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REVIEW OF THE CHEMISTRY OF CYCLOPROPENE COMPOUNDS

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I. INTRODUCTION

As a result of the bond strains that are set up in cyclopropene and cyclopropene derivatives, these compounds lend themselves nicely to a study of the effects of ring substituents on the properties of carbon–carbon bonds, on the carbon–hydrogen bond, and on the various orbitals. The effects of substituents are exaggerated in the unsaturated three-membered ring, and for this reason a considerable amount of attention has been given to the cyclopropenes. Moreover, the recent discovery (196) of naturally occurring fatty acids that contain the cyclopropene ring has fortified and intensified the interest in cyclopropene compounds. One of these fatty acids, malvalic acid, is a component of cottonseed oil triglycerides (235), one of our major sources of edible fats. This cyclopropene derivative has been indicted as the causative agent in the production of abnormalities among animals ingesting crude cottonseed oil (91, 194, 233, 234).

A review of the physiological properties of cyclopropene fatty acids is being prepared by several workers for publication in the near future (205). While passing reference is made to cyclopropene in various texts and in some reviews on other subjects (175, 189, 221, 267), no review of the chemistry of cyclopropene and cyclopropene compounds has appeared. Accordingly, this review covers the pertinent literature through December, 1963, and includes a few references

from early 1964. Some of the related cyclopropane compounds are mentioned briefly in this review only for coherence in the presentation. In general, the nomenclature recommended by *Chemical Abstracts* is used, although some of the names of the compounds used by the authors of reviewed articles are retained here.

II. CYCLOPROPENE AND SYNTHETIC CYCLOPROPENE DERIVATIVES

A. SYNTHESIS

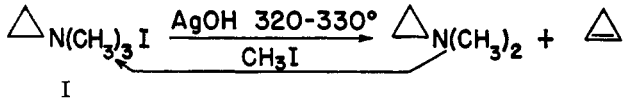
1. Cyclopropene

In 1897 Freundler (104, 106) reported the synthesis of cyclopropene by the pyrolysis of barium furoate. This gaseous substance with an alliaceous odor was reported to be slightly soluble in water, gave no precipitate with either ammoniacal cuprous chloride or silver nitrate, but did yield a precipitate from alcoholic solutions of mercuric chloride. The gas reacted with bromine to give a small quantity of dibromide [b.p. 50° (reduced pressure)] as well as one or more tetrabromides. The formation of the tetrabromide $CHBr_2$-CH_2CHBr_2 [b.p. 162° (20 mm.)] indicated that the unsaturated hydrocarbon synthesized was cyclopropene. Although furan was the principal product formed, the gas was obtained in 5 to 6% yields (105).

A later study of the method confirmed the formation of furan and other products but indicated no appreciable yields of cyclopropene (141). Possibly the temperature necessary for this dry distillation procedure caused the transformation of any cyclopropene formed into a polymer, methylacetylene, or some other substance. Methylacetylene was identified as a reaction product but was found only in small amounts.

The first confirmed report of the synthesis of cyclopropene was that of Dem'yanov and Doyarenko (69, 70), who obtained the hydrocarbon by the thermal decomposition of trimethylcyclopropylammonium hydroxide on platinized clay at approximately 300°. Trimethylamine and dimethylcyclopropylamine were also obtained. The reaction was carried out in an atmosphere of carbon dioxide and away from direct light in order to prevent extensive oxidation and polymerization of the synthesized cyclopropene. The cyclic compound reacted with bromine to give two bromides, a dibromide [b.p. 45° (27 mm.)] and a tetrabromide [b.p. 155° (19 mm.)]. Although the tetrabromide, $CHBr_2CH_2CHBr_2$, was stated to be reduced quantitatively to cyclopropene by zinc dust and ethyl alcohol, this reduction was not confirmed (229). The presence of a small amount of $CH_3CBr_2CHBr_2$ indicated that methylacetylene was also formed from the decomposition of the quaternary base. Further experiments (71) showed that an increase in the temperature for the decomposition resulted in an increase in methylacetylene formed and a decrease in the amount of cyclopropene.

The work of the Russians was confirmed in an extensive investigation (229) of the reaction conditions necessary for a preparative scale. Approximately a 4.7% over-all yield of cyclopropene was obtained at the optimum temperature of 320–330°. The pure compound was obtained by fractional distillation of the hydrocarbons formed from the pyrolysis of the quaternary base (I). Each step in the synthesis was studied from a preparative point of view. Dimethylcyclopropylamine and methylacetylene were also obtained, but the amine was reconverted quantitatively to the quaternary salt. Whereas the ratio of hydrocarbons to the amine seemed to be affected by the condition of the catalyst, the ratio of cyclopropene to methylacetylene depended mainly on the temperature.



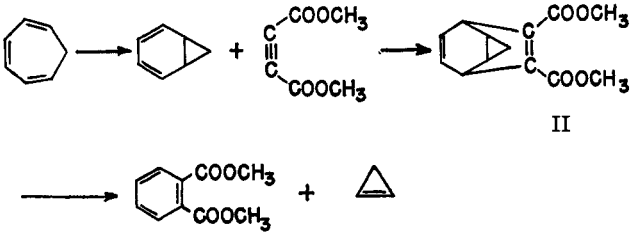
I

This procedure was modified (274) slightly by using the Schmidt reaction for the conversion of cyclopropanecarboxylic acid to cyclopropylamine. The cyclopropene was purified by vapor phase chromatography with the removal from the gaseous mixture of such impurities as ethylene, carbon dioxide, methylacetylene, and dimethyl ether.

A deuterated sample of cyclopropene has been prepared by equilibrating the cyclopropyltrimethylammonium hydroxide with deuterium oxide before pyrolysis (274). Mass spectrometric analysis showed that the cyclopropene sample obtained had 40% cyclopropene-d_2, 40% cyclopropene-d_1, and 20% cyclopropene-d_0 (148). An analysis of the n.m.r. spectrum of the dibromide derivative indicated that 80% of the deuterium was in the vinyl position, thereby supporting the evidence (273) that vinyl hydrogen in a cyclopropene derivative is moderately acidic (274).

A gas believed to be cyclopropene, along with a phthalic acid ester, was cleaved from an adduct (II) formed by the reaction of cycloheptatriene and dimethyl acetylenedicarboxylate (2, 3). In a further investigation (274), quantitative yields of the phthalate were obtained but only 1% of cyclopropene, as the remainder, was found in the form of a cyclopropene polymer.

Pentachlorocyclopropane was synthesized by the de-

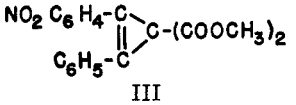


II

carboxylation of the sodium salt of trichloroacetic acid in dry 1,2-dimethoxyethane at 80° in the presence of excess trichloroethylene (255). When this highly chlorinated cyclopropane was treated with excess 18 *M* aqueous potassium hydroxide at 80–85°, tetrachlorocyclopropene was obtained in 85% yield [b.p. 129.5–130.0° (745 mm. under N_2)].

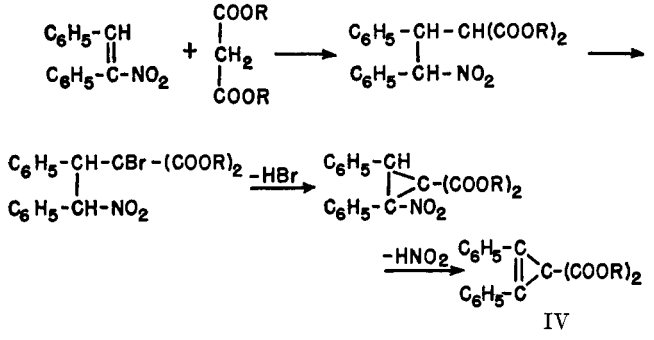
2. Aryl-Substituted Derivatives

In 1930 Kohler and Darling (160) showed that cyclopropene compounds could be obtained by the elimination of nitrous acid from the properly constituted nitrocyclopropane derivatives. The appropriate nitrocyclopropane derivative was prepared by brominating the γ-position of the addition product obtained by adding phenylnitromethane to a nitrobenzalmalonic ester, followed by the elimination of hydrogen bromide. When the nitrocyclopropane compound was treated with sodium methoxide it lost nitrous acid and formed the cyclopropene derivative III.



III

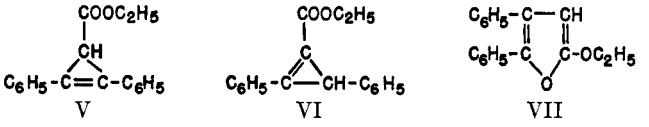
A second derivative of cyclopropene in which both phenyl groups are unsubstituted (IV) was prepared in a



IV

somewhat similar manner (67). The dibasic acid was obtained by hydrolysis. The structure of this derivative, 2,3-diphenyl-2-cyclopropene-1,1-dicarboxylic acid, was confirmed by its preparation (41, 42) by the reaction of diazomalonic ester with diphenylacetylene followed by alkaline hydrolysis. Electrolytic copper dust was used as a catalyst. The monoacid was prepared in a similar manner by the reaction of ethyl diazoacetate with diphenylacetylene. Both derivatives were found to be remarkably stable, probably as a result of the highly conjugating substitution (42).

Other workers have reported the use of copper sulfate as a catalyst in the low temperature reaction of ethyl diazoacetate with acetylenes to give cyclopropene derivatives (79, 80, 83). Isomers with different properties were obtained by the reaction of ethyl diazoacetate with diphenylacetylene. Structure V was assigned to the derivative formed when the copper powder catalyst was used (42), and structure VI to the isomer obtained with the copper sulfate catalyst (80). The position of the double bond in the cyclopropene ring was thought to be the significant difference in the isomers; however, the compound thought to have structure VI was shown later not to be the cyclopropene derivative but an isomer, 2-ethoxy-4,5-diphenylfuran (VII) (31, 81).



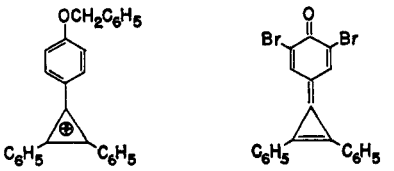
V VI VII

Subsequent work (82) indicated that a small amount of the cyclopropene with structure VI was actually formed as an impurity in the reaction using copper sulfate as a catalyst. When the reaction was carried out in the absence of any catalyst at 120–130°, isomer V was obtained with a yield of 17% (83). The implication that the copper sulfate catalyst can alter the course of the reaction pointed out the importance of exact reaction conditions for the synthesis of cyclopropenes (31).

In a similar reaction, diphenylacetylene was caused to react with phenyldiazoacetonitrile to give 1,2,3-triphenyl-2-cyclopropenecarboxylic acid nitrile (25). This compound was used as the starting material for the preparation of many cyclopropenyl derivatives (25, 43). Since this method is not readily adaptable to large-scale preparative work, an alternate method for the synthesis of the triphenylcyclopropenium ion was investigated.

The *sym*-triphenylcyclopropenium ion was synthesized by the reaction of diphenylacetylene with phenylchlorocarbene, which was generated *in situ* by the reaction of benzal chloride with potassium *t*-butoxide (30, 37). Aqueous washing of the reaction product gave the bisether which was then converted to the bromide by treatment with hydrogen bromide. Similarly, diphenylcyclopropenyl derivatives were synthesized by a reaction of phenylchlorocarbene with phenylacetylene (37) and arylcyclopropenyl ions by a reaction of arylchlorocarbene with the appropriately substituted acetylene (30).

The addition of phenylchlorocarbene to 4-benzyloxytolane gave the 1-(*p*-benzyloxyphenyl)-2,3-diphenylcyclopropeniun ion (VIII) (155). Pyrolysis of the bromide derivative resulted in debenzylation and produced phenolic cyclopropenium bromide, which in turn was converted by a tertiary amine to the corresponding quinocyclopropene (IX). The methylenecyclopropene grouping is found in this unusual compound.



VIII IX

Although attempts (258) to prepare dione derivatives of benzocyclopropene were not successful, 1,1-dimethyl-3-carbomethoxybenzocyclopropene was recently prepared by the irradiation (ultraviolet light) of methyl 3,3-dimethylindiazene-6-carboxylate (4). The major product, however, was methyl *p*-isopropenylbenzoate. The benzocyclopropene derivative was stable for several hours at room temperature but was completely destroyed when it was refluxed in benzene for 15 min. The derivative was sensitive to acids but not to bases.

Phenylketene dimethyl acetal has been found to react with benzal chloride and potassium *t*-butoxide to form the dimethyl ketal of diphenylcyclopropenone, which upon hydrolysis gave diphenylcyclopropenone (34). An independent synthesis for this compound used the more convenient reaction between diphenylacetylene, bromoform, and potassium *t*-butoxide (268). Very good yields (50–60%) of diphenylcyclopropenone were obtained by reacting α,α'-dibromodibenzyl ketone with 20% triethylamine at room temperature for 30 min. (40). Similarly, the reaction of ethylamine in chloroform with 2,8-dibromocyclooctanone gave a 50% yield of cycloheptenocyclopropenone. Dibromo- and dichlorocarbenes were caused to react with diphenylacetylene to form diphenylcyclopropenone (165). Similarly, by heating GeI_2 with diphenylacetylene, a stable addition product was obtained with the composition $C_{14}H_{10}GeI_2$ which was thought to be analogous to the cyclopropenone (269).

3. Alkyl-Substituted Derivatives

The structures of many cyclopropene derivatives reported in the literature have not been substantiated. Repetition (154, 246) of a few experiments have clarified the standing of several compounds, but in many cases (24, 145, 188), a re-opening of these investigations will be necessary for definite proof of the cyclopropene structure. A product isolated in a small amount from the reaction of methyl γ-bromocrotonate with dry sodium methoxide in benzene was originally reported to be methyl cyclopropenecarboxylate (198). The observations were confirmed, but the product was reported not to be the cyclopropene derivative but instead the dimer of the starting material, dimethyl 2,4,6-octatrienedioate (76).

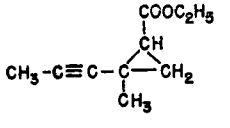
The synthesis of ethyl cyclopropenecarboxylate was attempted by the reaction of ethyl 2-bromocyclopropanecarboxylate with potassium *t*-butoxide in *t*-butyl alcohol (1, 273). Although the product obtained was ethyl 2-*t*-butoxycyclopropanecarboxylate, the cyclopropenecarboxylic ester was thought to be formed in the first step as an intermediate. Evidence for this intermediate was shown by carrying out the reaction in deuterium-labeled solvent and obtaining the product labeled with two deuteriums. The unsaturated intermediate thus exchanged its vinyl hydrogens with the deuterium of the solvent. This exchange was followed by an addition of *t*-butyl alcohol to give the observed product.

Since this theory indicated that the cyclopropene compound was reactive toward Michael addition of nucleophilic agents, an attempt was made to prepare the cyclopropene derivative by using a reaction which might be carried out in the absence of any nucleophilic agents (272). The thermal elimination of acetic acid from ethyl 2-acetoxycyclopropanecarboxylate to give the cyclopropenecarboxylic ester was tried on the supposition that introducing a double bond into the cyclopropane ring might prove to be easier than into the ethyl group. However, no cyclopropene derivative was obtained.

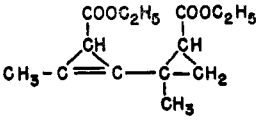
In 1960 the preparation of 1,2-dimethylcyclopropene and methyl 1,2-dimethylcyclopropene-3-carboxylate by the addition of methylene and carbomethoxycarbene, respectively, to 2-butyne was reported as the first illustrations of the synthesis of purely aliphatic cyclopropenes. The methylene and carbomethoxycarbene were generated photolytically from diazomethane and methyl diazoacetate, respectively. The photochemically and copper sulfate catalyzed reactions of *cis*- and *trans*-butene with methyl diazoacetate to form the cyclopropane derivatives were also investigated as a means of identifying the hydrogenation product of methyl 1,2-dimethylcyclopropene-3-carboxylate as the *cis* isomer (75). The compounds were purified with gas chromatographic columns.

In a continuation of the investigation of the nature and extent of the interaction of substituents with the cyclopropenyl ring, the dipropylcyclopropenyl and tripropylcyclopropenyl cations were prepared (35, 36). Copper dust was used as a catalyst in the reaction of 4-octyne with ethyl diazoacetate to form 2,3-dipropyl-2-cyclopropenecarboxylic acid from which the perchlorate and the fluoroborate were prepared.

The ethyl esters of 1-methyl-1-(propyn-1-yl)cyclopropane-2-carboxylic acid (X) and 2-methyl-1-(1-methyl-2-carbethoxycyclopropyl)-1-cyclopropene-3-carboxylic acid (XI) were formed by the reaction of 2-methyl-1-penten-3-yne with carbethoxycarbene, prepared by the catalytic decomposition of ethyl diazoacetate (78). Compound XI was hydrogenated to the "dicyclopropane" compound. Other workers (270) reported that the acetylene grouping of a conjugated enyne compound did not react with methylene to form a cyclopropene derivative; however, methylene does condense with 2-methyl-1-buten-3-yne, 1-ethynyl-1-methylcyclopropane, and 2-methyl-1-penten-3-yne.

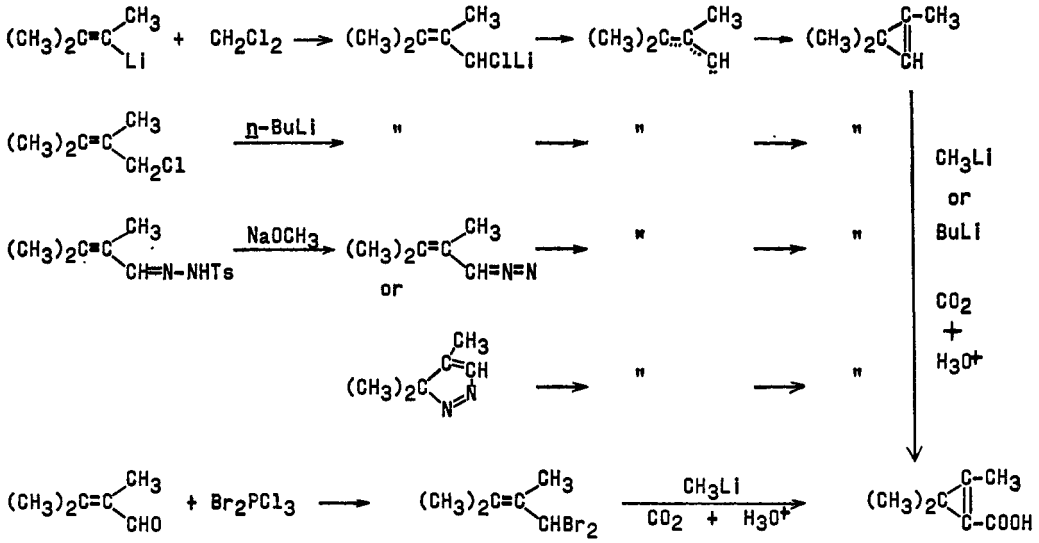


X



XI

SCHEME I



An unusual method for the synthesis of cyclopropene derivatives involved the addition of methylene chloride to a solution of 1,2-dimethylpropenyllithium in tetrahydrofuran at −35° to form 2,3,3-trimethylcyclopropenyllithium. The cyclopropene derivative gave 1,3,3-trimethylcyclopropene upon hydrolysis, underwent carboxylation to give 2,3,3-trimethylcyclopropene-1-carboxylic acid, and reacted with methyl iodide to form tetramethylcyclopropene (57). Yields of 40–50% were obtained for these compounds, the structures of which were determined by spectral and chemical evidence. The mechanism was postulated as a carbene reaction in which an alkenylcarbene served as a precursor of the cyclopropene. This concept was studied in considerable detail (56, 58, 59, 61), and the reactions shown in Scheme I were investigated.

Good yields of cyclopropenes were obtained from the base-induced decomposition of tosylhydrazones of α,β-unsaturated aldehydes and ketones when the β-carbon atom was fully substituted with alkyl groups. The yield was considerably diminished by the presence of one hydrogen atom at the β-position (61).

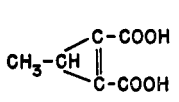
Difluorocarbene was generated and added to hexafluoro-2-butyne in the gas phase to form 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene. A second addition of difluorocarbene to the cyclopropene derivative gave 1,3-bis(trifluoromethyl)-2,2,4,4-tetrafluorobicyclobutane (25% yield), and 2,3-bis(trifluoromethyl)-1,1,4,4-tetrafluorobutadiene (8%) (182).

Sterculic acid, a naturally occurring fatty acid, was synthesized (50) through the reaction of stearolic acid and methylene iodide in the presence of a zinc–copper couple. The properties of the synthetic acid were found to be identical with those of an authentic sample. Only a 4% yield of the cyclopropene acid was obtained, although 51% was realized in the synthesis of the corresponding cyclopropane compound from methyl oleate (237).

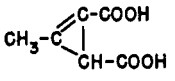
In order to determine if the phenyl groups contributed greatly to the unusual stability of diphenylcyclopropenone (34, 268), the dipropyl derivative was prepared for comparative purposes by the reaction of dipropylacetylene with dichlorocarbene (39). The modified Favorskii reaction of treating a dihaloketone with a base was used for the synthesis of dibutylcyclopropenone (40).

4. Feist's Acid

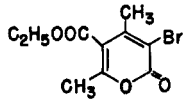
In 1893 Feist (101) reported the synthesis of two isomeric dicarboxylic acids which he described as symmetrical (XII) and asymmetrical (XIII) methylcyclopropenedicarboxylic acids. The existence of the two acids and their correct structure(s) have been the subject of considerable controversy. The symmetrical



XII



XIII

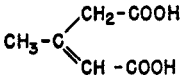


XIV

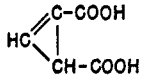
structure was assigned to the acid prepared by the reaction of alkali on ethyl dimethylbromocoumalinate (XIV). The acid was crystallized from water, sublimed to give needles which melted at 200°, and formed crystalline calcium and barium salts. An excess of bromine reacted with the acid to form the dibromocyclopropane derivative (m.p. 240° dec.), which in turn was reduced by sodium amalgam to yield an acid denoted as the asymmetrical isomer XIII. Acid XIII was crystallized from water, melted at 189°, and formed a calcium salt having crystals quite different in appearance from those of the calcium salt of acid XII (101). Later chemical reactions of the acid designated as XII were studied, but no mention was made of the second compound (146).

Approximately 30 years later, an acid, melting at 200°, was prepared by the action of concentrated

alkali on ethyl α,α'-dibromo-β-methylglutarate, but its structure was assigned as that of XIII (142). The synthesis was considered to be analogous to the formation of β-methylglutaconic acid (XV) from the monobromo ester. The corresponding cyclopropene acid (XVI) (m.p. 184°) was not obtained from the dibromo ester of glutaric acid, although it was reported to be prepared from the bromoglutaconic ester (96, 114).



XV



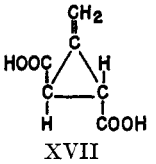
XVI

The acid melting at 189° was considered by some investigators (114, 116, 142) to be an impure form of the acid with the asymmetric structure which melted at 200°. Many of the differences attributed to the two isomers, such as the failure of the lower melting acid to sublime and the difference observed in the crystal forms of the calcium salts, are readily explained by the presence of an impurity. The acid melting at 189° was stated to melt at 200° when it was recrystallized from xylene.

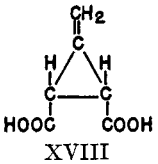
Feist (102) continued to claim the existence of both isomers and compared the physical and chemical properties of the acids and their derivatives. Acid XIII was reported to be labile and to be converted to XII by standing in the presence of concentrated sulfuric acid or by boiling with strong alkali.

Although the investigators in favor of the asymmetric structure for the acid melting at 200° believed that only one form of the acid existed, they also considered the acid to be a true glutaconic derivative and capable of three-carbon tautomerism (114–116). Three isomeric esters of the acid were reported, the normal, labile, and enol forms. The compound reported to be the labile ester was later identified as a straight-chain acetylene derivative, and the identification of the enol ester was questioned (161).

In 1952, the structure of Feist's acid, the acid formed by the reaction of alkali with 3-bromo-5-carbethoxy-4,6-dimethyl-2-pyrone (XIV), was reformulated as 1-methylenecyclopropane-*trans*-2,3-dicarboxylic acid (XVII) (88). This structure had earlier been rejected



XVII



XVIII

on the basis that only ethyl acetooxaloacetate was obtained on the ozonolysis of the compound (114). This latter observation was confirmed by other workers (161, 171, 172) who were not able to detect formaldehyde among the products of oxidation by ozone or other oxidizing agents. Formaldehyde was finally obtained by the oxidation of the acid by the method of Lemieux and Rudloff (168, 173).

The results of a study of the acid by X-ray methods indicated that in the solid state the methylenecyclopropane structure XVII was correct (171, 172, 202). Even so, one group (19) obtained infrared absorption bands that favored the cyclopropene structure. These data were discounted by Ettlinger and Kennedy (89) who presented infrared, ultraviolet, and n.m.r. data in support of structure XVII. The n.m.r. data were confirmed (22, 152, 153) and completely ruled out the cyclopropene structure.

A study of the exchange of hydrogens in the acid with deuterium showed that the hydrogen atoms α to the carboxyl groups were exchanged very rapidly in 0.25 *N* sodium deuteroxide at 100° (90). Similar replacement at the γ-position occurred in 2.5 *N* sodium deuteroxide when the temperature was increased to 110–120° and a longer reaction time was used. This exchange of the γ-hydrogens for deuterium was considered to provide evidence for the transient existence of a cyclopropene isomer but also indicated that an equilibrium between the two lies almost exclusively in the direction of the methylenecyclopropane compound.

The isolation of 1-methylenecyclopropane-*cis*-2,3-dicarboxylic acid (XVIII), an isomer of Feist's acid (XVII), served as final proof for the existence of structure XVII, as corresponding ultraviolet and proton magnetic resonance spectra of the stereoisomers were indistinguishable (90).

B. CHEMICAL REACTIONS

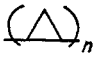
1. Cyclopropene

The properties of cyclopropene are of interest to investigators studying the effect of ring strain on bond hybridization and relativity. A number of cyclopropene reactions were investigated with special interest in the effect of bond angle deformation on the reactions.

The thermal isomerization of cyclopropene to methylacetylene was found to proceed slowly at 325° but fairly rapidly at 425°. Cyclopropene was not obtained in detectable quantities when methylacetylene was treated similarly (274).

The major portion of cyclopropene was polymerized upon attempted fractional distillation at −36°, its boiling point at atmospheric pressure. Polymerization occurred readily at room temperature and was assumed to be a free-radical chain reaction. The n.m.r. spectrum indicated the structure of the polymer to be that of a polycyclopropane (XIX) (274). Although cyclopropene could not be stored even at Dry Ice–acetone temperature, 1,2-dimethylcyclopropene

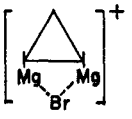
could be kept in the refrigerator without the occurrence of polymerization (75).



XIX

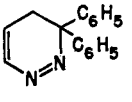
Cyclopropene was quantitatively removed from a mixture with nitrogen when the mixture was passed through an aqueous or ammoniacal silver nitrate solution (192, 274). The formation of the silver complex possibly imparted some sp^3 character to the double bond and thus was related to the relief of angle strain by the lengthening of the double bond.

Cyclopropene reacted with iodine in carbon tetrachloride solution to form 1,2-diiodocyclopropane, a very stable compound which did not react with iodide ion or with zinc dust to reform cyclopropene (274). Cyclopropene also readily added bromine to form a dibromide with the *trans* configuration. The dibromide formed a di-Grignard reagent with the probable structure formulated as XX, where the magnesium atoms and the bromine are associated in a way similar to an ion-triplet, or where there may be some covalent character to the association. An alternate structure for the Grignard reagent was suggested as XXI (10, 274). Other preliminary experiments (220) indicated that cyclopropene may not react with Grignard reagents under conditions where cyclopentadiene is converted to cyclopentadienylmagnesium compounds.



XX

XXI



XXII

Cyclopropene behaved as a dienophile and underwent the Diels–Alder reaction when it was passed into a cold solution of cyclopentadiene in methylene chloride. The expected adduct was obtained in 97% yield. Only a 37% yield was obtained with the less reactive butadiene (10, 274).

Diphenyldiazomethane reacted with cyclopropene, even in the presence of copper powder, to form a 1:1 addition compound with the probable structure XXII (274). A six-membered unsaturated ring was obtained in a similar fashion by the reaction of cyclopropene with diazoacetic ester, with the reaction proceeding rapidly even at temperatures as low as −40° (274).

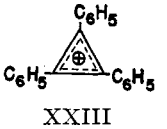
2. Cyclopropene Derivatives

a. Reactions Yielding Other Cyclopropene Derivatives

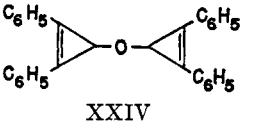
1,2,3-Triphenyl-2-cyclopropenecarboxylic acid nitrile, prepared by the reaction of diphenylacetylene with phenyldiazoacetonitrile (25), was treated with boron trifluoride etherate and a trace of water and thereby converted into 1,2,3-triphenylcyclopropenyl fluoroborate. The product was contaminated with some of the hydroxyfluoroborate. The nitrile derivative is covalent while the fluoroborate and the picrate derivative into which the fluoroborate can be converted are considered to be ionic. When the fluoroborate–hydroxyfluoroborate was treated with potassium cyanide under mild conditions, triphenylcyclopropenyl cyanide was reformed, showing that no rearrangement of the carbon skeleton had occurred.

In an expansion of this study, the properties of both covalent and ionic derivatives were determined (43). The fluoroborate–hydroxyfluoroborate derivative reacted with methanol to form 1,2,3-triphenylcyclopropenyl methyl ether, a convenient source of salts of the triphenylcyclopropenyl cation XXIII, which the ether yielded on acid treatment. The equilibrium between the ion and the covalent ether derivative was studied with the aid of ultraviolet spectroscopy. The extent of the contribution to the stability of the *sym*-triphenylcyclopropenyl cation by the phenyl groups and by the cyclopropenyl aromatic system was studied.

Diphenylcyclopropenium perchlorate was synthesized by the reaction of 10% perchloric acid in acetic anhydride with 1,2-diphenylcyclopropene-3-carboxylic acid. Hydrolysis of the perchlorate derivative resulted in the formation of 3,3-bis(1,2-diphenylcyclopropenyl) ether (XXIV) (97). The covalent ether was treated with dry hydrogen bromide to give the bromide and



XXIII



XXIV

with boron trifluoride etherate to give the fluoroborate salt (37). Aqueous alkali reconverted the bromide into the covalent ether. The cyanide derivative was also obtained from the bromide. Similarly, perchlorate and fluoroborate derivatives were prepared from dipropylcyclopropenecarboxylic acid (35, 36).

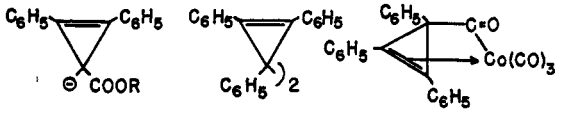
Tripropylcyclopropene was prepared from the fluoroborate, either by direct reaction with propyllithium or by conversion of the cation to 1,2-dipropyl-1-cyclopropenyl methyl ether and reaction of this compound with propylmagnesium bromide (36).

In a study of the solvolytic behavior of derivatives of the cyclopropenylcarbinyl cation, the acid chloride was first prepared from 2,3-diphenyl-2-cyclopropenecarboxylic acid and then reduced with an excess of lithium tri-*t*-butoxyaluminohydride to form the alcohol (38). Direct reduction of the acid with lithium aluminum hydride gave the saturated alcohol, although the unsaturated alcohol itself is not reduced by lithium aluminum hydride under the same conditions (18).

The carboxylic acids were readily converted into the

corresponding esters. In a study of the effect of substitution on the nonaromaticity of the cyclopropenyl anion XXV (27), 2,3-diphenyl-2-cyclopropenecarboxylic acid was converted by methylation and then ester exchange to the *t*-butyl ester.

Bistriphenylcyclopropenyl (XXVI), an undissociated dimer of the triphenylcyclopropenyl radical, was prepared by the reaction of *sym*-triphenylcyclopropenyl bromide with zinc dust in benzene. Treatment of the dimer with bromine gave the starting bromide. Although the purpose of the preparation was to obtain information on the stability of the radical for a comparison with the stable cation and the unstable anion, no evidence of radicals was noted in the dimer which was found to be remarkably stable (33).



XXV XXVI XXVII

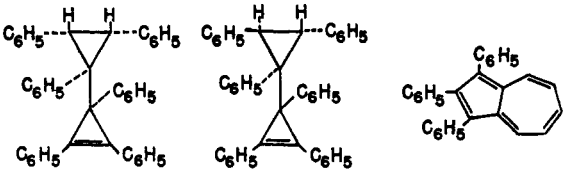
In an attempt to prepare a complex containing a cyclopropenyl ligand π-bonded to a metal, Coffey (62) reacted triphenylcyclopropenyl bromide with cobalt tetracarbonylate anion in acetonitrile to obtain a complex with the probable structure XXVII. The reaction with $[Fe(CO)_3NO]^-$ yielded a similar complex with Fe replacing Co and NO replacing one CO. The cyclopropene ring in the complex was shown to be intact, since triphenylcyclopropenylium tetrachloroferrate was obtained on the oxidation of the iron complex with 1,3-diphenylallyl chloride in hot toluene.

The reaction between triiron dodecacarbonyl and 1,3,3-trimethylcyclopropene gave bright yellow, air-stable crystals with the formula designated as $C_6H_{10}COFe(CO)_3$ (157). The infrared and n.m.r. spectra indicated that the complex consisted of an iron tricarbonyl group π-bonded to a $C_6H_{10}CO$ residue which acted as a four-electron donor and which contained three methyl groups and a single olefinic hydrogen atom.

Triphenylcyclopropenyl chloride in methanol was treated with potassium trichloro(ethylene)platinate to give the stable complex $C_{23}H_{19}Cl_3Pt$. The infrared spectrum had the characteristic absorption of the triphenylcyclopropenyl cation. Similarly, treatment of the cation with sodium chloroplatinate gave the complex salt $[C_3Ph_3]_2[PtCl_6]$ (54).

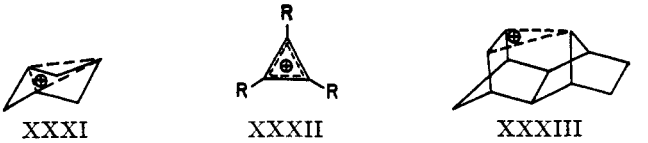
Several stable cyclopropenylium salts were prepared during an investigation (216) on the use of quinone dehydrogenation as a method of preparation of organic cations. Triphenylcyclopropene reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in methylene chloride to give a complex (79% yield). Triphenylcyclopropenylium perchlorate (95% yield) was prepared by the addition of perchloric acid to the complex or to a hot solution of triphenylcyclopropene and DDQ in acetic acid. Triphenylcyclopropene reacted with DDQ and picric acid to form triphenylcyclopropenylium picrate (88%) and with DDQ and sodium iodide to form a triphenylcyclopropenylium iodide complex (80% yield) (216).

The reaction of triphenylcyclopropene with potassium amide in liquid ammonia gave hexaphenylbenzene, but with sodium or lithium amide yielded the *cis* dimer triphenylcyclopropyltriphenylcyclopropene (m.p. 179.5–180.5°) (32). The *cis* dimer (XXVIII) was also formed when triphenylcyclopropene was heated in a solution in organic solvents. The *trans* dimer (XXIX) (m.p. 155–157°) was obtained by converting *trans*-chloro-1,2,3-triphenylcyclopropane to its Grignard reagent and reacting it with triphenylcyclopropenyl bromide. The spectra of the two isomers were very similar. When the dimer was heated at 280°, triphenylazulene (XXX) and *trans*-stilbene were formed.



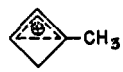
XXVIII XXIX XXX

Winstein and Sonnenberg (281) prepared 3-deuterated 3-bicyclo[3.1.0]hexanols and acetolyzed the corresponding toluenesulfonates to study the occurrence of a uniquely symmetrical nonclassical cation as an intermediate in solvolysis of the *cis*-toluenesulfonate. The results indicated that tris(homocyclopropenyl) cation XXXI was the intermediate. This cation was considered to be the first example of a homoaromatic structure, and the theoretical relationship between it and cyclopropenyl cations XXXII was considered.

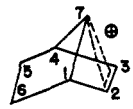


XXXI XXXII XXXIII

A number of investigators recently have been interested in studies concerning intermediate cations possessing three-center bonding (227, 278). An octahydrodimethanonaphthyl cation (XXXIII) was described as a nonclassical homocyclopropenyl cation (279). Similarly, the enhancement of the rate of solvolysis of 1-methylcyclobut-2-enyl bromide was associated with the 1,3-π-type electronic interaction attributed to a homocyclopropenyl cation (XXXIV) (156). The intermediate nonclassical bis(homocyclopropenyl) cation XXXV accounted for the high rate of solvolysis of *anti*-7-norbornenyl *p*-toluenesulfonate (280).



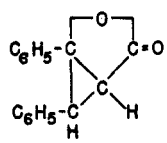
XXXIV



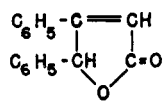
XXXV

b. Reactions Involving Ring Expansion

1,2-Diphenylcyclopropene-3,3-dicarboxylic acid melted at approximately 190° with the evolution of carbon dioxide to form a lactone instead of the expected monobasic acid. The structure of the lactone was believed to be that of XXXVI (67). Later workers (41, 42) disagreed with this structure and designated it as diphenylcrotonolactone (XXXVII). This structure was confirmed by comparison with an authentic sample. The lactone was also formed by pyrolysis of the monocarboxylic acid.



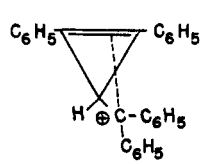
XXXVI



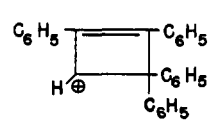
XXXVII

Pyrolysis of 3,3-bis(1,2-diphenylcyclopropenyl) ether for a short time at 180° gave a mixture of products that included 1,2,4,5-tetraphenylbenzene and 2,3,4,6-tetraphenylphenol (97). Bis(triphenylcyclopropenyl) was transformed quantitatively to an isomer, hexaphenylbenzene, when held at its melting point for a few seconds, refluxed in xylene for a few hours, or irradiated with ultraviolet lamp at room temperature (33). Analogous results were obtained with 3,3-bis(1,2-diphenylcyclopropenyl) (108).

The preparation and unusual rearrangement of diphenyl(1,2-diphenyl-1-cyclopropenyl)carbinol were studied under a variety of dehydrating conditions in an attempt to prepare the derivative tetraphenylmethyleneecyclopropene (11). Instead of the desired derivative, two hydrocarbons were formed by a rearrangement, the major one identified as 1,2,4-triphenylnaphthalene and the minor one as 1,2,3-triphenylazulene. The mechanism postulated involved the rearrangement of the carbonium ion XXXVIII to the cyclobutenyl cation XXXIX. The resulting allylic cation could attack a neighboring phenyl group to form spirocyclic systems which would then undergo well-established rearrangements to give the products obtained (28).



XXXVIII

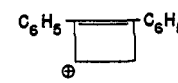


XXXIX

Since the pyrolysis of triphenylcyclopropyltriphenylcyclopropene at 280° gave triphenylazulene as well as *trans*-stilbene, the mechanisms of such reactions were investigated further (32).

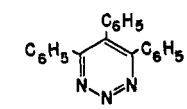
During an investigation of the solvolytic behavior of derivatives of the cyclopropenylcarbinyl cation XL, the solvolysis of the tosylate in aqueous acetonitrile indicated that the process also proceeded with ring expansion to the diphenylcyclobutenyl cation XLI. For rate studies diphenylcyclopropenylcarbinyl, diphenylcyclopropylcarbinyl, and *p*-anisylphenylcyclopropenylcarbinyl tosylates were solvolyzed in absolute ethanol. The rapid rates indicated that solvolyses of the first two proceeded through nonclassical carbonium ions. Studies on the third tosylate indicated that the double bond is not directly involved in the ionization but that the process involved delocalization of a ring single bond. The lack of an appreciable effect on the solvolysis rate by both the double bond and the extra methoxyl group pointed to a transition state that resembled the starting cyclopropenylcarbinyl system, both geometrically and stereoelectronically, but in which σ-electrons were delocalized. The slight rearrangement of the cyclopropenylcarbinyl cation was sufficient to transform an unstable primary carbonium ion into a strongly stabilized species. The results indicate the unusual stability of the bicyclobutonium ion XLII (38).

XL



XLI

XLII



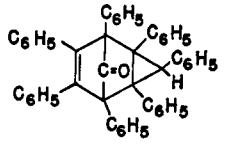
XLIII

Chandross and Smolinsky (52) reported on the preparation of 1-azido-1,2,3-triphenylcyclopropene by the reaction of sodium azide with the bromide derivative and its rearrangement at room temperature to 4,5,6-triphenyl-*vic*-triazene (XLIII) and a second product. Their properties and the mechanism of the rearrangement were studied. This rearrangement was also noted in a study (29) of similar reactions in which ring expansion occurred by the internal attack of a substituent attached to the saturated carbon of a diphenylcyclopropene derivative. In an attempt to prepare the hydrazone of 1,2-diphenyl-3-benzoylcyclopropene, the reaction of the ketone with hydrazine hydrate in refluxing ethanol led to 3,4,6-triphenyldihydropyridazine. Similarly, tetraphenylpyrrole was formed when triphenylcyclopropenyl cyanide was treated with phenyllithium. The reaction of 2,3-diphenyl-2-cyclopropenecarboxylic acid chloride with phenylcadmium reagent in benzene at 0° yielded the expected phenyl ketone, but at 60° only 2,3,5-triphenylfuran was isolated (29).

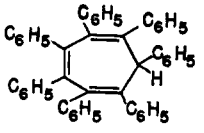
c. Diels–Alder Reactions

sym-Triphenylcyclopropene reacted as a dienophile in the Diels–Alder addition of tetraphenylcyclopenta-

dienone to give a ketone (XLIV), which on heating gave the reactants and heptaphenyltropilidene (XLV). Although the ketone was isolated, it was quite unstable to heat and was readily converted to the triene (12). Similarly, *sym*-triphenylcyclopropene reacted with acecyclone in refluxing xylene, refluxing benzene, or benzene–chloroform at room temperature to give $C_{47}H_{32}$,

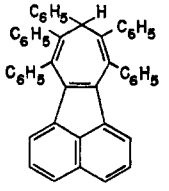


XLIV

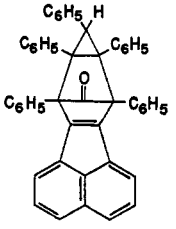


XLV

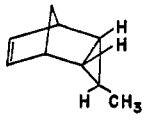
thought to be 9H-cyclohept[*a*]acenaphthalene (XLVI). A bright yellow crystalline ketone, $C_{48}H_{32}O$ (XLVII), was also obtained in the room temperature reaction. An acid was formed by the reaction of acecyclone with 2,3-diphenyl-2-cyclopropenecarboxylic acid, and a bromo derivative was prepared by using 3-bromoacecyclone as the diene (13).



XLVI



XLVII



XLVIII

The unstable 3-methylcyclopropene reacted with cyclopentadiene at 0° to give the tricyclic compound XLVIII. The n.m.r. and infrared spectra of this adduct and the cyclopropene adduct (274) of cyclopentadiene are very similar. The dimethyl derivative failed to add to cyclopentadiene, however, even at elevated temperatures (61).

d. Miscellaneous Reactions

The ring-opening reactions of the reactive tetrachlorocyclopropene ring systems were investigated (255). Tetrachlorocyclopropene reacted with water at room temperature to give CHCl=CClCOOCOCCl=CHCl (90% yield), with alcoholic ammonium hydroxide at 50° to give CHCl=CClCN (30% yield), and with alcohols in the presence of zinc at 50–80° to give the mixtures of CHCl=CClCOOR, CCl_2=CHCOOR, and ROOCCH$_2$COOR esters (R = Me, Et, *n*-Bu, or *i*-Pr). The addition of a neutral solvent molecule to the double bond of the cyclopropene was believed to form an unstable cyclopropane intermediate which then underwent the ring-opening reactions to give the observed products. Tetrachlorocyclopropene was found to be quantitatively converted to hexachlorocyclopropane (256) when it was chlorinated in ultraviolet light.

The oxidation of 1,2-diphenylcyclopropene-3,3-dicarboxylic acid with potassium permanganate in alkaline solution formed dibenzoylmethane (27). Similarly, the dipropyl derivative gave dibutyrylmethane and the dibutyl derivative gave di-*n*-valerylmethane (83). The nitrophenylphenyl derivative was oxidized by the permanganate to give a nitrodibenzoylmethane (160). The ester of this dicarboxylic acid added bromine to form the dibromocyclopropane derivative, which upon boiling with excess concentrated potassium hydroxide would reform the cyclopropene acid.

Evidence was obtained to indicate that the cyclopropenecarboxylic esters were particularly reactive in Michael addition reactions (273). The reactivity was attributed to the considerable acetylenic character of the cyclopropene ring.

1,2-Diphenylcyclopropene-3-carboxylic acid, however, was shown to be quite stable, most likely due to the heavy conjugation of the substituents (42). The ester was not affected by refluxing with potassium *t*-butoxide in *t*-butyl alcohol for 60 hr. or by 40% sulfuric acid in methyl alcohol at room temperature.

sym-Triphenylcyclopropene reacted with sodium *p*-toluidide in *p*-toluidine or with lithium propylamide in propylamine to give, on hydrolysis, benzyldeoxybenzoin (32). The hydrocarbon reacted with sodium methoxide to give the methyl ether, which in turn was quantitatively hydrolyzed with acid to benzyldeoxybenzoin.

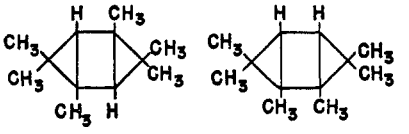
Aqueous alkali reacted with 1,2,3-triphenylcyclopropenyl fluoroborate to open the ring and form a benzylidene desoxybenzoin isomer (43). Diphenylcyclopropenium perchlorate was hydrolyzed by aqueous potassium hydroxide to form α-phenylcinnamaldehyde (97). Chromatography of the bis(diphenylcyclopropenyl) ether on alumina converted it to α-phenylcinnamaldehyde (37).

1,3,3-Trimethylcyclopropene was hydrogenated using 5% palladium on charcoal at 0° to give 1,1,2-trimethylcyclopropane as the major product. The minor component, which had a shorter retention time on a gas chromatographic column, was not identified (59). 3,3-Dimethylcyclopropene was hydrogenated under the same conditions to give 95% 1,1-dimethylcyclopropane (59, 61), whereas 1,3-dimethylcyclopropene was hydrogenated in *n*-heptane with platinum oxide as catalyst at 0° to form three compounds in the ratios of 10:1:6. The three compounds were isolated by gas chromatography and identified as *cis*-1,2-dimethylcyclopropane, *trans*-1,2-dimethylcyclopropane, and isopentane (61). 1,2-Dimethylcyclopropene was hydrogenated in isooctane with the platinum oxide catalyst to produce 70% of *cis*-1,2-dimethylcyclopropane and two minor components identified by mass spectroscopy as *n*-pentane and isopentane (75). Hydrogenation of methyl 1,2-dimethylcyclopropene-3-carboxylate produced methyl *cis*-1,2-dimethylcyclopropane-3-(*cis*)-carboxylate with no detectable amount of another stereoisomer (75).

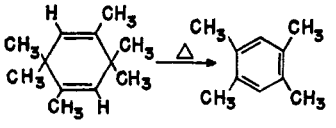
Similarly, hydrogenation (Pd, $CaCO_3$) of the ethyl ester of 1,2-di-*n*-butyl-1-cyclopropenecarboxylic acid gave the corresponding *cis*-cyclopropane compound. Reduction of the cyclopropene derivative with lithium aluminum hydride under mild conditions gave 1-methylol-2,3-di-*n*-butyl-2-cyclopropene (162).

Sterculene, 1,2-dioctylcyclopropene, was used in a study designed to determine the products formed when the cyclopropene ring is destroyed by rearrangement with activated alumina. The major products indicated by spectral, hydrogenation, maleic anhydride adduction, and ozonolysis data were: 9-methylene-10-octadecene, 9-methyl-8,10-octadecadiene, and 9-methyl-9,11-octadecadiene (236).

The dimerization of 1,3,3-trimethylcyclopropene with benzophenone as the sensitizer was shown to form the tricyclic compounds XLIX and L. The dimeric compounds underwent thermal isomerization to form compounds LI and LII. When copper catalysts were employed in the reaction, the expected dimerization did not occur, but instead, the ring was opened and a conjugated triene was formed (247).



XLIX L



LI LII

e. Cyclopropenone Reactions

Dipropylcyclopropenone is more basic than the corresponding diphenyl compound, has a much greater stability toward base, and has a greater thermal stability (203). However, it is moderately sensitive toward oxygen and has to be handled under nitrogen. The diphenyl ketone was 90% converted to stilbenecarboxylic acid in 3 min. at 31° in 0.1 *N* ethanolic sodium hydroxide solution, whereas the dipropyl derivative was unaffected after 1 hr. at the same conditions (39). The results were attributed to a greater stabilization by the phenyl groups of the transition states in the decompositions rather than to a greater stabilization by the propyl groups on the ketone.

The treatment of either diphenylcyclopropenone or diphenylacetylene with nickel carbonyl and hydrochloric acid in ethanol–benzene gave *trans*-α-phenylcinnamic acid and its ethyl ester. When the reaction was carried out with nickel carbonyl in benzene, the results indicated that diphenylcyclopropenone was first converted into diphenylacetylene and then into α-phenylcinnamic acid and thus did not support the suggestion that cyclopropenones served as intermediates in the carbonylation of acetylenes to acrylic acids (14).

Nevertheless, the hypothetical cyclopropenone–Fe$(CO)_3$ complex was included in a study (49) of the nature of the bonding occurring in complexes of the general type $C_xH_xCOFe(CO)_3$ (x = 2, 4, 6). The complexes were shown to differ only in the variation in the number of occupied orbitals of different n and m. On the basis of the simple molecular orbital theory, a simple and unified picture of the bonding in this series was provided. The investigator (49) concluded that the effective atomic number rule has little significance.

Diphenylcyclopropenone underwent thermal decomposition at 130–140° to liberate carbon monoxide and to form diphenylacetylene (34). The cyclopropene ring was also opened when the ketone reacted with 10% potassium hydroxide solution to form α,β-diphenylacrylic acid (165). 2,3-Diphenyl-1-hydroxycyclopropane was formed from the ketone by hydrogenation with platinum oxide as the catalyst or by reduction with lithium aluminum hydride. Other workers (203) reported dibenzyl ketone was formed by hydrogenation of the ketone. Possibly the most interesting property of diphenylcyclopropenone is its reaction with mineral acids to form diphenylhydroxycyclopropenylium salts. The reaction is reversible in aqueous solution of sodium bicarbonate (203, 268). The cyclopropenone will also form a 2,4-dinitrophenylhydrazone (165). The ketone reacts with hydroxylamine to form 3,4-diphenylisoxazolone and a small amount of desoxybenzoin oxime (203).

Pyrolysis of cycloheptenocyclopropenone gave carbon monoxide and tris(cycloheptenobenzene). Cycloheptene-1-carboxylic acid was formed when the cyclopropenone was refluxed with aqueous potassium hydroxide (40).

C. PHYSICAL AND PHYSICAL–CHEMICAL PROPERTIES

1. Cyclopropene

The physical and physical–chemical properties of cyclopropene and its derivatives are of interest since the extreme of chemical bonding is encountered in the small bonding angles in this three-membered unsaturated ring. The availability of cyclopropene through an improved method of synthesis (229) stimulated investigations of the structure of this molecule which the classical Baeyer strain theory predicted to be so highly strained. The stabilities of cyclopropene and cyclopropane structures were compared on a theoretical basis (271b).

Data reported for bond angles and interatomic distances as determined by microwave spectra and electron methods are included in Table I. The data indicated the shortening of the C–C bond relative to ethane,

TABLE I

STRUCTURAL PARAMETERS OF CYCLOPROPENE

Bond and bond angle	Microwave spectra (148)	Electron diffraction (77)	Calculated (238)
C—C	1.515 Å.	1.525 ± 0.02 Å.	
C=C	1.300 Å.	1.286 ± 0.04 Å.	
C—H (methylene)	1.087 ± 0.004 Å.	1.087 ± 0.04 Å.	1.073 Å.
C—H (vinyl)	1.070 Å.		1.083 Å.
C=C—H angle	149° 55′	152 ± 12°	
H—C—H angle	114° 42′ ± 10′	118° (assumed)	117.5°
C—C—C angle	50° 48′	49.9°	
CH_2 or CH orientation			32° 30′

propane, and cyclopropane (1.54 Å.) and the C=C bond relative to ethylene (1.34 Å.) (148, 200). The major differences in cyclopropene from cyclopropane were the shortened C–C single bond distance and the smaller internuclear ring angle at the methylene position. The angle between the carbon orbitals at the methylene position which are used in the bonding to the ring was calculated to be 105° 35′. These orbitals formed bonds which lie 27° 24′ outside of the direct internuclear line and which are known as "bent-bonds." The value of 1.574 Å. was calculated for the "bent-bond" distance along a 27° 24′ arc and indicated that the C–C single bonds in cyclopropene should be weaker than the bonds in cyclopropane (148).

The chemical bonding in cyclopropene has been the subject of several research papers. The method of antisymmetrized products of molecular orbitals was used to calculate the lower excited energy levels of the cyclic polyenes, radicals and ions with three to eight carbon atoms. The interelectronic integrals were calculated without empirical data, except for the carbon–carbon distance (23). The results were compared with the calculations obtained using a semiempirical molecular orbital method (174). The cyclopropene radical was stated to have degenerate doublet ground states as well as several degenerate excited states. While different results were obtained from the calculations, the qualitative trends were the same if all the compounds studied were considered. Data are reported in Table II.

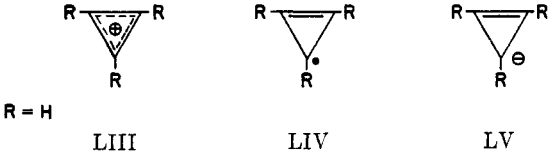
The molecular orbital theory as developed by Hückel (140) predicts that compounds of the completely conjugated planar monocyclic polyolefins which possess

TABLE II

Electronic Energy Levels

Ion or radical	Symmetry	Excitation energy, e.v. Singlet (174)	Singlet (23)	Triplet (174)	Triplet (23)
Cyclopropene cation	E′ (D_{3h})	8.25	10.09	6.09	4.42
Cyclopropene radical	$^2E''$	0	0		
	$^2E''$	7.17	7.26		
	$^2A_2''$	7.17	9.89		
	$^2A_1''$	7.17	10.30		
	$^4A_1''$	5.02	1.58		

$(4n + 2)$ π-electrons (n = 0, 1, 2, 3, ...), are peculiarly stable by having fully filled molecular orbitals with substantial electron delocalization (resonance) energies as compared to the classical valence bond structures. Since the theory was stated to be applicable to the cyclopropenyl cations, anions, and free radicals, the molecular orbital (LCAO) method was used to calculate the electron delocalization energy, bond order, and free-valence index of cyclopropene and other related compounds. The values obtained for delocalization energies were: cyclopropenyl cation LIII, 2.00β; radical LIV, 1.00β; anion LV, 0.00β, with a predicted triplet ground state. The bond order was given as 1.50 (220).



LIII LIV LV

Bond energies of cyclopropene and other hydrocarbons were calculated, taking into consideration all valence electrons by the valence bond method and using bond equations (159). Although the results agreed quite well with experimental values for alkanes and olefins, the results for cyclopropenes and cyclopropanes did not coincide with experimental data at all. The ω-technique in the simple LCAO theory, a self-consistent field method which recognized the fact that electron repulsion will be less in the cation than in the radical, was used to calculate an ionization potential of 5.80 e.v. for the cyclopropenyl radical, 6.38 e.v. for the 1,2,3-triphenylcyclopropenyl radical, and 11.29 e.v. for cyclopropane (250). The ionization potential of cyclopropene as measured by electron impact was 9.95 v., which was close to the value of 9.84 v. obtained for propylene (63).

In a study of the microwave spectra of four isotopic species of cyclopropene, three rotational constants for each isotopic species were determined (148). The moments of inertia of cyclopropene, as calculated from these data, are: $I_A = 2.792 \times 10^{-39}$ g. cm.^{2}, $I_B = 3.846 \times 10^{-39}$, $I_C = 6.085 \times 10^{-39}$ (274). In turn, from these data and vibrational frequencies, the fol-

lowing thermodynamic functions at 25° were calculated: $(F° - H_0°)/T = -49.15$; $(H° - H_0°)/T = 9.23$; $S° - 58.38$.

Cyclopropene is rapidly isomerized to methylacetylene when it (mixed with helium) is passed through a glass tube packed with glass helices at 425°. The entropy of isomerization was calculated to be 1.9 e.v. and the enthalpy of the isomerization less than −3.4 kcal./mole. From the known heat of formation of methylacetylene (44.3 kcal./mole) and the above value for the enthalpy of isomerization, the heat of formation of cyclopropene was calculated to be at least 47.7 kcal./mole. The heat of hydrogenation to cyclopropane was calculated to be less than −35 kcal./mole. The extra strain energy of cyclopropene compared to cyclopropane was estimated from the thermodynamic data to be at least 8 kcal./mole (274).

The heat of combustion of cyclopropene was determined by the use of a flame calorimeter to be 485 ± 0.6 kcal./mole (275). The heat of formation of cyclopropene was calculated from this value to be 66.6 ± 0.6 kcal./mole. Other values derived from these data include −53.9 kcal./mole for the heat of hydrogenation to cyclopropane and −22 kcal./mole for the heat of isomerization to methylacetylene. From these calculations the extra strain energy in cyclopropene over that in cyclopropane was calculated to be on the order of 27 kcal./mole, somewhat higher than the value (274) estimated above.

The infrared, ultraviolet, and n.m.r. spectra of cyclopropene and a number of related compounds have been reported (276). The assignment of the 1641-cm.$^{-1}$ absorption band for the carbon–carbon double bond in cyclopropene was supported by Raman data.

Cyclopropene was found to have a dipole moment of 0.455 ± 0.01 D. (148).

In a study pertaining to acidities of hydrocarbons as determined by the simple molecular orbital theory, the pK of cyclopropene was calculated to be approximately 48. The value was compared with a pK of 28 obtained for 1,2,3-triphenylcyclopropene (251). However, the pK_{R^+} values of substituted cyclopropenyl cations were compared, and by extrapolation of these values the pK_{R^+} of the unsubstituted cyclopropenyl cation was predicted to be −6.3 (36). The value is quite low but may be influenced by such factors as destabilization by ring-strain effects and from coulombic repulsion.

2. *Cyclopropene Derivatives*

The reversible reduction potentials of a series of cyclopropene cations were determined by the technique of triangular wave potential oscillopolarography (7, 26). The reduction potential was used as an experimental measure of the difference between the resonance energies of the cations and their respective radicals with triphenylmethyl cation being used as a reference. At 150 c.p.s., the anodic and cathodic peak currents were found to be equal, thereby indicating that the radical could be reoxidized completely before dimerization occurred. The reductions were shown to involve one electron.

According to the molecular orbital theory, the sum of the energies of the occupied orbitals makes up the π-electron energy of a molecule, and thus the energy difference between the cation and radical is given by the energy of the orbital into which the reducing electron goes (7). For the triphenylcyclopropenyl cation, the electron enters an antibonding orbital and destabilizes the system by 0.504β, the predicted value for ΔDE. The value β is of the order of −2 e.v. for the simple MO theory. When Streitwieser's "ω-technique" (250), in which coulombic effects were considered, was used to calculate the ionization potential of the cation (6.38 e.v.) and the radical (7.26 e.v.), the difference (ΔDE) was 0.88 e.v. This value is not too different from the value (1.04 e.v.) of the difference in the reduction potentials of the triphenylcyclopropenyl and triphenylmethyl cations (7, 26). The simple molecular orbital method (LCAO) was also used to calculate DE values for cyclopropenyl cations, anions, and free radicals (183). Reversible reduction potentials for a number of cyclopropene cations are given in Table III.

The properties of these substituted derivatives were studied to determine the precise role of the substituent groups on the stability of the cyclopropenyl cation. The pK values of the triaryl-substituted cations were determined in 23% aqueous ethanol, since the related carbinols are not soluble in water (30, 53). The pK_{R^+}

$$R^+ + H_2O \rightleftharpoons ROH + H^+$$

value was determined by getting the midpoint of a spectrophotometric titration by plotting the absorbency at a wave length characteristic of the cation against the pH. The pK of the diphenyl cation was more sensitive to the nature of the medium than that of the triphenylcyclopropenyl cation. In water its pK_{R^+} was 0.3 as compared with 3.1 for the triphenyl cation, and in

TABLE III

REVERSIBLE REDUCTION POTENTIALS AND pK VALUES

Cation	$E_{1/2}$	23% aqueous ethanol solution	50% aqueous aceto-nitrile
Triphenylmethyl	−0.09	−6.63	
Diphenylcyclopropenyl	−1.02	−0.67	
Triphenylcyclopropenyl	−1.13	2.80 ± 0.05	3.1
p-Anisyldiphenyl-cyclopropenyl	−1.24	4.00 ± 0.05	
Di-*p*-anisylphenyl-cyclopropenyl	−1.37	5.22 ± 0.05	5.2
Tri-*p*-anisylcyclopropenyl	−1.49	6.42 ± 0.05	6.5
Propyldiphenylcyclopropenyl		3.8	
Dipropylcyclopropenyl			2.7
Tripropylcyclopropenyl			7.2

TABLE IV: PHYSICAL PROPERTIES OF CYCLOPROPENE DERIVATIVES

Compound	B.p., °C. (mm.)	$n^{20}D$	M.p., °C.	Ref.
1-Cyclopropene				
1,2-Bis(trifluoromethyl)-3,3-difluoro-	11			182
Dibromodiphenylquino-			>230 dec.	155
1,2-Dimethyl-	v.p. 150 mm. at 0° cor. to *ca.* 40°			75
1,3-Dimethyl-	33			61
3,3-Dimethyl-	14			58
	14.5			61
1,2-Dioctyl- (sterculene)	102 (0.04)	1.4541		195
3-Methyl-	−5 (est.)			61
3-Methyl-1,2,3-triphenyl-			95.5–97.5	32
1,2,3,3-Tetrachloro-	129.5–130 (745, under N_2)			255
1,2,3,3-Tetramethyl-	67 (755)	1.4021		57, 59
1,3,3-Trimethyl-	45 (750)	1.3893		57
	43.3	1.3892		59
	42.5–43.5	1.3892		61
1,2,3-Triphenyl-			110	12
			112–113	32
3β-(1β,2β,3β-Triphenylcyclopropyl)-1,2,3-triphenyl- (*cis* dimer)			179.5–180.5	32
3β-(1β,2β,3β-Triphenylcyclopropyl)-1,2,3-triphenyl- (*trans* dimer)			155–157	32
1,2,3-Tripropyl-	82–83 (27)			36
2-Cyclopropene-1-carbonitrile				
2,3-Diphenyl-			115–116	37
1,2,3-Triphenyl-			145–146	25, 43
2-Cyclopropene-1-carboxylic acid				
2,3-Dibutyl-	107.5–108 (0.2)	1.4612		83
2,3-Dibutyl-, ethyl ester	79–80 (0.2)	1.4479		83
2,3-Dimethyl-, methyl ester	45–60 (2) (impure)	1.4412 (purified)		75
2,3-Diphenyl-			209–211.5	27, 42
			210–211	83
2,3-Diphenyl-, ethyl ester			75.5–76.5	38
			77–78	83
2,3-Diphenyl-, methyl ester			83–85	42
2,3-Diphenyl-, *t*-butyl ester			88.5–89.5	27
2,3-Dipropyl-	101 (0.7)			36
	92–92.5 (0.5)	1.4625		83
2-(*p*-Methoxyphenyl)-3-phenyl-			179.5–181.5	38
2-Cyclopropene-1-carboxylic acid				
2-(*p*-Methoxyphenyl)-3-phenyl-, ethyl ester			69.5–71	38
2-Methyl-1-(1-methyl-2-carboethoxycyclopropyl)-, ethyl ester	104–106 (0.5)	1.4731		78
2-Methyl-3-phenyl-			137–139	82
2-Methyl-3-phenyl-, ethyl ester	86–87 (0.3)	1.5361		84
1-Cyclopropene-1-carboxylic acid				
2,3,3-Trimethyl-			48.5	57
			48.5–49.0	59
2,3,3-Trimethyl-, methyl ester	57 (15)			57
2-Cyclopropene-1,1-dicarboxylic acid				
2,3-Diphenyl-			205 dec.	42
			190 dec.	67
2,3-Diphenyl-, dimethyl ester			143–143.5	42
			140–142	67
2-*m*-Nitrophenyl-3-phenyl-			216	160
2-*m*-Nitrophenyl-3-phenyl-, dimethyl ester			176–178	160
1-Cyclopropene-1-heptanoic acid				
2-Octyl- (malvalic acid)			10.3–10.6	233, 234
2-Cyclopropene-1-methanol				
2,3-Diphenyl-			71–72	38
2,3-Diphenyl-, acetate			55.5–58.0	18
2,3-Diphenyl-, 3,5-dinitrobenzoate			155–156.5	18

TABLE IV (*Continued*)

Compound	B.p., °C. (mm.)	$n^{20}D$	M.p., °C.	Ref.
2,3-Diphenyl-, *p*-toluenesulfonate			70–71	38
2-*p*-Methoxyphenyl-3-phenyl-			72.5–73.5	38
2-*p*-Methoxyphenyl-3-phenyl-, *p*-toluenesulfonate			74 dec.	38
Diphenyl(2,3-diphenyl)-			173.5–174.5	28
Phenyl(2,3-diphenyl)-			82.0–82.5	18
1-Cyclopropene-1-octanoic acid				
2-Octyl- (sterculic acid) synthesized			18.9–19.6	50
2-Octyl- (sterculic acid) isolated			18.2–18.4	45, 99, 196
			19.3–19.9	218
			17.9–18.7	234
2-Octyl-, methyl ester (methyl sterculate)	123 (0.35)	1.4571		195
2-Octyl-3-carbethoxy-, methyl ester	200 (0.5)			46
1-Cyclopropene-1-octanol				
2-Octyl- (sterculyl alcohol)		1.4647		195
			10.6	196
Cyclopropenone				
Dibutyl-	95–97 (0.3)			40
Diphenyl-			121–121.5	34, 165
			121	268
Diphenyl-, 2,4-dinitrophenylhydrazone			248–249.5	165
			248–249	268
Diphenyl-, HBr salt of			148.5–149	268
Dipropyl-	66 (0.3)			39
Cyclohepteno-			52–53	40
Cyclopropenyl				
3,3-Bis(triphenyl)-			225–226	33
Cyclopropenylium bromide				
1,2-Bis(*p*-methoxyphenyl)-3-phenyl-			178–179 dec.	30
1-(3,5-Dibromo-4-hydroxyphenyl)-2,3-diphenyl-			278–280 dec.	155
2,3-Diphenyl-			105–106 dec.	37
2,3-Diphenyl-1-(*p*-hydroxyphenyl)-			280–282 dec.	155
2,3-Diphenyl-1-(*p*-methoxyphenyl)-			173–174 dec.	30
1,2,3-Triphenyl-			269–271 dec.	30, 43
1,2,3-Tris(*p*-methoxyphenyl)-			210–212 dec.	30
Cyclopropenylium fluoroborate				
2,3-Diphenyl-1-propyl-			179 dec.	36
2,3-Dipropyl- (impure)			70	36
Cyclopropenylium fluoroborate–hydroxyfluoroborate				
1,2,3-Triphenyl- (impure)			300 dec.	25, 43
Cyclopropenylium perchlorate				
1-(Benzyloxyphenyl)-2,3-diphenyl-			248–250 exptl.	155
2,3-Diphenyl-			149.5–150.5 dec.	97
2,3-Diphenyl-1-propyl-			196–197 dec.	36
2,3-Dipropyl-			80 dec.	35, 36
1,2,3-Triphenyl-			229–231 dec.	216
1,2,3-Tripropyl-			184–185 dec.	36
Cyclopropenylium picrate				
1,2,3-Triphenyl-			195–196	25
			194–197	43
			193–197	216
Complexes				
1,3,3-Trimethylcyclopropene complex				
With triiron dodecacarbonyl			69	157
1,2,3-Triphenylcyclopropenyl complex				
With cobalt tetracarbonylate anion			134–135.5	62
With $Fe(CO)_3NO^-$			119–121	62
With trichloro(ethylene) platinate			210–215 dec.	54
1,2,3-Triphenylcyclopropenylium tetrachloroferrate			253–254	62
Ethers				
3,3-Bis(1,2-diphenyl-1-cyclopropenyl) ether			170–172 dec.	37
			163–165 dec.	97
3,3-Bis(1,2,3-triphenyl-1-cyclopropenyl) ether			175–177 dec.	30
1,2-Dipropyl-1-cyclopropen-3-yl methyl ether	94 (53)			36
1,2,3-Triphenyl-1-cyclopropen-3-yl methyl ether			69–70	43
1,2,3-Triphenyl-1-cyclopropen-3-yl *t*-butyl ether			143–144.5	30

23% aqueous ethanol, −0.67 as compared with 2.80 (37). The difference is less than that predicted by simple Hückel molecular orbital calculations by the ω-technique as the prediction in this case was modified by both an inductive effect and an effect on the solvation energy of the ion (37). For the triaryl series, the pK values of the cations were found to be roughly proportional to the increase of DE on ionization as obtained by the first iteration of the ω-technique and by the simple Hückel approximations with the choice of special parameters for oxygen (30). The pK values are also directly proportional to the reduction potential, as shown in Table III (7, 26).

In both the triphenylmethyl (used as reference) and triphenylcyclopropenyl series there was no evidence for a special symmetry effect on stability (30). However, a comparison of the pK values of the dipropyl- and tripropyl-, diphenyl- and propyldiphenylcyclopropenyl cations (2.7, 7.2; 0.67, 3.8) indicates that the alkyl groups have a considerable effect on the stability of the cyclopropenyl cation (36). A potentiometric titration was used to determine the pK_{R^+} values of the alkyl-substituted cations which could not be determined by ultraviolet spectroscopy. The propyl groups are apparently more effective in stabilizing the cations and the phenyl groups, the covalent carbinols. The propyl groups contribute stabilization mainly by an inductive effect involving the single bonds, and hyperconjugation is most likely unimportant. This interpretation was reinforced by n.m.r. studies. In contrast, the phenyl groups contribute stabilization by conjugation, the extent of which is not large.

The gain in conjugation energies of the phenyl-, diphenyl-, and *sym*-triphenylcyclopropenyl cations, as calculated according to the π-electron approximation method, indicated the additive nature of the conjugation energies of the compounds in respect to the number of phenyl groups (15–17).

A comparison of the pK_{R^+} values and reduction potentials of the various substituted derivatives (Table III) indicates the effect of the methoxyl group on the properties of aryl-substituted cyclopropenes. The pK_{R^+} value increased 1.2 units per methoxyl group, corresponding to a $\Delta F°$ of ionization of 1.7 kcal./mole. The methoxyl group has a small but not appreciable effect on the rate of solvolysis, as is shown by the comparison of the rate in absolute ethanol at 30° of diphenylcyclopropenylcarbinyl tosylate as 1.36×10^{-4} sec.$^{-1}$, with *p*-anisylphenylcyclopropenylcarbinyl tosylate as 4.50×10^{-4} sec.$^{-1}$. By comparison, the rate of bromination of *p*-anisylphenylcyclopropenylcarboxylic ester is of the order of 1000 times that of the bromination of the diphenyl derivative (38, 239). The ultraviolet spectrum of triphenylcyclopropenyl cation was similar to the spectra of covalent triphenylcyclopropenyl derivatives with the position of the major absorption band of each only a few millimicrons apart. With anisyl compounds, however, the addition of the methoxyl group shifted the major absorption peak to longer wave lengths until for the tri-*p*-anisylcyclopropenyl derivative, the peak is 25 mμ apart from that of the triphenylcyclopropenyl derivative (30).

Since a knowledge of the geometry of the cation is important for computation of delocalization energy, charge density, and bond orders, a crystallographic study of *sym*-triphenylcyclopropenyl perchlorate was made (253). The cation as a whole was found to be nonplanar, with the phenyl groups twisted out of the plane of the cyclopropenyl group at an average angle of 21°. The average C–C bond distance in the ring is 1.40 Å., and the average exocyclic C–C bond is 1.45 Å.

The ^{13}C–H coupling constants in 3,3-dimethylcyclopropene and 1,3,3-trimethylcyclopropene were measured (55, 166) by observing the proton-resonance satellites of hydrogen on carbon-13 in natural abundance. The values indicated that a model for cyclopropenes should be essentially similar to that for cyclopropane with "bent" ring-skeleton bonds and increased s-character of the exocyclic atomic orbitals. With regard to the vinyl-hydrogen bonds, cyclopropenes should be more closely related to acetylenes than to olefins. A comparison of the data obtained for 1,3,3-trimethylcyclopropene and tricyclo[4.1.0.0]heptane indicated a qualitative analogy between the cyclopropene and the bicyclobutane ring system (60).

The dipole moments and infrared absorption spectra have been obtained for diphenylcyclopropenone and related compounds (20, 21). A study comparing the spectra of this unusual ketone with its hydrogen bromide salt indicated the transition of the ketone into the cationic enolic form, with formation of a nonbenzenoidal aromatic ring system (284, 285). Since diphenylcyclopropenone exists in neutral solutions in the form of neutral molecules and in acid solutions in the form of cations, the polarography of this compound was investigated. In neutral solutions, the cyclopropene derivative gives either a single wave of the reduction of the double bond in the ring or this wave plus a wave of the reduction of the carbonyl group. In acid solution a wave has a diffusion character in weakly acid solutions and a mixed diffusion–kinetic character in strongly acid solutions. The wave results from simultaneous single electron reduction of cationic form of the ketone with dimerization of the radicals and catalytic evolution of hydrogen (287).

A number of cyclopropene derivatives and their physical properties are listed in Table IV.

III. Naturally Occurring Cyclopropene Fatty Acids

A. Occurrence

Considerable interest in the cyclopropene com-

TABLE V

PLANTS OF THE ORDER MALVALES GIVING A POSITIVE HALPHEN TEST

Family and species	Common name[a]	References
Malvaceae		
Abutilon incanum	Indian mallow	86
Abutilon theophrasti	Chingma, velvetweed	85, 86, 139
Althaea officinalis	Marsh mallow	201
Althaea rosea	Hollyhock	86, 139, 176, 201
Gossypium hirsutum	Upland cotton	139, 233, 235
Hibiscus abelmoschus	Musk mallow	139
Hibiscus cannabinus	Kenaph	85, 86
Hibiscus esculentus	Okra	121, 139
Hibiscus manihot	Sunset hibiscus	207, 208
Hibiscus moscheutos	Rose mallow	85, 86, 139
Hibiscus palustris	Common rose mallow	86
Hibiscus plantanifolius	Sycamore leaf hibiscus	86
Hibiscus roseus		201
Hibiscus sabdariffa	Roselle	201
Hibiscus syriacus	Shrub althea	85, 86, 139
Hibiscus trionum	Flower of an hour	86
Kosteletzkya virginica	Virginia salt marsh mallow	86
Lavatera assurgentiflora	California tree mallow	176, 177
Lavatera trimestris	Herb tree mallow	85, 139
Malope sp.	Malope	201
Malope trifida	Malope	139
Malva moschata	Musk mallow	139
Malva parviflora	Little mallow, cheeseweed	86, 176, 177, 201, 233, 235
Malva rotundifolia	Running mallow	201
Malva verticillata	Cluster mallow	233, 235
Sida hederacea	Alkali sida	176
Sida spinosa	Prickly sida	86
idalcea hybridum Gray		139
Sphaeralacea coccinea	Scarlet globe mallow	86
Thespesia populnea Soland	Portia tree	139
Urena lobata	Cadillo	86
Sterculiaceae		206
Brachychiton acerifolius	Flame tree	85, 86, 235
Brachychiton populneum	Kurrajong bottle tree	235
Cola vera		201
Firmiana simplex (Sterculia platanfolia)	Chinese parasol tree	85, 86, 201
Sterculia foetida	Hazel sterculia	5, 98, 186, 235
Sterculia tragacantha		201
Tiliaceae		143, 144, 206
Glyphaea grewioides		201
Tilia cordata	Little leaf linden	201
Tilia platyphilla	Big leaf linden	201
Tilia tomentosa	Silver linden	201
Bombacaceae		143, 206
Adansonia sp.	Baobab	190, 201
Bombax oleagineum		65
Ceiba acuminata		86, 87
Ceiba pentandra or sp.	Kapok	86, 190, 257

[a] Mostly from H. P. Kelsey and W. A. Dayton, "Standardized Plant Names," 2nd Ed., J. Horace McFarland Co., Harrisburg, Pa., 1942.

pounds was stimulated by the association of a positive Halphen test (119) with the occurrence of cyclopropene fatty acids in oils from certain plants (74, 234, 235). Although the Halphen test has been used since 1897 for the detection of cottonseed oil in mixtures of vegetable oils, investigators have found that the Halphen reaction is not specific for cottonseed oil but is given by oils from many species of the order Malvales. The four families included in this order are: *Malvaceae*, *Sterculiaceae*, *Bombacaceae*, and *Tiliaceae*. Species that have been reported to give positive Halphen tests are listed in Table V.

B. THE HALPHEN TEST

The many conflicting statements found in the early literature on the Halphen test were due mainly to the effect of modifications of the experimental procedure on the sensitivity of the test. Investigators studied the effect of various treatments of the oils on the Halphen reaction and attempted to determine the chemical reactions that occur in the test. Possibly many conclusions obtained from these early studies were erroneous as a result of inadequate equipment and procedure. The early interest in the reaction was stimulated by the need of a good test for the adulteration or substitution of one vegetable oil by another.

In the original method described by Halphen (119), equal volumes (about 1–3 ml. of each) of the oil under examination, amyl alcohol, and carbon disulfide containing 1% free sulfur, were placed in a tube and then heated in a boiling bath of aqueous sodium chloride for 10–15 min. A red or orange coloration developed in the presence of cottonseed oil. Modifications of the test included differences in heating time (64, 113, 223, 252), temperature of the bath (184), excess of sulfur (109), the use (197, 243) or omission (164, 224, 242, 259) of amyl alcohol, addition or substitution of an additional reagent such as pyridine (110–112, 209, 259), and use of sealed tubes or pressure flasks (212, 226, 249, 271a) in place of condensing tubes (232, 282).

Many investigators attempted to make the test quantitative (222, 225), but, in general, most workers felt that the test would not give reliable results (187, 213). Recently Deutschman and Klaus (72) studied the reaction conditions for carrying out the Halphen test and proposed a procedure claimed to give reproducible color development.

Many experiments have been described in which

cottonseed oils were subjected to various treatments for the purpose of identifying and inactivating the material responsible for a positive Halphen reaction. Oils heated to 260–270° (107), oxidized with potassium permanganate in the presence of cold dilute sulfuric acid (214), or exposed to infrared radiation (199) did not give positive tests. Similarly, cottonseed oil mixed with sulfur and exposed for a long time to sunlight became indifferent toward Halphen's reagent (215). Oils treated with bromine or iodine did not give the reaction, confirming Halphen's statement (120) that fully brominated cottonseed oil gave a negative test. Concentrated hydrochloric acid inactivated the factor after long shaking with the oil which, after such treatment, contained a slight amount of chlorine in combination (163). Treatment of *Sterculia foetida* oil with either hydrogen chloride or sulfur dioxide destroyed the Halphen reactivity of the oil (73).

Much of the literature is filled with contradictory reports which are difficult to explain. For example, although the Halphen reaction was considered by many workers (245) to be more characteristic of old oils, a rancid oil that was 3 years old was reported to give a negative test (244). Similarly, although no change in the intensity of the color development was detected when the oil tested was previously treated with zinc and sulfuric acid, a negative reaction was obtained with oils subjected to the action of sulfurous acid and then washed with alcohol to remove the free acids formed (103). The refraction and iodine and saponification values of these latter oils were not altered to any extent by the treatment.

Recently activated aluminas that were treated with various inorganic and organic acids were tested for their efficiency as bleaching agents and for their ability to eliminate the response of bleached cottonseed oil to the Halphen test (211). An alumina containing a catalytic amount of sulfurous acid proved to be the best of these adsorbents. The response to the Halphen test became negative with exposure of the refined oil to the alumina for 30 min. at 225°.

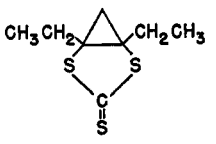
The Halphen response of a cottonseed oil fraction obtained by an additional hot hexane extraction was almost three times that of the oil from the initial extraction at room temperature (9). The addition of commercial soybean phosphatides enhanced the Halphen response of refined cottonseed oil but had no significant effect on the response of the crude oil. Possibly the crude oils gave fictitiously high responses as they contain phosphatides similar to those of soybeans. The test was found to be sensitive to a number of nitrogen-containing substances. Although small amounts of primary amines reduced the color intensity, the presence of secondary amines or urea increased the intensity and suppressed the formation of a second pigment absorbing at 540 mμ (9). This effect of urea should be particularly noted as the use of urea clathrates has played an important role in the isolation of fatty acids from these oils.

Most of the early workers (120, 204) believed the factor in the seed oils which was responsible for the Halphen reaction to be an unusual, unsaturated fatty acid. Raikow (214) thought that perhaps the acid had a side chain, while other workers (163) concluded that the factor was a glyceride containing an unsaturated fatty acid which was either an ethylene derivative with an abnormal carbon chain or an acetylene derivative. It was not until 1955 that a very small amount of a fatty acid with a cyclopropene ring was suggested as the material in cottonseed oil responsible for a positive Halphen reaction (74, 118).

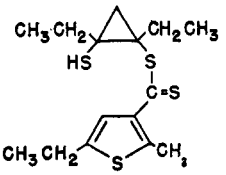
The investigation (98) of the reaction with sterculic acid, a fatty acid containing a cyclopropene ring (196), indicated that the reaction involved an opening of the ring across the single bonds. As the Halphen color developed, there was a gradual disappearance of the absorption bands at 5.35 and 9.92 μ which were attributed to the cyclopropene ring. The rapid appearance of a strong band at 4.88 μ and its subsequent disappearance were attributed to the double bond in the grouping —S—C=S, which was first formed by reaction between carbon disulfide and the cyclopropene ring, and afterwards polymerized across the C=S double bond. The addition of sulfur and amyl alcohol did not appear to be essential (98).

Positive Halphen reactions given by sterculyl alcohol and sterculene (1,2-dioctylcyclopropene) indicated that the color of the test was not affected by the carboxyl group of the fatty acids (195). However, methyl ω-(2-*n*-octyl-3-carbethoxycycloprop-1-enyl)octanoate, which contains a cyclopropene ring in which one hydrogen of the methylene group has been substituted, failed to give the reaction (45). The test, therefore, was thought to be characteristic of the unsubstituted methylene group in the cyclopropene ring.

In recent studies the structures of two of the colored products formed in the Halphen test with 1,2-diethylcyclopropene were established as LVI and LVII. The



LVI



LVII

structures were established by a combination of infrared, ultraviolet, n.m.r., and mass spectral methods (283).

C. ISOLATION OF CYCLOPROPENE FATTY ACIDS

In 1941 a description (124) was given of the com-

ponent acids of *Sterculia foetida* seed fat, a very unusual oil that polymerizes suddenly to a solid gel upon heating to 250°. Somewhat over 70% of the component acids of the oil was reported to consist of a branched-chain polyethenoid acid of the C_{19} series, but attempts to isolate it by the lead salt–alcohol separation procedure were unsuccessful. On the basis of results of degradative experiments on the mixed methyl esters, the acid was thought to be 12-methyl octadeca-9,11-dienoic acid. Steger and van Loon (248) believed this unusual acid to be a saturated hydroxy acid, probably $C_{18}H_{34}O_3$.

In 1952, Nunn (196) reported the isolation of this acid, sterculic acid (LVIII), from the oil by means of its urea clathrate and proposed its structure to be ω-(2-*n*-octylcycloprop-1-enyl)octanoic acid. The acid was isolated by saponification of the oil in the cold and then separated by fractional crystallization of the urea clathrates of the acids from methanol. Sterculic acid appeared in the last fractions and was further purified by low-temperature crystallization from acetone.

Chemical studies (233) to determine the biologically active fatty acid in *Malvaceae* were carried out on the oils extracted from the leaves and seeds of *Malva verticillata* and *M. parviflora* and from cottonseed, *Gossypium hirsutum*. The Halphen test was used to follow the fractionation in the isolation procedure, as the biologically active acid seemed to be the factor in malvaceous oils responsible for the Halphen reaction. The solvent-extracted oils were saponified under mild conditions, and the total fatty acids were subjected to low-temperature crystallization from acetone solutions. Saturated acids were absent in the filtrate which contained almost all the Halphen-positive acids. The enriched fractions were further purified by reversed phase partition chromatography and by six to ten crystallizations from cold acetone and petroleum ether. There was some doubt as to the extent of purity of the "Halphen acid" isolated, but characteristics were described for the richest fractions obtained. In 1957, this biologically active acid was indicated to be a homolog of sterculic acid and was assigned the name malvalic acid (178).

A preliminary account (74) of the isolation of "bombacic acid" from kapok seed oil indicated that the new acid was a C_{18} fatty acid with a structure similar to that of sterculic acid. In 1963, the cyclopropene fatty acids of *Bombax oleagineum* seed oil were reported as approximately 22% sterculic acid and 5% malvalic acid as determined by g.l.c. analyses (65). The methyl esters of the cyclopropenoid material were isolated on a Kieselgel silver nitrate column and were being investigated further.

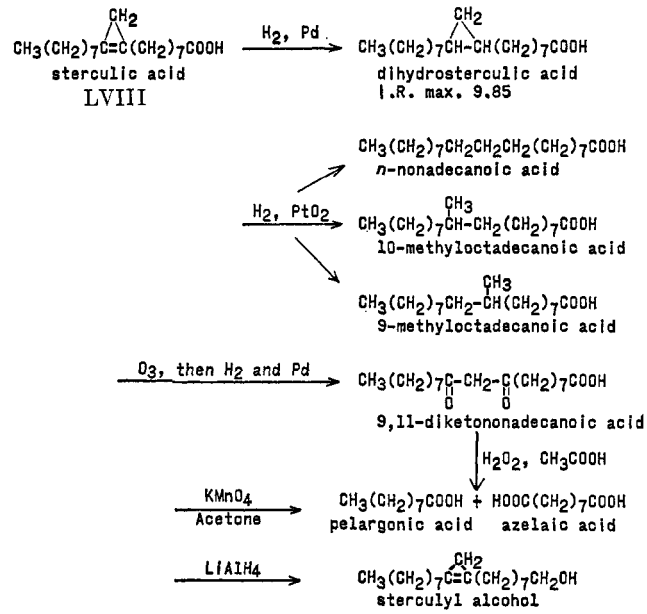
In a further study (235) of the occurrence of cyclopropene acids in plants of the order Malvales, the concentrations of malvalic and sterculic acids were determined for the seed and leaf oils of three species from each of the families *Malvaceae* and *Sterculiaceae*. The two cyclopropene acids were cleanly separated by reversed phase column chromatography and then assayed by a modification of the Halphen test and by an estimation of the products of partial hydrogenation of the fatty acids. Both acids were found in all oils with the concentration of malvalic acid exceeding that of sterculic acid except for the oils from *Sterculia foetida* (235) or *Bombax oleagineum* (65). Chromatograms gave evidence of the presence of other cyclopropene acids, but insufficient quantities prevented further identification.

In general, the isolation procedures used by the various workers in their studies of these cyclopropene acids either followed the urea complex fractionation or the low-temperature fractional crystallization methods (158, 194, 195, 263).

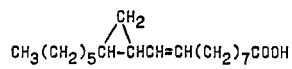
D. PROOF OF STRUCTURE

The structure of ω-(2-*n*-octylcycloprop-1-enyl)octanoic acid (LVIII) was assigned to sterculic acid on the basis of the reactions (196) shown in Scheme II.

SCHEME II



Varma and his co-workers (262, 264, 265) rejected this structure and instead proposed the structure ω-(2-*n*-hexylcyclopropyl)dec-9-enoic acid (LIX) on the basis of an incorrect interpretation of infrared data, the supposed synthesis of the methyl ester of the acid of structure LVIII, and the isolation of certain compounds from the oxidation of the isolated acid. Their

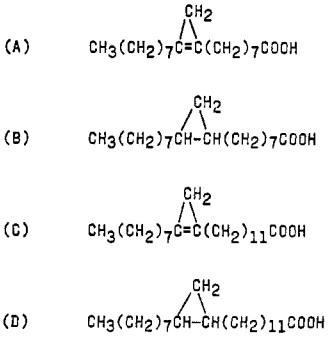


LIX

product gave infrared absorption bonds at 9.96 and 6.09 μ which were assigned, respectively, to the cyclo-

propane ring and to the double bond in the chain (264). The band at 6.09 μ was reported not to be present in samples of freshly prepared sterculic acid, but only in samples in which some polymerization had occurred (99). In support of Nunn's structure, other workers (74) stated that the difference in the absorption maximum noted between sterculic acid (1009 cm.$^{-1}$) and dihydrosterculic acid (1021 cm.$^{-1}$) was greater than that which would be expected from the cyclopropane ring conjugated with a double bond and, furthermore, that the change was in the wrong direction.

The methyl esters of four carboxylic acids (A–D) were reported (260) to be synthesized by the reaction of diazomethane with the appropriate unsaturated acid (stearolic, oleic, behenolic, and erucic acids). The



infrared absorption spectra obtained for the synthesized compounds which were thought to be cyclopropenes and cyclopropanes were compared with those for sterculic and dihydrosterculic acids. Since the spectra were found to be different, the Indian workers (260) concluded that sterculic acid could therefore not be compound A. Other workers indicated that the cyclopropene and cyclopropane acids (A–D) could not be synthesized by the action of diazomethane on the appropriate unsaturated acid and that only the carboxyl groups of the initial acids had been esterified (45).

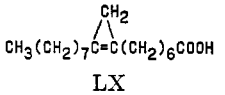
Further support for structure LIX was obtained by the potassium permanganate oxidation of sterculic acid to form heptanoic acid, azelaic acid, and a small amount of *n*-hexyl methyl ketone (266). The same products had been obtained previously by the oxidation of the total fatty acids of *Sterculia foetida* oil (124). Hydroxylation of sterculic acid with potassium permanganate gave a $C_{19}H_{34}O_4$ compound which was characterized as an α-ketol. Periodic acid oxidation of this product gave azelaic semialdehyde and a steam-volatile liquid consisting mostly of an acid containing a cyclopropane ring and a very small amount of an aldehyde (262).

The $C_{19}H_{34}O_4$ compound was suggested (45) to be 9,11-dioxononadecanoic acid, which had been described by previous workers (99, 196) as the product obtained from ozonolysis of sterculic acid. The diketone was synthesized independently in three laboratories (44, 169, 193) by different methods. The acids were compared with each other and with the product obtained from sterculic acid (99) and found to be the same. Further work (46) was carried out on the synthesis of the diketone and related compounds and their reduction to glycols by the use of sodium borohydride. The corresponding cyclopropanes were synthesized *via* the glycols and dibromides by debromination with zinc and sodium iodide in acetone.

In 1957, *dl-cis*-9,10-methyleneoctadecanoic acid was synthesized and identified as dihydrosterculic acid (47, 132, 136). X-Ray diffraction studies (48) of the synthetic acid and dihydrosterculic acid and their amides verified that the acids were identical. In a much simpler synthesis (237), dihydrosterculic acid was prepared in 51% yield by the treatment of methyl oleate with methylene iodide and a zinc–copper couple.

An investigation (218) of the structure of sterculic acid with nuclear magnetic resonance showed that the acid lacked olefinic hydrogens, thus again eliminating the possibility of Varma's structure being the correct one. This conclusion was further supported (137, 138) by a comparison of the spectra of *Sterculia foetida* oil, sterculic acid, dihydrosterculic acid, and methyl dihydrosterculate. The n.m.r. spectrum of sterculic acid showed a sharp peak at 9.2 p.p.m. indicative of the CH_2 of a cyclopropene group, but no peak for ordinary olefinic unsaturation at 4.7 p.p.m. or for the cyclopropane ring at 10.3 p.p.m. (parts per million of the total magnetic field, in gauss or milligauss).

In 1960, sterculic acid was synthesized (50) from the reaction of stearolic acid and methylene iodide in the presence of a zinc–copper catalyst by the general method of Simmons and Smith (237). The properties of the synthetic acid were compared with those of the isolated acid and were found to be identical.

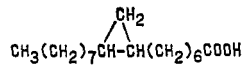


LX

A comparison of the infrared spectra of malvalic acid (LX) and dihydromalvalic acid with sterculic and dihydrosterculic acids indicated that the acids were analogous (178). Both cyclopropene fatty acids gave bands at 1008 and 1872 cm.$^{-1}$. Hydrogenation with a palladium catalyst to form the dihydro acids resulted in the disappearance of the band at 1870 cm.$^{-1}$ and the shifting of the 1008-cm.$^{-1}$ band to 1021 cm.$^{-1}$. In the high frequency region of the spectra no absorption was noted for malvalic or sterculic acid or for their methyl esters. Absorption attributed to the stretching frequencies of carbon–hydrogen groups in the cyclopropane ring was recorded at 3056–3058 and 2988–2990 cm.$^{-1}$ for the dihydro acids and for lactobacillic acid, a naturally occurring cyclopropane fatty acid (125).

A crystal structure analysis (66) of dihydromalvalic

acid showed it to be *dl-cis*-8,9-methyleneheptadecanoic acid (LXI).



LXI

Both malvalic and sterculic acid were found together in oils of *Hibiscus syriacus* and *Lavatera trimestris* (241). Analyses by gas–liquid chromatography were carried out on methyl esters of the cyclopropene acids and the acids obtained by hydrogenation. Saponification of the permanganate–periodate oxidized oils gave products that included 8,10-dioxooctadecanoic and 9,11-dioxononadecanoic acids, which were characterized by gas–liquid chromatography of the products obtained by peracetic acid oxidation.

E. CHEMICAL REACTIONS

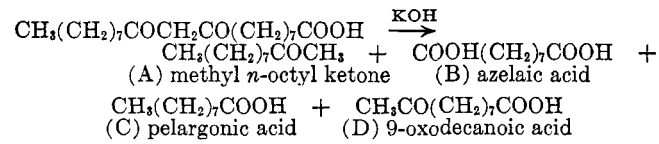
1. Hydrogenation

Hydrogenation (196) of sterculic acid in ethanol in the presence of palladized calcium carbonate brought about the absorption of hydrogen equivalent to one double bond, with the formation of dihydrosterculic acid. Dihydromalvalic acid (178) was obtained in a similar manner from malvalic acid by hydrogenation with the use of a palladium catalyst. Nunn found that dihydrosterculic acid absorbed a second mole of hydrogen in the presence of Adams' platinum catalyst. This product is a mixture of *n*-nonadecanoic acid and two methyl-substituted octadecanoic acids. Hydrogenation studies (277) of oils containing both sterculic and malvalic acids showed that prolonged hydrogenation in ethanol produced dihydro derivatives and branched-chain products but none having straight chains. The use of Adams' catalyst in glacial acetic acid gave both branched-chain and straight-chain hydrogenolysis products.

2. Oxidation

Pelargonic and azelaic acids were the main products obtained from the oxidation of sterculic acid with potassium permanganate in acetone. Ozonolysis of the cyclopropene acid in acetic acid gave an ozonide which was decomposed with acetic acid–hydrogen peroxide to give pelargonic and azelaic acids. Ozonolysis in ethyl acetate at low temperature gave an ozonide which was reduced with hydrogen in the presence of palladized charcoal to form 9,11-diketononadecanoic acid which in turn was oxidized by hydrogen peroxide in acetic acid to give again pelargonic and azelaic acids as the only fission products (196).

Alkaline hydrolysis of the dioxo acid should yield four products, of which three (A, B, and D) have been isolated and identified (99).



(A) methyl *n*-octyl ketone (B) azelaic acid

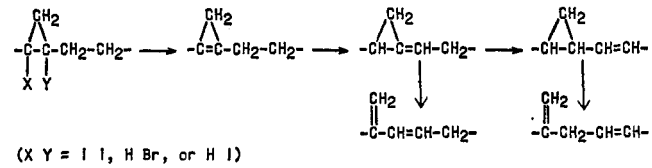
(C) pelargonic acid (D) 9-oxodecanoic acid

3. Reduction

Reduction (196) of sterculic acid with lithium aluminum hydride gave sterculyl alcohol. The alcohol was hydrogenated in the same stepwise manner as the acid, indicating that the cyclopropene ring was kept intact. Sterculyl alcohol was methylated to form the methyl sterculyl ether and reduced to form the hydrocarbon, sterculene (1,2-dioctylcyclopropene) (194, 195). Infrared data obtained from these preparations were compared with those of sterculic acid, its methyl ester, and the corresponding polymers.

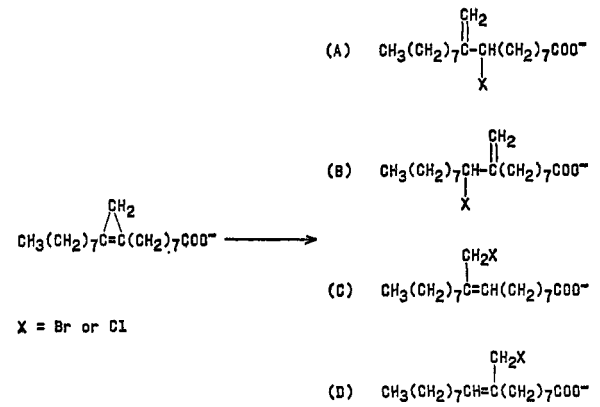
4. Halogenation

A diiodide was formed by heating methyl sterculate under reflux in acetone with sodium iodide. A series of products was obtained upon heating the diiodo ester at various temperatures up to 190°, heating under reflux with zinc dust in acetone, heating with pyridine, quinoline, or potassium hydroxide. The decomposition of hydrobromides or hydriodides of methyl sterculate gave similar products. The following reactions were thought to occur with the products obtained depending upon the severity of the method used for the decomposition (100).



(X Y = I I, H Br, or H I)

Iodine values and infrared absorption measurements indicated to other workers (8) that the reaction of cyclopropenoid fatty acids with hydrogen halides involved the formation of four isomeric monounsaturated monohalo moieties as shown. The mechanism



X = Br or Cl

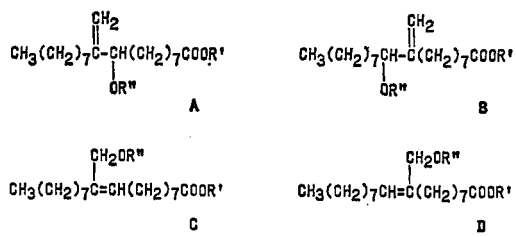
was analogous to that postulated for the polymerization of sterculic acid (219).

5. *Polymerization*

Nunn (196) suggested that sterculic acid polymerized by the addition of the carboxyl group across the double bond. The polymerization occurred quite rapidly at room temperature, and even slowly at 0°, as indicated by the increase of the equivalent weight with time. Saponification of partly polymerized material yielded an acid with nearly the same equivalent weight as the original sterculic acid, but the isolated acid was not investigated further.

The instability of the free acid was shown by a study (99) of the infrared spectrum of the polymerized material, to be due to the opening of the cyclopropene ring across the single bonds by interaction with the carboxyl group. The band at 5.35 μ for the cyclopropene ring completely disappeared, and only a weak absorption remained at 9.9 μ. The very broad absorption between 3 and 4 μ, the broad, strong band at 10.7 μ, and the band at 7.78 μ, which are characteristic of fatty acid spectra and are associated with the presence of the carboxylic acid group, disappeared. The C=O stretching absorption shifted from 5.86 μ in the acid to 5.76 μ in the polymerized material, and a new strong band appeared at 8.58 μ which suggested that an ester or lactone had formed. The appearance of a double bond absorption band at 6.07 μ in the spectrum of the polymerized material which was not present in the fresh sterculic acid spectrum, together with an increase in the methyl group absorption at 7.27 μ, indicated that the reaction occurred by the splitting of the C–C linkages and the subsequent opening of the ring.

In 1959 the polymerization was described (219) as proceeding by isomerization of the cyclopropene ring with carboxylic acid addition to form a mixture of polyesters (A–D), shown below, where R′ and R″ are sterculic acid residues. The spectral data agreed



essentially with those previously described (99). The polymer gave no color with the Halphen reagent and was insoluble in hot methanol. In a more detailed study (217) of the polymerization and acetolysis of sterculic acid, the polymer was saponified to the corresponding unsaturated hydroxy acids, which in turn were acetylated to the unsaturated acetoxy acids. The acetoxy acids were also obtained by heating sterculic acid in excess glacial acetic acid. The isomeric products were identified by oxidative degradation.

6. *Reaction with Mercaptans*

A possible mechanism of the reaction of the cyclopropene ring with sulfhydryl groups of proteins was investigated by reacting mercaptans with sterculic acid and sterculene (158). The sulfhydryl group of methyl mercaptan or β-mercaptopropionic acid added to the double bond of the cyclopropene ring and formed the cyclopropylmethyl and 2-carboxyethyl derivatives. Hydrogen peroxide in acetic acid oxidized these derivatives to sulfones without opening the cyclopropane ring. The reactions of the cyclopropene ring with the mercaptans were thus in contrast to those with carboxylic acids and halides where the ring was opened. Infrared and n.m.r. spectra, as well as gas–liquid chromatography, were used to check the purity of the derivatives prepared.

F. ANALYSIS OF CYCLOPROPENE FATTY ACIDS

A study (72) of the Halphen reaction led to the development of a proposed quantitative procedure for the cyclopropene acids in oils. The accuracy reported was 10% with 95% confidence at the midpoint of the desired range of 0.1 to 0.7 mg. of sterculic acid per gram of oil. The method as published has been modified further and has been found to give consistent estimations of cyclopropenoid fatty acids in mixtures of *S. foetida* oil and corn oil. Critical points in the procedure were found to be the use of pyridine of high purity and the use of a standard temperature and a standard time for the reaction (149).

A titration method was developed when sterculic acid was found to add hydrogen bromide very rapidly in the benzene–acetic acid medium normally used for the Durbetaki titration in the determination of oxirane oxygen (87). The epoxy acids in the oil were reduced by lithium aluminum hydride to monohydroxy compounds which no longer gave the Durbetaki reaction, whereas sterculic acid was reduced to sterculyl alcohol with the cyclopropene ring intact and therefore still reactive with hydrogen bromide (240, 241). A modification of this method allowed the determination of both epoxy and cyclopropenoid acids by first titrating at 3° to determine the epoxy compounds and then continuing the titration at 55° to determine the cyclopropenoid components (122). When traces of interfering substances in vegetable oils were removed by adsorption on activated alumina, the cyclopropenoid fatty acids in crude and refined cottonseed oils were determined by this method to within 0.01% (123).

The quantitative addition of a molecule of hydrogen chloride at the cyclopropene ring when the sample is shaken with concentrated hydrochloric acid is the basis of another proposed analytical method. The cyclopropenoid content was calculated from the increase in the chlorine content of the sample. Interfering substances such as epoxy compounds and hydroperoxides

must first be removed (181). Interference from such substances was circumvented by taking advantage of the strong infrared absorption noted at 11.05 μ for the products obtained by treatment of cyclopropene materials with either hydrochloric acid (or hydrogen bromide). The band was attributed to the group

$$-CH_2-\overset{CH_2}{\overset{\|}{C}}-CHCl-$$

which was formed by the opening of the cyclopropene ring. The data presented indicated that the sterculic acid content could be determined to within one percentage unit (180).

The 9.92 μ infrared absorption band, characteristic of the cyclopropene ring (incorrectly considered by the investigators as characteristics of the cyclopropane ring), was used to estimate the sterculic acid content as 71.8% of the total fatty acids in *S. foetida* oil (261). The value was considerably higher than values obtained by the Halphen test or the hydrogen bromide titration (123). The three major glycerides in the oil were computed from the infrared data as 31.4% tristerculin, 17.4% monopalmitin, and 11.5% monoolein disterculin.

The methyl esters of the cyclopropene fatty acids and their corresponding cyclopropane acids have been prepared and analyzed by gas–liquid chromatography on both polar (Resoflex 446) and nonpolar (Apiezon L) columns (191, 241, 277). Since the malvalate peak coincided with that of the linoleate, the samples were usually hydrogenated to form the dihydro compounds. A gas–liquid chromatogram (DEGS column) of the methyl esters of fatty acids from *Sterculia foetida* oil is shown in Fig. 1 (94).

Methyl sterculate was noted by other workers (158) to give two peaks. The relative sizes of the peaks are apparently dependent upon such experimental conditions as the port and column temperatures, column packing, and the particular instrument in use. The spectral properties and Halphen response of methyl sterculate were studied (185) before and after chromatography and were found to be altered considerably. The Halphen test became negative and the infrared absorption bands normally attributed to the cyclopropene structure disappeared. The ultraviolet spectrum of methyl sterculate after 180-min. isomerization at 198° was very similar to that of the ester after gas chromatography at 210°. The investigator (185) believed that isomerization of the sterculate during gas chromatography resulted in the formation of a mixture of methyl 10-methyleneoctadec-8-enoate and methyl 9-methyleneoctadec-10-enoate. Gas–liquid chromatography has been used to determine the purities of isolated compounds and derivatives, including methyl sterculate, sterculyl alcohol, sterculyl alcohol derivatives, sterculene, and derivatives formed by the addition of mercaptans to methyl sterculate and sterculene (158, 195).

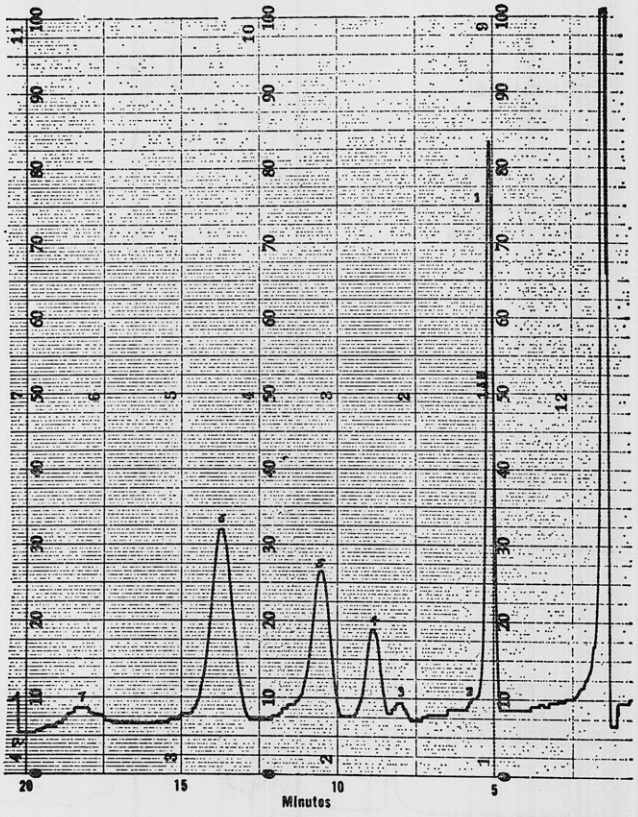


Fig. 1.—Gas–liquid chromatogram of methyl esters of fatty acids from *Sterculia foetida* seed fat. Peaks are as follows: 1, palmitate; 2, palmitoleate; 3, stearate; 4, oleate; 5, linoleate; 6, sterculate; and 7, an unknown fatty acid methyl ester associated with sterculate, perhaps a C_{20} cyclopropene fatty acid [from Fig. 1, R. J. Evans, J. A. Davidson, and S. L. Bandemer, *J. Nutr.*, **73,** 284 (1961)].

Nuclear magnetic resonance studies were utilized in the determination of the structure of sterculic acid (138, 218) and may prove to be useful in quantitative determination of the cyclopropene ring in the future (138). A comparison of the spectra of *Sterculia foetida* oil, sterculic acid, dihydrosterculic acid, and methyl dihydrosterculate is illustrated in Fig. 2 (138).

G. PHYSIOLOGICAL PROPERTIES

The pink-white discoloration of stored eggs has long been associated with the feeding of meal or oils of plants of the order Malvales to laying hens. The discoloration was explained as a pink iron–conalbumin complex formed by iron diffusing from the yolk through the vitellin membrane into the white where it chelated with conalbumin (228). The yolks of the abnormal eggs had a higher water content and thus were larger than normal. They were claylike in consistency at cold storage temperatures and rubbery when cooked (176). The pH values of the yolk and the white tended to converge (233).

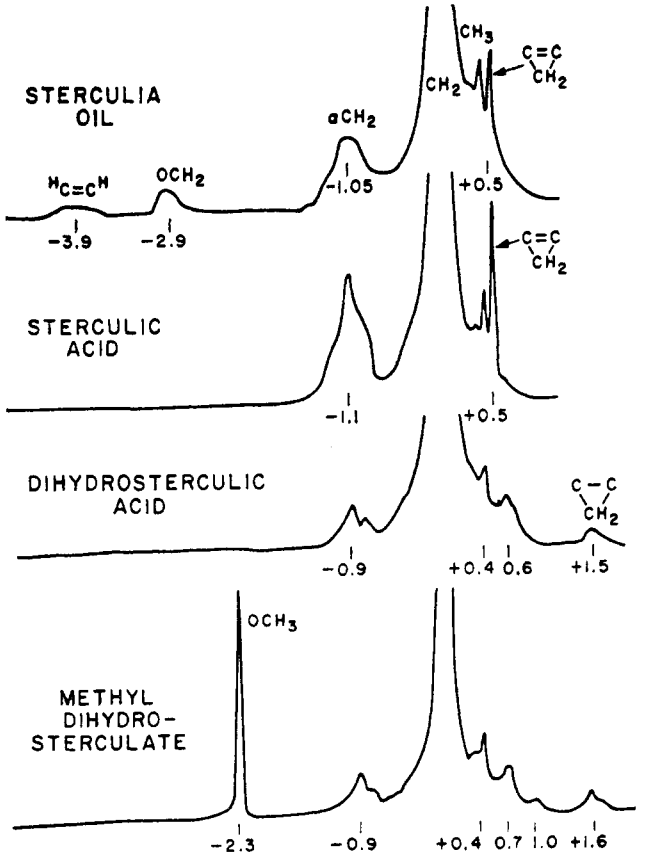


Fig. 2.—Proton resonance spectra of *Sterculia* oil, sterculic acid, and two derivatives; the signal of the CH_2 group of the cyclopropane ring is at +1.5 p.p.m. [from Fig. 6, C. Y. Hopkins and H. J. Bernstein, *Can. J. Chem.*, **37**, 781 (1959)].

As early as 1933 the component causing the pink discoloration was suggested as the same component responsible for the Halphen reaction of the oil (176, 177). The feeding of isolated sterculic and malvalic acids, which are characterized by a cyclopropene ring and positive Halphen tests, caused pink-white discoloration (186, 233). Since hydrogenation of cyclopropene acids to the cyclopropane compounds eliminated the discoloration, the cyclopropene ring was believed to increase the permeability of the vitellin membrane and thus cause the discoloration. Feeding of methyl sterculyl ether and sterculene to laying hens also produced pink discoloration of eggs, whereas the polymer prepared from the acids of *S. foetida* oil did not (194, 195). Destruction of the Halphen reactivity by treating the oil with either hydrogen chloride or sulfur dioxide likewise eliminated the development of the pink whites (73).

In apparent contradiction, a crude cottonseed oil heated at 150° for 4 hr. or 200° for 1 hr. still caused egg-white discoloration but no longer gave a positive Halphen reaction. Discoloration was not obtained when the oil was heated at 200° for 8 hr. or at 240° for 1 hr. (92). This study was extended by the isolation of a fraction of crude cottonseed oil, which did not give a positive Halphen test and yet produced the pink-white discoloration. The investigators believed the fraction contained a fatty acid other than malvalic or sterculic acid, but they did not eliminate the possibility that the acid was formed from malvalic or sterculic acid during the isolation procedure (93).

Discoloration in the eggs from hens given crystalline gossypol was intensified when either crude cottonseed oil or *S. foetida* oil was given simultaneously to laying hens (150, 151).

Feeding 250 mg. of malvalic acid daily caused cessation of egg production (234). Feeding as little as 25 mg. of *S. foetida* oil in gelatin capsules per day per hen caused an 82% suppression of the hatchability of the eggs (231). The study was extended to determine the effect of feeding the oil to immature chickens. Daily feeding of 200 mg. of the oil resulted in a delayed development of the ovary and oviduct with almost complete suppression of egg production, the enlargement of the liver and gall bladder, and a change in the composition of the depot fat from the normal fat, a fairly unsaturated type to a highly saturated type (230).

A comparison of the fatty acid distribution in the tissues and egg yolk lipids of normal chickens with that of hens fed cottonseed oil or *S. foetida* seeds indicated that the fatty acid metabolism of the hen was disturbed by the cyclopropene fatty acid-containing materials. Hens fed the test rations had higher levels of stearic acid in the fatty acids of the egg yolk lipids, their livers, blood plasma, and ovaries than hens fed the normal laying diet. Only slight changes were noted in the fatty acid distribution of depot fat or heart lipids (91, 94). Further study indicated that the mechanism regulating the equilibrium that normally existed between stearic and oleic acids was upset so that a greater proportion of stearic acid was produced at the expense of oleic acid (95).

Recently, a mechanism postulated to account for the biological activity of the cyclopropene compounds was the reaction of the cyclopropene ring with the sulfhydryl groups in proteins which are closely associated with the lipids. The physical and biochemical properties of the protein molecule would be greatly altered by the irreversible addition of protein sulfhydryl groups to the cyclopropene ring (158).

H. RELATED NATURALLY OCCURRING CYCLOPROPANE FATTY ACIDS

Dihydrosterculic acid has played such an important role in the elucidation of the structure of sterculic acid that considerable attention has been focused upon the cyclopropane fatty acids occurring naturally. The speculation that the cyclopropane compounds serve as precursors for the cyclopropene derivatives is supported by finding dihydrosterculic acid with sterculic and

malvalic acids in *Hibiscus syriacus* and other oils (241).

The lipids of *Lactobacillus arabinosus* (129, 130), *L. casei* (125, 134), and *L. delbrueckii* (126) were found to contain significant amounts of an unusual fatty acid of the composition $C_{19}H_{36}O_2$. Hydrogenation gave nonadecanoic acid and an apparent mixture of methyloctadecanoic acids. The resistance of the acid to oxidation and the infrared absorption maximum at 9.8 μ which disappeared on hydrogenation supported the conclusion that a cyclopropane ring was present (129). X-Ray diffraction studies of the synthesized compounds, *trans-dl*-9,10-methyleneoctadecanoic and *trans-dl*-11,12-methyleneoctadecanoic acids, suggested that the 11,12-position was a likely location for the cyclopropane ring (125). This position was confirmed by a micromethod (131) for the degradation of long-chain cyclopropane fatty acids, in which the cyclopropane ring was opened by the addition of hydrogen bromide.

Dihydrosterculic acid, an isomer of lactobacillic acid, was obtained by hydrogenation of *S. foetida* oil, saponification, and fractional distillation of the methyl esters (127). A comparison of the crystallographic data of dihydrosterculic, lactobacillic, and four synthetic cyclopropane fatty acids confirmed the structure of dehydrosterculic as *cis-dl*-9,10-methyleneoctadecanoic acid and indicated the structure of lactobacillic as probably the *cis-d-* or *-l*-11,12-methyleneoctadecanoic acid (48).

A C_{17} fatty acid with a cyclopropane ring was found in the lipids of *Escherichia coli* (68) as well as in *Pasteureila pestis* and *Bacillus subtilis* (6). Similarly, C_{17} and C_{19} cyclopropane fatty acids were found in *Salmonella typhimurium* (117, 179). The C_{17} acid was isolated and identified as *cis*-9,10-methylenehexadecanoic acid; the C_{19} component was identified as a mixture of lactobacillic and dihydrosterculic acids (147). Lactobacillic acid was also isolated from *Agrobacterium* (*Phytomonas*) *tumefaciens* (135) where it had been previously described as "phytomonic acid."

Gas–liquid chromatography proved to be an important tool in both isolation and analytical procedures (51, 117, 254). Acid hydrolysis, which was necessary to obtain the total fatty acids from the bacterial lipids, resulted in the destruction of lactobacillic acid by the breaking of the cyclopropane ring (254). Since the position of the peak of lactobacillic acid was the same as that of a C_{19} acid with one double bond, the destruction of the cyclopropane fatty acid by acid hydrolysis was used as a measure of its concentration. Considerable differences were found in the fatty acid patterns of the whole bacterial cells and in those of a membrane fraction. Lactobacillic acid appeared to be a less important constituent of the membrane than of the whole cells (254).

Although early studies (133) established the biotin-sparing activity of the cyclopropane fatty acids in lactobacilli, the over-all role of these acids in the bacterial cell remains obscure (167).

The biosynthesis of lactobacillic acid by *L. arabinosus* was shown to involve the addition of a one-carbon fragment such as formate or the methyl carbon of a methionine group across the double bond of *cis*-vaccenic acid (128, 170). Ninety-two per cent of the radioactivity of *cis*-vaccenic acid-1-^{14}C added to the culture medium was found in the lactobacillic acid isolated from the cultured cells. Studies of the incorporation of [Me-^{14}C] and [Me-^{3}H] methionine into the cyclopropane fatty acids of a number of microorganisms indicated that the hydrogen as well as the carbon of methionine methyl groups were incorporated into the cyclopropane ring (167, 210).

Studies on the enzymatic synthesis of cyclopropane fatty acids catalyzed by cell-free extracts of *Serratia marcescens* or *Clostridium butyricum* suggested that the synthesis required S-adenosylmethionine and a phospholipid, probably phosphatidylethanolamine, as substrates (286).

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