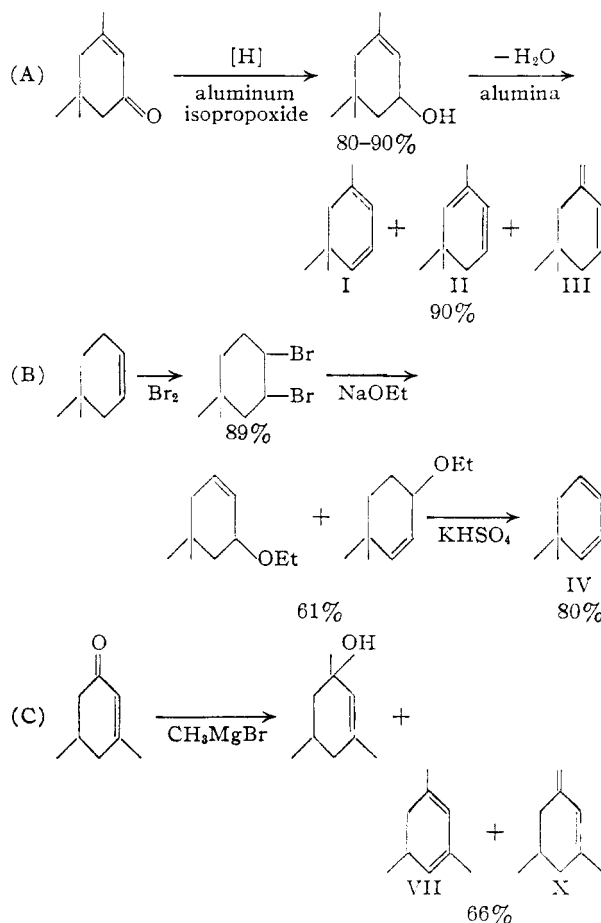
(4) (a) G. Dupont and R. Dulou, *Compt. rend.*, **201**, 219 (1935); (b) G. Dupont and R. Dulou, *Atti X Congr. intern.*, **3**, 123 (1939); *C. A.*, **33**, 9312 (1939).

(5) L. A. Goldblatt and S. Palkin, *THIS JOURNAL*, **66**, 635 (1944).

(6) E. D. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950).

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

The dienes I to IV and 1,3,5-trimethyl-1,3-cyclohexadiene (VII) were prepared according to the schemes

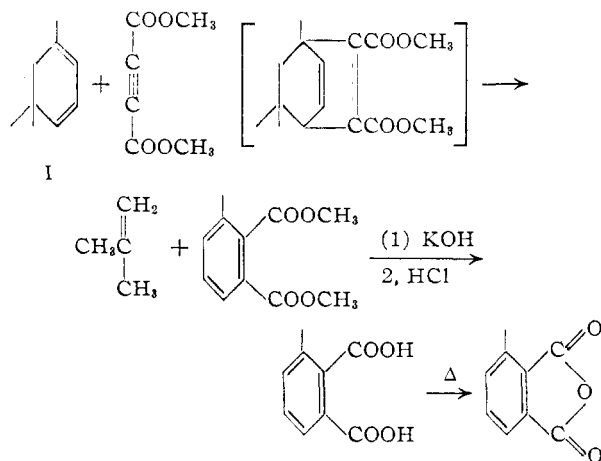


The structures of these dienes were substantiated by hydrogenation to known cyclohexane compounds, infrared and ultraviolet spectral analysis, and their reaction with the dimethyl ester of acetylenedicarboxylic acid.

The Diels–Alder reaction of 1,3-cyclohexadienes with dimethyl acetylenedicarboxylate was used extensively throughout the work to show the type and/or amount of cyclohexadienes that were present. Alder and Rickert⁸ found that the adducts

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

of the diethyl ester of acetylenedicarboxylic acid with cyclohexadienes decompose on heating to give ethylene and the diethyl ester of phthalic acid or homologs of these compounds depending on the cyclohexadiene used. Dupont and Dulou^{4b} used dimethyl acetylenedicarboxylate in their study of the pyrenenes. Parker and Goldblatt⁶ used this reaction to determine the structures of the many dienes obtained in their study of the thermal isomerization of alloöcimene. Using diene I as an example, the reaction is illustrated by the scheme



The gases obtained from this type of reaction were

Results of the Thermal Reactions
1,5,5- and 3,5,5-Trimethyl-1,3-cyclohexadienes (I and II).—These dienes underwent a reversible isomerization of the double bond system when passed over quartz chips at 300–450° and at H.L.S.V.⁹ of 0.4. The ratio of the dienes obtained in the mixture depended on the temperature of the reaction. Table I summarizes the results of six experiments carried out in a flow system at temperatures from 300–450°. In none of the thermal isomerization reactions stated above was there any indication of 5,5-dimethyl-3-methylenecyclohexene (III) being formed.

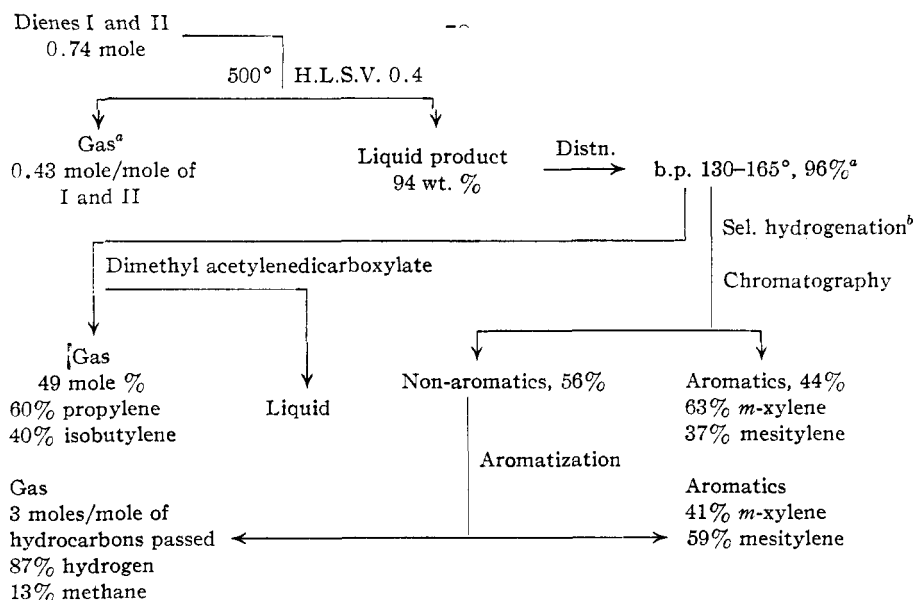
TABLE I
THERMAL REACTION OF A MIXTURE OF DIENE I AND II AT 300–450°

Expt.	Composition of dienes charged ^a I	Composition of dienes charged ^a II	Temp., °C.	Composition of recovered product I	Composition of recovered product II
1	80	20	300	76	24
2	77	23	350	63	37
3	34	66	350	53	47
4	70	30	400	55	45
5	33	67	400	56	44
6	53	47	450	26	50 ^b

^a Calculated by means of infrared spectroscopy, accuracy $\pm 5\%$. ^b The remaining 24% consisted of 1,3,5-trimethyl-1,3-cyclohexadiene and *m*-xylene.

When a mixture of dienes I and II was passed over quartz chips at 500° gaseous and liquid prod-

TABLE II
THERMAL REACTION OF A MIXTURE OF DIENES I AND II. OUTLINE OF ANALYTICAL PROCEDURE



^a Composition is given in Table III. ^b One mole of hydrogen was absorbed per mole of hydrocarbons charged.

identified by mass spectral analysis. The dimethyl esters of the phthalic acids were identified by conversion to their corresponding acids and anhydrides.

The physical properties of the dienes, their infrared and ultraviolet spectral data and the results of their reactions with dimethyl acetylenedicarboxylate are given in tabular form in the Experimental Part.

ucts were obtained. The procedure used for the investigation of the liquid product and the results obtained are shown schematically in Table II. The composition of the liquid and gaseous products is summarized in Table III.

The liquid product was fractionally distilled under a blanket of nitrogen at atmospheric pres-

(9) Hourly liquid space velocity or volume of liquid passed per volume of contacting medium per hour.

TABLE III

RESULTS OF THE THERMAL REACTION OF A MIXTURE OF CONJUGATED 1,1,3-TRIMETHYLCYCLOHEXADIENES (I AND II)

A. Composition of Liquid Product ^a			B. Composition of Gaseous Product ^c	
	Compound	Wt. % ^b	Gas ^d	Mole %
I + II	1,1,3-Trimethylcyclohexadienes	22	Hydrogen	18
			Methane	73
VII	1,3,5-Trimethyl-1,3-cyclohexadiene	30	Ethylene	6
			Ethane	3
VIII	<i>m</i> -Xylene	28		
IX	Mesitylene	16		
X	1,5-Dimethyl-3-methylenecyclohexene	4		

^a The liquid product does not include 4 wt. per cent. of high and low boiling material. ^b Accuracy $\pm 2\%$. ^c The gas produced amounted to 0.43 mole per mole of dienes passed. ^d Analyzed by means of a mass spectrograph.

sure. Ultraviolet and infrared spectral analyses were used to follow the course of the fractionation. Many of the fractions exhibited a maximum absorption in the ultraviolet range from 260–270 $m\mu$. The maximum extinction coefficient (absorptivity)¹⁰ in units of absorbance per gram per liter per centimeter of light path, symbolized by $A^{g/l}_{1cm}$ is plotted in Fig. 1, together with boiling point and refractive index, as a function of weight per cent. of the charge distilled.

A representative sample of the distilled liquid product was allowed to react with an excess of dimethyl acetylenedicarboxylate which afforded a liquid and gaseous product, the latter consisting of isobutylene and propylene. Since the liquid product obtained from this reaction was probably a mixture of esters, it was not further investigated. The fact that the reaction proceeded to an extent of 49% indicated that there was at least that percentage of *endo*-cyclohexadienes in the former mixture. The composition of the gaseous product indicated the presence of dienes I and/or II and 1,3,5-trimethyl-1,3-cyclohexadiene (VII). This was confirmed by further chemical investigation

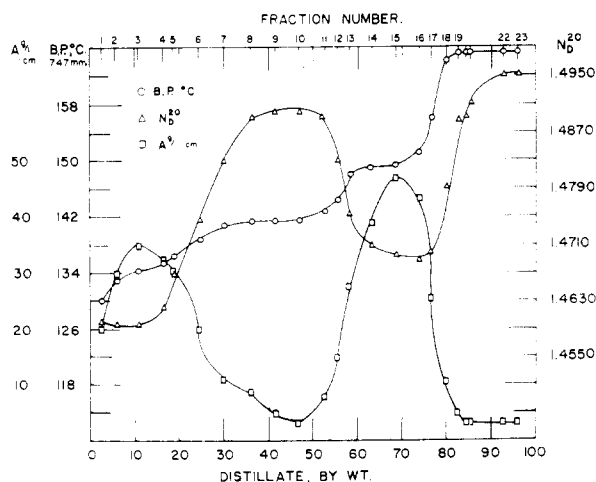


Fig. 1.—Fractional distillation of the thermal reaction product of dienes I and II at 500°.

(10) H. K. Hughes, *et al.*, *Anal. Chem.*, **24**, 1349 (1952).

along with the ultraviolet absorption characteristics of the liquid product and its various fractions. In the latter case, Woodward's Rule¹¹ allowed an insight as to the type of dienes present.

A composite mixture of the above distilled liquid product of the thermal reaction was selectively hydrogenated in the presence of copper chromite catalyst which converted only the unsaturated hydrocarbons to saturated ones, while the aromatic hydrocarbons remained unchanged. The amount of hydrogen uptake indicated that about 50% of the charge consisted of trimethylcyclohexadienes.

The aromatic hydrocarbon fraction which was separated chromatographically from the saturated hydrocarbons was composed, according to infrared spectral analysis, of *m*-xylene and mesitylene.

A comparison of the infrared spectrum of the non-aromatic hydrocarbons obtained from the chromatographic separation with those of 1,1,3- and 1,3,5-trimethylcyclohexane indicated the presence of only these hydrocarbons in the mixture.

These non-aromatic hydrocarbons were aromatized at 500° using chromia-alumina as a catalyst.¹² The gas evolved consisted of methane and hydrogen. The aromatic hydrocarbons derived from this reaction were composed of *m*-xylene and mesitylene. The combination of the above results indicated that 40 ± 2 wt. % of 1,1,3-trimethylcyclohexane and 60 ± 2 wt. % of 1,3,5-trimethylcyclohexane were in the non-aromatic portion of the chromatographic separation.

Further confirmation of the presence of diene VII was obtained by allowing a representative sample of cuts boiling between 148° and 152° to react with dimethyl acetylenedicarboxylate. Mass spectral analysis indicated the gaseous degradation product to be propylene. The liquid product was shown to be the dimethyl ester of 3,5-dimethylphthalic acid. Also, the infrared spectrum of cut boiling at 140° was shown to be identical with that of 1,3,5-trimethyl-1,3-cyclohexadiene (VII) independently synthesized.

Indication of the presence of 1,5-dimethyl-3-methylenecyclohexene (X) in cuts boiling at 156–164° of Fig. 1 was shown by the maximum absorption peak at 235 $m\mu$ and strong peaks in the 11–12 μ region.

5,5-Dimethyl-3-methylenecyclohexene.—At 400°, under the same conditions as used above for the thermal reactions, diene III isomerized very little, if at all, to diene I and/or II.

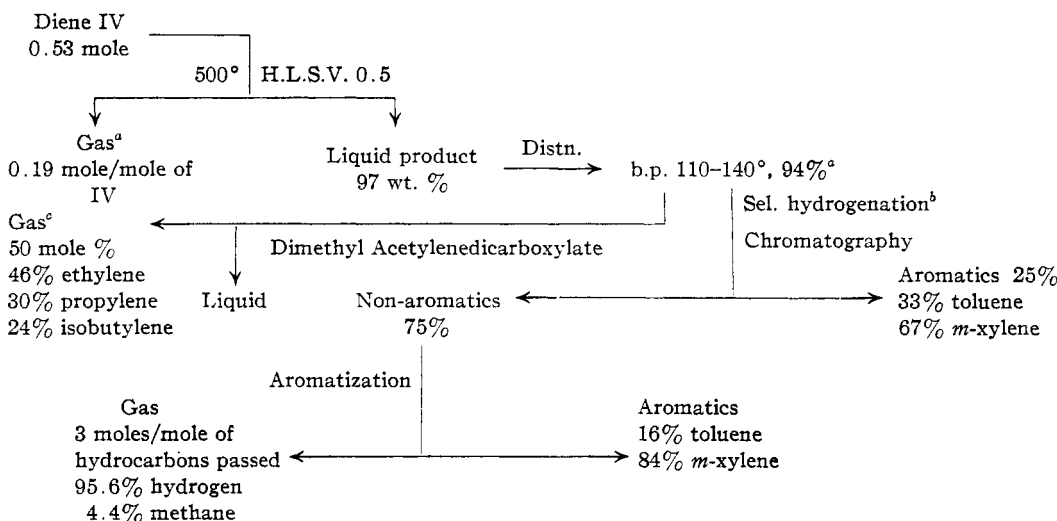
The reaction at 500° under similar conditions gave a gaseous and liquid product. The gas amounting to about 0.09 mole per mole of the diene was shown to consist of methane and hydrogen in the ratio of about 2 to 1. The infrared spectrum of the liquid product indicated the possible presence of small amounts of dienes I and/or II, mesitylene, *m*-xylene and diene VII.

5,5-Dimethyl-1,3-cyclohexadiene.—When diene IV was passed at 500° over quartz chips and at an H.L.S.V. of 0.5, liquid and gaseous products were formed. The results are given in Tables IV and V.

(11) R. B. Woodward, *This Journal*, **64**, 72 (1942).

(12) H. Pines, E. F. Jenkins and V. N. Ipatieff, *ibid.*, **75**, 6226 (1953).

TABLE IV
THERMAL REACTION OF 5,5-DIMETHYL-1,3-CYCLOHEXADIENE. OUTLINE OF ANALYTICAL PROCEDURE



^a Composition is given in Table V. ^b 1.5 Moles of hydrogen was absorbed per mole of hydrocarbons charged. The calculation was based on the data given in Table VI.

TABLE V
RESULTS OF THE THERMAL REACTION OF 5,5-DIMETHYL-1,3-CYCLOHEXADIENE(IV) AT 500°

A. Composition of Liquid Product ^a		
Compound		Wt. % ^b
IV	5,5-Dimethyl-1,3-cyclohexadiene	15
XI	Toluene	8
VIII	<i>m</i> -Xylene	17
XII	1,5-Dimethyl-1,3-cyclohexadiene	20
XIII	3,5-Dimethyl-1,3-cyclohexadiene	28
XIV	1,3-Dimethyl-1,3-cyclohexadiene	12
XV	1-Methyl-3-methylenecyclohexene	
XVI	5-Methyl-3-methylenecyclohexene	
B. Composition of Gaseous Product ^a		
Gas ^d	Mole %	
Hydrogen	35	
Methane	61	
Ethane	3	
Propane	1	

^a The liquid product does not include 6 wt. per cent. of high and low boiling material. ^b Accuracy $\pm 2\%$. ^c The gas produced amounted to 0.19 mole per mole of dienes passed. ^d Analyzed by means of a mass spectrograph.

The liquid product amounting to 97% of the reactant passed was distilled and the fractionation followed by means of infrared and ultraviolet analysis.

Many of the cuts exhibited a maximum absorption in the ultraviolet range from 255–265 μ . The maximum extinction coefficient for this wave length is plotted in Fig. 2, together with boiling point and refractive index, as a function of weight per cent. of distillate.

The distilled liquid product was analyzed by reaction with dimethyl acetylenedicarboxylate, selective hydrogenation, chromatography and catalytic aromatization. The procedure used in investigating the reaction products is shown schematically in Table IV.

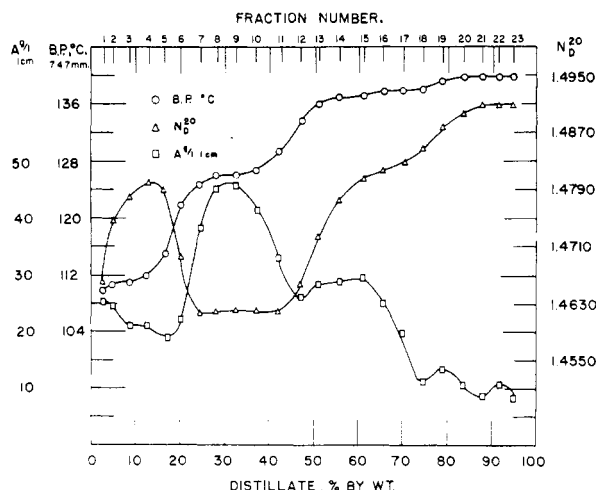


Fig. 2.—Fractional distillation of the thermal reaction product of 5,5-dimethyl-1,3-cyclohexadiene at 500°.

After selective hydrogenation the product was shown to be composed of 25% aromatic hydrocarbons and 75% dimethylcyclohexanes. The latter according to catalytic aromatization were found to be composed of $15 \pm 2\%$ of 1,1-dimethylcyclohexane and $85 \pm 2\%$ 1,3-dimethylcyclohexane.

Confirmation of the presence of the individual dimethylcyclohexadienes was obtained by the following procedure. The investigation of the physical properties, including ultraviolet and infrared spectra, of the distillation cuts (Fig. 2) allowed the selection of those to be combined into representative fractions for analysis. These combined fractions were treated with dimethyl acetylenedicarboxylate. The results of this reaction combined with ultraviolet spectral analysis of the fractions are given in Table VI.

Mechanism of the Thermal Reaction

The experimental results obtained from the thermal reactions of 1,1,3-trimethylcyclohexadienes

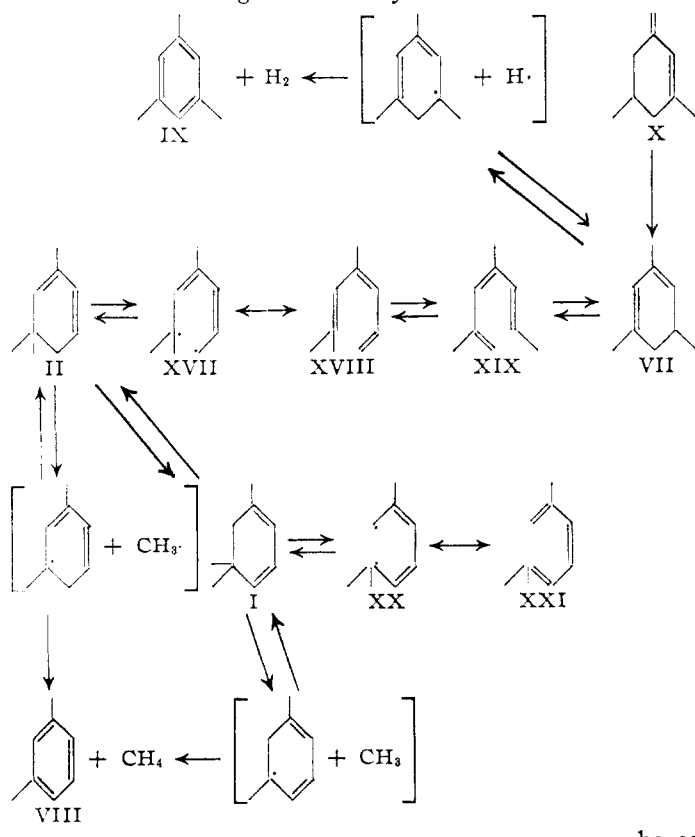
(I and II) and that of 5,5-dimethyl-1,3-cyclohexadiene (IV) suggest the following generalization: (a) at below 300° the dienes are fairly stable, (b) from 300–400° there is a shifting of double bonds in the endocyclic system, (c) at 400–450° a skeletal rearrangement begins to take place, seemingly competing with an aromatization reaction.

The skeletal isomerization of the dienes I, II and IV can be explained by a mechanism proposed previously,⁷ which involves the formation of a bialllyl biradical as an intermediate step in the reaction. The competing aromatization reaction most probably proceeds through a formation of an allyl radical. The various steps of the mechanism are outlined using diene II as an example.

The first step, the scission of the 5,6-bond, is predictable from the fact that a stable bialllyl biradical XVII may be formed. The second step can be explained as a mere redistribution of odd electrons to form a stable triene system. Once this triene system is formed there could be a facile reversible double bond isomerization to triene XIX (step three).

Step four appears to be a cyclization of the conjugated triolefin XIX by an intramolecular diene synthesis¹³ which may involve a concerted mechanism to give rise to diene VII. However, triene XVIII cyclizing in this way, as shown, would revert to diene II.

Diene I in equilibrium with diene II could form triene XXI through the bialllyl biradical XX.

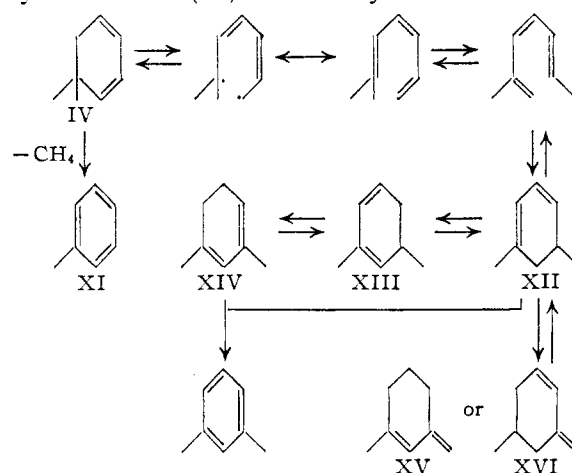


(13) K. Adler and M. Schumacher, "Umwendungen der Dien-Synthese für die Erforschung von Naturstoffen" in "Progress in the Chemistry of Organic Natural Products," Springer Verlag, Wien, 1953, pp. 10, 52.

This triene is a symmetrical one and therefore cyclization in this case would result in diene I again.

Also, diene I and II could lose methane to form *m*-xylene (VIII) whereas diene VII could lose hydrogen to form mesitylene (IX). The steps in the demethanation and the dehydrogenation reactions of I, II and VII most probably involve the intermediate formation of bialllyl radicals as indicated in the above outline.

The above discussed mechanism may also be applied to the thermal reactions of 5,5-dimethyl-1,3-cyclohexadiene (IV) as shown by the outline



The reaction of 5,5-dimethyl-3-methylenecyclohexene (III) at 500° gave only a small amount of product which appeared to be the same as that obtained from the isomeric *endo*-cyclohexadienes. This can be explained by the prior isomerization, to a small extent, of diene III to diene I and/or II followed by reaction of the latter dienes as shown previously. This and the fact that practically no reaction of diene III was observed at 400° indicates that the *trans*-diene which cannot form directly a bialllyl biradical skeleton is relatively stable toward isomerization.

The reverse isomerization does not seem to be facile since none of diene III was found in the reaction of dienes I and II at 300–500°. Yet a small amount of *trans*-dienes was found in the reaction products of the *endo*-cyclohexadienes at 500°. However, these dienes appear to result from the non-geminal type substituted cyclohexadienes.

The fact that all the possible predictable dienes occurring through the above proposed bialllyl biradical mechanism were shown to be present and/or isolated in the study at hand seems to verify the mechanism.

On the basis of the present investigation and the results previously reported,⁷ it can be concluded that the bialllyl biradical mechanism appears to be applicable in explaining thermal reactions of *gem*-dimethyl type and perhaps other conjugated cyclohexadienes.

TABLE VI
THERMAL REACTION OF 5,5-DIMETHYL-1,3-CYCLOHEXADIENE.
RESULTS OF INVESTIGATION OF COLLECTIVE CUTS

Cut	B.p., °C.	% ^a	endo-Dienes ^b	Gas, kind ^c	Dienes present Kind	%
1-6	110-122	20.2	75	Isobutylene	IV	15.1
7, 8, 10	122-127	13.0	83	Propylene	XII + XIII	10.8
9 ^f	126	3.6	100	Propylene	XII + XIII	3.6
11-13	127-136	13.7	73	Propylene and ethylene ^e	XII + XIII XIV	4.5 5.5
14-16	136-138	15.0	77	Ethylene	XIV	12.4
17-23	138-140	28.2	37	Ethylene	XIV	10.5

^a Weight per cent. of distilled product (Fig. 2). ^b Weight per cent. based on ultraviolet spectral analysis. ^c Gas resulting from the reaction with dimethyl acetylenedicarboxylate. ^d Weight per cent. of given diene in the total product. ^e Ethylene 55 mole %, propylene 45%. ^f Anal. Calcd. for C₈H₁₂: C, 88.81; H, 11.19; MRD, 36.01. Found: C, 89.08; H, 11.30; MRD, 36.52; *n*_D²⁰, 1.4623; *d*₄²⁰, 0.8148.

TABLE VII
PHYSICAL PROPERTIES OF SYNTHESIZED CYCLOHEXADIENES

Diene	B.p., °C. ^a	Mm. ^a	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	Obsd. MRD	Calcd. ⁱ	Found C	Analyses, % H	Calcd. C	H
I	130.0-130.4	745	1.4585	0.8057	41.42	40.63	88.42	11.61	88.45	11.55
	131-134 ^b									
	132-135 ^c									
II	133.3-133.4	750	1.4608	.8152	41.15	40.63	88.88	11.35	88.45	11.55
III	140.0-140.3	750	1.4760	.8205	42.02	40.63	88.46	11.50	88.45	11.50
IV	111.6-111.8	749	1.4558	.8081	36.38	36.01	89.16	11.16	88.81	11.19
	111	770 ^d		.8153 ^d						
	110	111 ^e	1.4563/18 ^o	.814 ^e						
	112.1-112.3 ^f			.80809 ^f						
VII	148.0-148.4	748	1.4688	.8197	41.50	40.63	88.21	11.48	88.45	11.55
	147 ^g			.8260 ^g						
	150.2-152.5 ^h		1.4807 ^h	.8280 ^h						
	146-147	747 ⁱ	1.4740 ⁱ	.8279 ⁱ	41.48 ⁱ					

^a Fractionally distilled in a Podbielniak¹³ Whirling Band Column using fresh mid-cuts for the analyses. ^b L. L. Gershebein, H. Pines and V. N. Ipatieff, THIS JOURNAL, 69, 2888 (1947). ^c M. S. Kharasch and P. O. Tawney, *ibid.*, 63, 2314 (1941). ^d At 15°, A. Crossley and H. Le Sueur, *J. Chem. Soc.*, 81, 832 (1902). ^e At 18°, C. Harries and W. Antoni, *Ann.*, 328, 88 (1903). ^f G. Chiurdoglu, P. J. Fiereus and C. Henkart, *Bull. soc. chim. Belg.*, 59, 140 (1950). ^g *d*₄¹⁸, O. Wallach, *Ann.*, 323, 135 (1902). ^h *d*₄²⁰, K. Auwers and G. Peters, *Ber.*, 43, 3076 (1910). ⁱ *d*₄²⁰, Ya. Levina, K. D. Gir and N. P. Shusharina, *J. Gen. Chem.*, (USSR), 25, 768 (1955). ^j The following values were used for refractive constants: C, 2.418; H, 1.100; double bond, 1.733.

Experimental Part

Apparatus.—The apparatus consisted of a Pyrex reaction tube having a reaction zone of 2.0 cm. outside diameter heated by a thermostatically controlled vertical furnace. The dienes were introduced into the tube, packed with 32 cc. of approximately 1/8 inch quartz chips in the reaction zone, by means of a motor driven syringe. The lower end of the reaction zone was attached to a liquid receiver, which in turn was attached through wet ice and Dry Ice-acetone cooled traps to a gas measuring and sampling bottle.

The procedure used for the determination of the various hydrocarbons is given in Tables II and IV.

Analytical Procedures. Fractional Distillation.—All precision fractional distillations were performed on a Podbielniak¹⁴ Whirling Band Column at atmospheric pressure and under a blanket of nitrogen.

TABLE VIII
INFRARED SPECTRA OF THE SYNTHESIZED
CYCLOHEXADIENES
Wave length, μ ^a

I ^b	II ^b	III ^c	IV ^d	VII ^e
6.00w	6.05m	5.70w	5.80w	6.00m
6.05m	6.10w	5.80w	6.10w	6.20w
6.30m	6.30w	6.10s	6.30w	6.85s

(14) Podbielniak, Inc., Chicago, Illinois.

6.85s	6.85s	6.25s	6.80s	7.00s
6.95s	6.90s	6.85s	6.95s	7.15s
	7.05m	7.05s	7.10w	7.50w
7.30m	7.15m	7.25s	7.20w	7.75w
7.35s	7.25m	7.35s	7.35s	7.85w
7.70w	7.35s	7.50m	7.55w	7.20w
7.90w	7.50m	7.85m	8.35w	8.60w
8.10w	7.70w	8.55s	8.50w	8.95w
8.30w	8.10w	8.85m	8.65w	9.20w
8.55w	8.30w	9.95s	8.90w	9.60w
8.75w	8.55w	10.05s	9.80w	9.80w
8.90w	8.75w	10.40m	9.90m	10.0w
9.50w	8.90w	11.15s	10.50w	10.60w
9.90w	9.60m	11.40s	10.90m	11.2w
10.25w	9.90m	11.65s	11.70m	11.55m
10.70w	10.05m	12.40s	13.05m	11.90m
10.90w	10.70w	13.00s	14.10s	12.00m
11.05w	10.85w	14.55m	14.5s	12.45s
11.45m	11.05w	15.25m		12.60s
12.00m	11.40w			
12.45m	12.25s			
13.8s	12.40s			
14.65w	13.90s			
	15.15w			

^a The peaks are referred to as: s = strong, m = medium, w = weak. ^b 0.027-mm. cell. ^c 0.030-mm. cell. ^d 0.019-mm. cell. ^e 0.022-mm. cell.

TABLE IX
ULTRAVIOLET SPECTRAL CHARACTERISTICS OF SYNTHESIZED
CYCLOHEXADIENES

Diene	Obsd. λ_{max}	Calcd. ^a	$A_{1\text{cm}}^{1\%}$ ^b	$A_{1\text{cm}}^{1\%}$ ^c
I	261	262	51	46
II	260	262	34	37
III	231	232	126	134
IV	258	257	51	..
VII	267	267	50	..

^a Calculated according to Woodward's Rule.¹¹ For endocyclic conjugated dienes a displacement value of 30 $m\mu$ is used. ^b Absorptivity⁷ in ethyl alcohol. ^c Absorptivity⁷ in isoöctane.

scribed by Mair.¹⁸ Absolute ethanol was used as eluent.

Catalytic Aromatization.—The alkylcyclohexanes obtained from the selective hydrogenation were aromatized in the presence of chromia-alumina¹⁹ at 500° and an H.L.S.V. of about 0.2 according to the procedure described previously.¹² The aromatic compounds thus obtained were identified by infrared spectral analysis. The gaseous products obtained from the aromatization were analyzed by means of a mass spectrograph.

Infrared Spectral Analysis.—The analyses were made on a Baird double beam recording infrared spectrophotometer having rock salt optics.²⁰

Ultraviolet Spectral Analysis.—All absorption measurements were made on a Cary model 11 recording quartz spectrophotometer²¹ which recorded absorbance *versus* wave length. Absolute ethanol or isoöctane was used as solvent.

TABLE X
RESULTS OF THE REACTIONS WITH DIMETHYL ACETYLENEDICARBOXYLATE

Compound	Reacn. temp., °C. Init. ^a Final	Gas, % ^b	Gas, prod. ^c	Ester prod. ^d	Acid	Melting points, °C. Anhyd.	Others
II	95 125–138	91	<i>i</i> -Bu	4	150–152 ^{e,f}	91.5–92.5 ^{f,g}	
I	89 130–133	97	<i>i</i> -Bu	3		116–117 ^{g,h}	188.5–189.5 ^{h,i}
IV	95 130	74	<i>i</i> -Bu	0		193–195 ⁱ	209–209.5 ^j
VII	90 150–160	95	Pro	3, 5	179–179.5 ^{k,v}	114.5–115.5 ^{l,w}	
Cuts 130–165 ^{om}	170	49	Pro <i>i</i> -Bu				
Cuts 145–156 ^{om}	158	75	Pro	3, 5	"	"	
Cuts 110–140 ^{op}	157	58	Pro <i>i</i> -Bu Eth				
Cuts 110–122 ^{op}	133	38	<i>i</i> -Bu Pro				
Cuts 122–127 ^{op}	85 150	76	Pro	3 and 4 ^g			
Cuts 127–136 ^{op}	143	64	Pro Eth				
Cuts 136–138 ^{op}	80 145	70	Eth	3, 5	"	"	
Cuts 138–140 ^{op}	146	35	Eth				

^a Temperatures at which a vigorous evolution of gas and exothermic reaction began. ^b In mole %, based on the total weight of reactant calculated as the cyclohexadiene. ^c Analyzed by mass spectrometry. Legend: *i*-Bu = isobutylene, Pro = propylene, Eth = ethylene. ^d Given as the position of methyl substitution on the dimethyl ester of phthalic acid. ^e M.p. 152°, St. v. Niementowski, *Monatsh.*, **12**, 627 (1891). ^f M.p. 92°, ref. *e*. ^g M.p. 118–119°, cf. ref. 5. ^h 3-Methylphthalimide, m.p. 188.5–189°, M. Hayashi, *et al.*, *Bull. Chem. Soc. Japan*, **11**, 184 (1936). ⁱ Sealed tube; m.p. 203–207°, open tube and rapid heating. ^j No depression in melting point when mixed with an authentic sample of phthalanil. ^k M.p. 181°, M. Freund and K. Fleisher, *Ann.*, **411**, 33 (1916). ^l M.p. 116°, W. A. Noyes, *THIS JOURNAL*, **20**, 810 (1898). ^m Cf. Fig. 2. ⁿ No depression of melting point was observed when mixed with sample of respective acid or anhydride ^k or ^l. ^o Cf. Fig. 3. ^p The melting range of the acid and anhydride and elemental analysis substantiated that this mixture was present. ^q Calcd. for C₉H₈O₄: C, 60.00; H, 4.47. Found: C, 59.62; H, 4.43. ^r Calcd. for C₉H₈O₃: C, 66.67; H, 3.73. Found: C, 66.57; H, 3.61. ^s Calcd. for C₉H₈O₃: C, 66.67; H, 3.73. Found: C, 66.96; H, 3.66. ^t Calcd. for C₉H₇O₂N: C, 67.06; H, 4.38; N, 8.69. Found: C, 67.03; H, 4.15; N, 9.01. ^u Calcd. for C₁₀H₁₀O₄: C, 61.85; H, 5.19. Found: C, 62.07; H, 5.19. ^v Calcd. for C₁₀H₈O₃: C, 68.18; H, 4.58. Found: C, 67.56; H, 4.60.

Hydrogenation.—The hydrogenations were carried out in a 125-ml. capacity rotating autoclave at temperatures above 100° and in the presence of 100–120 atmospheres of initial hydrogen pressure. Copper chromite¹⁵ was used as a catalyst for selective hydrogenations and nickel-on-kieselguhr,¹⁶ which was reduced at 350°, for the others. The amount of catalyst used was 5–10% by weight of the material to be hydrogenated. The degree of unsaturation was calculated from the drop in pressure.

Chromatographic Separation.—Aromatic hydrocarbons were separated from the non-aromatic hydrocarbons by means of silica gel.¹⁷ The procedure used was essentially that de-

Synthesis of the Dienes. 1,5,5-Trimethyl-1,3-cyclohexadiene (I). 3,5,5-Trimethyl-1,3-cyclohexadiene (II) and 5,5-Dimethyl-3-methylenecyclohexene (III).—The above mixture was prepared by the alumina dehydration of isophorol. The latter was obtained in 90% yield by the aluminum isopropoxide reduction of isophorone²² using a modified procedure of Macbeth and Mills.²³

The dehydration was conducted at 300° in a flow type apparatus using an H.L.S.V. of approximately one. The product, 90% yield, after a preliminary separation of the resulting diene mixture from unreacted higher boiling mate-

(18) B. J. Mair, *ibid.*, **34**, 435 (1945).

(19) R. C. Archibald and B. S. Greensfelder, *Ind. Eng. Chem.*, **37**, 356 (1945).

(20) Baird Associates, Inc., Cambridge, Mass.

(21) Allied Physics Corporation, Pasadena, California.

(22) M. S. Kharasch and P. O. Tawney, *THIS JOURNAL*, **63**, 2314 (1941).

(23) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 2646 (1949).

(15) W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 142.

(16) Obtained from Harshaw Chemical Co., Elyria, Ohio; it contained 44% nickel.

(17) B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151 (1944); **32**, 165 (1944).

rials, contained 30% diene III and 70% of a mixture of dienes I and II, according to ultraviolet analysis.

The dienes were fractionally distilled under a blanket of nitrogen at atmospheric pressure in a Podbielniak¹⁴ Hypercal column. The lower boiling cuts rich in dienes I and II were separately refractionated. The higher boiling cuts rich in diene III were treated with maleic anhydride to remove dienes I and II and refractionated.

The samples used for the thermal reaction at 500° had the following physical constants: mixture of dienes I and II, b.p. 131–133°, n_D^{20} 1.4594; diene III, b.p. 139–140°, n_D^{20} 1.4752. Their spectra showed that only the designated dienes were present.

1,3,5-Trimethyl-1,3-cyclohexadiene (VII).—Diene VII was isolated from the products obtained in the reaction of 3,5-dimethyl-2-cyclohexenone²⁴ with an excess of methylmagnesium bromide. The general procedure of Kharasch and Tawney²⁵ was employed using commercial magnesium turnings. The 66% yield of dienes boiling between 47–79° (18 mm.), n_D^{20} 1.4776, was shown to consist of 45% of diene VII and 55% of diene X. Diene VII was fractionally distilled from diene X.

5,5-Dimethyl-1,3-cyclohexadiene. 4,4-Dimethylcyclohexene.—This compound was prepared by a previously described method.²⁵

5,5-Dimethyl-1,3-cyclohexadiene (IV).—The diene was synthesized by brominating 4,4-dimethylcyclohexene and treating this dibromide with sodium ethoxide followed by

(24) E. C. Horning, M. O. Denekas and R. C. Field, *Org. Syntheses*, **27**, 24 (1937).

(25) H. Pines, F. J. Pavlik and V. N. Ipatieff, *THIS JOURNAL*, **73**, 5738 (1951).

the reaction of the resulting ether with potassium bisulfate according to a procedure of Hofmann and Damm.²⁶

The diene used for the thermal reaction had the following properties, b.p. 111–114°, n_D^{20} 1.4558. Its spectra showed it to contain only diene IV.

The physical properties, infrared spectra and ultraviolet spectral data of all the above synthesized cyclohexadienes are given in Tables VII, VIII and IX, respectively.

The Reaction with Dimethyl Acetylenedicarboxylate.—The method and apparatus used was essentially that described by Parker and Goldblatt.⁶

This reaction with the cyclohexadienes gave liquid and gaseous decomposition products. The liquid products were identified in some cases by saponification of the resulting esters and determination of the corresponding phthalic acids. The gaseous products were identified by mass spectrometry.

The results of the reactions of the various dienes with dimethyl acetylenedicarboxylate are given in Table X. The reaction was conducted at the temperature designated (starting at room temperature with slow heating) until no more gas was evolved (0.5–3 hr.). About 2.0–5.0 g. of reactant was used with an excess of the acetylenedicarboxylate.

Acknowledgment.—The authors express their thanks to Dr. D. F. Mason of the Chemical Engineering Department for the mass spectrographic gas analyses and to Miss H. Beck for the elementary analyses.

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

EVANSTON, ILLINOIS

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY AND THE INSTITUTO DE QUIMICA DE LA UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO]

Terpenoids. XXIV.¹ The Structure of the Cactus Triterpene Queretaroic Acid

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From two Mexican cacti, *Lemaireocereus queretaroensis* and *L. beneckei*, there has been isolated a new triterpene acid named queretaroic acid. Degradation experiments are reported which establish its constitution as 30-hydroxyoleanolic acid. Queretaroic acid is the only known naturally occurring triterpene, other than glycyrrhetic acid, which is oxygenated at C-30.

In continuation of our work on cactus triterpenes, especially of the genus *Lemaireocereus*,⁴ there have been examined two additional Mexican representatives of this genus, *L. queretaroensis* and *L. beneckei*.⁵ In each instance, the acidic triterpene fraction could be separated into oleanolic acid and a new triterpene acid, now named "queretaroic acid." The present paper is concerned with a description of the relevant experiments which led to the structure elucidation of this new pentacyclic triterpene.⁶

Analysis indicated the empirical formula C₃₀—

(1) Paper XXIII, C. Djerassi and R. Hodges, *THIS JOURNAL*, **78**, 3534 (1956).

(2) Postdoctorate research fellow at Wayne University, 1954–1955, on funds supplied by the Division of Research Grants of the National Institutes of Health (grant No. G-3863).

(3) Postdoctorate research fellow at Universidad Nacional Autonoma de Mexico, 1954–1955, on funds supplied by the Rockefeller Foundation.

(4) For leading references, see Paper XXII, C. Djerassi, A. Bowers, S. Burstein, H. Estrada, J. Grossman, J. Herran, A. J. Lemin, A. Manjarrez and S. C. Pakrashi, *THIS JOURNAL*, **78**, 2312 (1956).

(5) Cf. H. Bravo, "Las Cactaceas de Mexico," Mexico, D. F., 1937, pp. 252, 265.

(6) A preliminary account of part of this work has been published (C. Djerassi, J. A. Henry, A. J. Lemin and T. Rios, *Chemistry & Industry*, 1520 (1955)).

H₄₈O₄ for queretaroic acid (Ia) and the nature of all four oxygen atoms was proved by formation of a monomethyl ester Ib, a diacetate Id and a diacetoxymethyl ester Ic. Queretaroic acid is thus a dihydroxycarboxylic acid and its membership in the β -amyrin series of triterpenes was established by the ready oxidation of the diacetoxymethyl ester Ic with selenium dioxide to a hetero-annular diene II with the characteristic triple ultraviolet maxima at 243, 251 and 260 m μ .⁷ In view of the co-existence of queretaroic acid with oleanolic acid in the cactus, it was assumed that the former was most likely x-hydroxy-oleanolic acid and all subsequent experiments were predicated on such a working hypothesis.

In order to locate the unknown hydroxyl group, methyl queretaroate (Ib) was subjected to chromium trioxide-sulfuric acid oxidation⁸ and led in good yield to a ketodicarboxylic acid monomethyl ester Vb. The new functional groups were charac-

(7) This reaction, typical of β -amyrins, was discovered by L. Ruzicka, G. Müller and H. Schellenberg (*Helv. Chim. Acta*, **22**, 767 (1939)) while the location of the double bonds was established by D. H. R. Barton and C. J. W. Brooks (*J. Chem. Soc.*, 257 (1951)).

(8) Cf. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *ibid.*, 39 (1946).