with activated charcoal.[17] The decolorized solution was evaporated almost to dryness and the residue was dissolved in 200 ml. of 80% ethanol. If necessary, a few drops of hydrochloric acid was added to make the residue completely soluble in the alcohol solution. Addition of propylene oxide precipitated 28 g. (46% from diethyl acetamidomalonate) of product, which at times could not be purified completely by recrystallization from water. Preferably the crude solid was dissolved in a minimum of water, and the solution was passed through 400 ml. of Dowex 50W-X8 resin (H^+ form). A strongly acidic impurity passed through rapidly, washing with distilled water caused the eluate to become neutral, and more water caused XI to be eluated as a mildly acidic eluate. Finally, washing the column with 3 *N* hydrochloric acid removed a small amount of an amino acid impurity that was not identified. Evaporation of the XI eluate to a small volume, adding alcohol until the hot solution began to cloud, followed by chilling produced highly purified XI as a white solid, m.p. 226° dec. Titration of this compound gave no break at the isoelectric point, pH 2.1, but gave moderately strong breaks at pH 4.8 and 8.7 and a weak break at pH 11 (Fig. 2).

Anal. Calcd. for $C_4H_{10}NO_5P$: C, 26.24; H, 5.50; P, 16.92; neut. equiv., 183. Found: C, 26.30, 26.23; H, 5.63, 5.58; P, 16.78, 16.82; neut. equiv., 185.

For some reason, the first preparation of the N-benzoyl derivative gave a solid, m.p. 205.5°, from water, but subsequent preparations, after alternate recrystallizations from water and from dioxane, melted at 197°. A potentiometric titration of this compound produced the first sharp break at pH 6.0, the amount of base consumed being twice that required for attaining the second break in the titration curve at pH 10.2. Thus, the first end point included the neutralization of two acidic hydrogens (Fig. 2).

Anal. Calcd. for $C_{11}H_{14}NO_6P$: C, 46.00; H, 4.91; P, 10.79; neut. equiv., 95.7. Found: C, 45.77, 45.83; H, 4.45, 4.98; P, 10.73, 10.65; neut. equiv., 95.7.

Hydrolysis of the benzoyl derivative produced XI, m.p. 226° dec.

2-Amino-3-phosphonopropionic Acid (XV).—A mixture of 12.9 g. (0.10 mole) of N-acetyl-α-aminoacrylic acid[12] (XII), 12.4 g. (0.10 mole) of trimethyl phosphite, and 14 ml. of dimethyl phosphonate was heated on a steam bath until XII had dissolved. This required 10–15 min. The solution was heated for an additional 60 min. on the steam bath and then was allowed to stand at room temperature for 36 hr. Volatile materials were removed by heating the mixture to 130° in a dibutyl phthalate bath at a pressure of 0.7 mm. The residue was hydrolyzed by refluxing with 130 ml. of concentrated hydrochloric acid for 55 hr. The hydrolysate was filtered to remove a small amount of dark, insoluble material and the filtrate was evaporated almost to dryness *in vacuo*. The residue was dissolved in 200 ml. of water and the hot solution was treated with carbon and filtered, producing a colorless filtrate. This filtrate was concentrated to about 20 ml., 100 ml. of ethyl alcohol was added, followed by butylene oxide dropwise until no more solid separated from solution. This compound also was purified best by the Dowex 50 treatment described for XI. The yield of XV was 8.45 g. (50% from XII), m.p. 228° dec. The titration curve was very similar to that of XI, giving no break at the isoelectric point (pH 2.2), moderate breaks at pH 4.5 and 8.8, and a very weak break at pH 11.

Anal. Calcd. for $C_3H_8NO_5P$: C, 21.32; H, 4.77; P, 18.33; neut. equiv., 169. Found: C, 21.09, 21.17; H, 4.59, 4.88; P, 18.26, 18.26; neut. equiv., 172.

An attempt was made to prepare the N-benzoyl derivative of XV, but this was not entirely satisfactory, since no good method was found to purify the product.

General Properties and Reactions with Ninhydrin.—Compounds VIIa, VIIb, and XV were soluble in cold water, but VIIc and XI were appreciably soluble only in hot water. They were all insoluble in the usual organic solvents.

Dilute solutions of VIIa, VIIb, VIIc, XI, and XV were mixed with a 0.1% aqueous solution of ninhydrin and were heated to boiling. All produced pale blue to red colors. When the same tests were carried out after the acidic solutions of the amino acids had been neutralized with sodium bicarbonate, intense violet solutions resulted.[18] It was further noted that the characteristic odor of phenylacetaldehyde was produced during the ninhydrin reaction with VIIc.

To the lavender solution from the ninhydrin reaction with VIIa, excess 6 *N* nitric acid was added, followed by a solution of ammonium molybdate. There resulted the characteristic positive test for the phosphate ion. When the same procedure was employed with VIIa with the exception that no ninhydrin was added, the resulting phosphate test was negative.

Acknowledgment.—We wish to express our appreciation to the Robert A. Welch Foundation and to the National Institutes of Health (GM 09014–02) for grants which supported this work.

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(17) If much hydrochloric acid were left in this solution, the charcoal would not remove the color. However, if all the hydrochloric acid were removed, the solid residue had a low solubility in water.

(18) D. A. MacFadyen [*J. Biol. Chem.*, **153**, 507 (1944)] has shown that α-amino carboxylic acids react with ninhydrin at pH 5–7 to give the characteristic purple-colored solution, whereas at pH 2.5 or less no colored product results.

Synthesis of 3-Phospholenes by Reduction of Diene–Phosphonous Dichloride Adducts[1]

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Department of Chemistry, Duke University, Durham, North Carolina

Received August 29, 1963

Seven 3-phospholenes were prepared in moderate yield by reduction with magnesium of the cyclic chlorophosphoranes resulting from addition of phosphonous dichlorides to 1,3-dienes. This class of compounds has not been characterized previously. They react rapidly with air but readily form stable quaternary salts. Infrared and n.m.r. spectra confirm the 3-phospholene structure.

Cyclic chlorophosphoranes (I) are formed by a Diels–Alder reaction between 1,3-dienes and phosphonous dichlorides.[3] The reaction generally is conducted at room temperature without a solvent, in the presence of a polymerization inhibitor. The adducts, which are probably ionic as are other trialkyldichlorophosphoranes,[4] are hydrolyzed readily to 3-phospholene oxides; and over-all yields of 60–70% are, in fact, common. The reaction constitutes one of the simplest methods of constructing a phosphorus-containing ring system. It has the additional valuable feature of providing a system

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(1) From a portion of the Ph.D. dissertation of D. A. M., Duke University, 1963. Presented in part before the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962. Support of some of this work by the Research Corporation, through a Frederick Gardner Cottrell grant, is gratefully acknowledged.

(2) Philip Morris Research Assistant, 1961–1962.

(3)(a) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (Dec. 22, 1953); (b) B. A. Arbuzov and L. A. Shapshinskaya, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 65 (1962); (c) I. G. M. Campbell, R. C. Cookson, and M. B. Hocking, *Chem. Ind.* (London), 359 (1962); (d) T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Am. Chem. Soc.*, **84**, 3673 (1962).

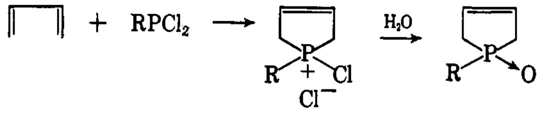
(4) K. Issleib and W. Seidel, *Z. anorg. allgem. Chem.*, **288**, 201 (1956); J. Goubeau and R. Baumgärtner, *Z. Elektrochem.*, **64**, 598 (1960).

TABLE I

3-PHOSPHOLENES AND THEIR QUATERNARY SALTS

			Quaternary salt							
					Carbon, %		Hydrogen, %		Phosphorus, %	
Compound	Yield %	B.p., °C. (mm.)	M.p., °C.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
IIa	39[a]	135–138 (760)	142–143[b]	$C_{13}H_{18}BrP$	54.75	54.71	6.36	6.65	10.86	10.63
IIb	38[c]	135–136 (760)	158–159[b]	$C_{13}H_{18}BrP$	54.75	54.70	6.36	6.72	10.86	11.27
IIc	20[a]	159–160 (760)	153–154[b]	$C_{12}H_{15}BrClP$	47.16	46.86	4.95	4.67	10.14	10.00
IId[d]	39[c]	133–134 (16)[e]	84–85.5[f]	$C_{13}H_{18}IP$	47.00	47.08	5.46	5.56	9.33	9.16
IIe	28[c]	158–160 (20)	220–221[b]	$C_{19}H_{22}BrP$	63.17	62.91	6.14	6.16	8.57	8.63
IIf	20[a]	179–180 (22)	168–170[b]	$C_{17}H_{17}BrClP$	55.53	55.20	4.66	4.60	8.42	8.32
IIg	16[c]	165–166 (20)	181–182.5[b]	$C_{19}H_{22}BrP$	63.17	63.36	6.14	6.65	8.57	8.76

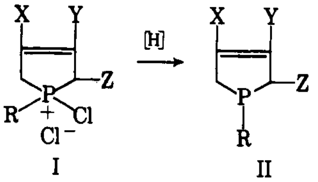
[a] Based on weight of adduct charged. [b] Benzyl bromide salt. [c] Based on phosphonous dichloride used for adduct preparation. [d] *Anal.* Calcd. for $C_{11}H_{13}P$: C, 74.98; H, 7.44; P, 17.58. Found: C, 74.71; H, 7.17; P, 17.72. [e] Lit.[7] b.p. 150–151° (30 mm.). [f] Ethiodide.



I

with the functionality of the double bond, which should permit access to numerous derivatives. Advantage has already been taken of this reactivity to produce 3,4-dibromophospholane 1-oxides, and, from these, phosphole 1-oxides by dehydrohalogenation.[5]

We have devised a method for the reduction of the adducts (I) to the phosphines (II) and have demonstrated the generality of the method by the preparation of seven representative compounds. The dual functionality of the tricovalent phosphorus and the double bond should make these compounds valuable intermediates.



I II

	R	X	Y	Z
a,	CH_3	CH_3	H	H
b,	CH_3	H	H	CH_3
c,	CH_3	Cl	H	H
d,	C_6H_5	CH_3	H	H
e,	C_6H_5	CH_3	CH_3	H
f,	C_6H_5	Cl	H	H
g,	*p*-$CH_3C_6H_4$	CH_3	H	H

The reduction[6] of I has been accomplished by treating a suspension of I in tetrahydrofuran (THF) with magnesium turnings, which was suggested by its efficacy in another chlorophosphorane reduction.[8] The mixtures were worked up in an appropriate manner, and the phosphines (II) were obtained by distillation. A successful analysis was obtained on one phosphine (IId); the rapid uptake of oxygen, however, made it difficult to obtain good values for these compounds, and the expedient of converting the phosphines to the stable quaternary salt form for analysis (Table I) was adopted. Benzyl bromide was particularly useful for forming crystalline salts.

Granular aluminum, also effective for certain chlorophosphorane reductions,[9] failed to reduce Id or f in THF. Some aluminum was consumed, but no product was obtained. Another reducing agent, methyl phosphorodichloridite (CH_3OPCl_2),[10] likewise failed to reduce Ic or d in THF. Although a smooth reaction occurred in converting the slurry to a solution, no phosphine was obtained on distillation. The reaction was not examined further. On the other hand, lithium aluminum hydride[7] did effect the reduction when tried on Ia. The yield (28%) was somewhat lower than that (39%) obtained on magnesium reduction of another portion of the same batch of Ia. However, the isolation procedure is simpler, and this agent is worthy of consideration for this reduction.

Tetrahydrofuran is the preferred medium for the magnesium reduction, although it dissolves little I. Methylene chloride, a good solvent for I, permitted no reduction. Other solvents investigated included benzene, chlorobenzene, ether, dioxane, diglyme, and ethyl and isopropyl acetates, all tried in the reduction of Ia. None was a good solvent, and in no case was reduction observed.

The yields (Table I) of 3-phospholenes from reduction of I appear to run below those reported[3a] for 3-phospholene 1-oxides from hydrolysis of I. However, the reduction reaction itself appears largely complete, judging visually from the amount of magnesium consumed. Some loss undoubtedly occurs in the isolation of the 3-phospholenes, as these are oxidized very rapidly. Most of the yields in Table I are from single runs, and it is felt that improvements can be made with further study of the process. The reductions of adducts Ic and f, both vinylic chlorides, were performed at lower temperatures to prevent Grignard reagent formation, which might have occurred in refluxing THF. The yields may be particularly low in these cases due to incomplete reduction.

In conventional Diels–Alder reactions, steric prevention of the diene from attaining a planar cisoid conformation hinders the addition of the dienophile.[11] McCormack[3a] cited certain structural features, which offer this hindrance, as being important also where a phosphonous dichloride is the dienophile. Unreactive dienes were stated to include (A) those containing two substituents on one or both of the 1 and 4 positions, (B) those having a *cis* arrangement of one vinyl group with respect to a 1 or 4 substituent, when present, and (C) those having three carbons of the diene system incorporated in an alicyclic structure. We attempted to treat two dienes of type A (hexachloro-1,3-butadiene and 2,5-dimethyl-2,4-hexadiene) with the strongly

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(5) E. Howard, Jr., and R. E. Donadio, Abstracts of Papers, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 100P.

(6) After much of this work was complete, we found that Balon[7] had effected the reduction of Id with lithium aluminum hydride. However, the yield was not given, and no product analysis or characterization was provided.

(7) W. J. Balon, U. S. Patent 2,853,518 (Sept. 23, 1958).

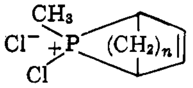
(8) L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **83**, 4124 (1961).

(9) L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **27**, 4120 (1962).

(10) L. D. Quin and C. H. Rolston, *ibid.*, **23**, 1693 (1958).

(11) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

dienophilic methylphosphonous dichloride, but, as predicted, no reaction was observed on prolonged standing. We also exposed two alicyclic dienes to the same dichloride, hoping to form the interesting bicyclic compounds, III (from cyclopentadiene) and IV (from 1,3-cyclooctadiene).



III, $n=1$

IV, $n=4$

Neither adduct formed after several days at room temperature. Cyclopentadiene is, of course, well-known to participate in Diels–Alder reactions; its failure to react here may be due to the strain involved in constructing the four-membered ring component of III. 1,3-Cyclooctadiene is not known to react with dienophiles,[11] and its inactivity here was not unexpected. The requisite planar cisoid conformation can only be achieved with considerable ring strain.[12]

The infrared spectra of IIa, c, and d showed C=C stretching peaks (weak but sharp) as expected[13a] at 1656, 1639, and 1623 cm.$^{-1}$, respectively. Compound IIe, a tetrasubstituted ethylene, had very weak, ill-defined absorption[13a] in the same general region. The stretching vibration of the vinyl hydrogen in IIa was detectable at 3020 cm.$^{-1}$; this absorption was poorly defined in the spectrum of IIc, and in IId could not be distinguished from aromatic hydrogen absorption. Trisubstituted ethylenes show C–H out-of-plane deformation[13a] in the region 800–840 cm.$^{-1}$, and in IIa, a peak of medium intensity was located at 839 cm.$^{-1}$. However, IIc had two peaks in this region (819 and 845 cm.$^{-1}$), while IId had a peak at 812 cm.$^{-1}$. Compound IIe, with no vinyl hydrogen, also absorbed at 817 cm.$^{-1}$. Until additional structures have been examined, it does not appear possible to associate confidently absorption in the 800–840-cm.$^{-1}$ region with this vibrational mode. Compounds IId and e showed strong absorption at 1437 and 1439 cm.$^{-1}$, respectively. This frequency has been associated with the P-phenyl grouping.[13b] Characteristic phenyl absorptions appeared at 694 and 741 cm.$^{-1}$ in both compounds.

In one case (IIe), the 60-Mc. n.m.r. spectrum was obtained and found to be in accord with the assigned structure. A sharp singlet at τ 8.43 was assigned to hydrogens of the two equivalent methyls, a broad symmetrical singlet at τ 7.51 to the ring methylene hydrogens, and a complex centered at τ 2.73 to the phenyl hydrogens. Splitting of the methylene hydrogen peak by phosphorus–hydrogen coupling was not apparent under the conditions used.

Experimental

General.—Melting and boiling points are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. All preparations and manipulations of chlorophosphorane adducts and phosphines were conducted in a nitrogen atmosphere.

Phenylphosphonous dichloride was obtained from Eastman. Methylphosphonous dichloride was kindly supplied by U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, Md. *p*-Tolylphosphonous dichloride was prepared according to *Organic Syntheses*.[14] Dienes were obtained from commercial sources, and, except for chloroprene, used as received. Chloroprene was received in xylene solution; the pure diene was recovered by vacuum distillation and was used immediately. Tetrahydrofuran was purified by distillation from lithium aluminum hydride.

Formation of Diene–Phosphonous Dichloride Adducts.—An equimolar amount of phosphonous dichloride was added to the diene containing about 2–4 wt. % of cupric stearate. The flask was stoppered and allowed to stand until solidification of the mixture was complete, or until no further solid seemed to be forming. In general, reactions with methylphosphonous dichloride were complete in a few days, while with arylphosphonous dichlorides, reaction periods of 1–2 weeks were required. The adduct then was broken up in the flask and washed with pentane. Some of the adducts were recovered by filtration in a drybox and the yield was determined as follows: Ia, 0.21 mole run, 84% after 5 days; Ic, 0.36 mole run, 82% after 1 week; If, 0.85 mole run, 39% after 2 weeks.

Preparation of P-Methyl-3-Phospholenes. A. Magnesium Reduction.—The adduct was suspended in THF in a ratio of about 25 g./150 ml. and stirred vigorously while 1 molar equiv.[15] of dry, ether-washed magnesium turnings was added in small portions. Reductions of Ia and b were generally exothermic, and some moderation with an ice bath was required during magnesium addition to maintain gentle reflux. The mixtures were refluxed 1 hr. after the reaction subsided. However, occasional reductions were only mildly exothermic and required several hours at reflux. The reduction of Ic was performed at low temperatures to prevent Grignard formation; magnesium was added over a 4-hr. period with ice-bath cooling, and the mixture then was stirred 14 hr. at room temperature. Final reaction mixtures were generally cloudy solutions or thin slurries containing some residual magnesium and occasionally a gummy deposit.

The mixtures were treated slowly with cold water to destroy remaining phosphorus chlorides. The solutions were made strongly acidic with 8 *N* hydrochloric acid and then distilled until all THF was removed. The residual solutions were made basic with concentrated sodium hydroxide and then steam distilled. The products were removed from the distillates by ether extraction. The ether extracts were dried with sodium sulfate and distilled at atmospheric pressure. By this procedure, **1,3-dimethyl-3-phospholene (IIa)**, **1,2-dimethyl-3-phospholene (IIb)**, **and 3-chloro-1-methyl-3-phospholene (IIc)** were prepared. Additional data appear in Table I.

Attempts to separate a mixture of IIa and THF by distillation with a Vigreux column were unsuccessful, even though there is a 70° range in boiling point. These two compounds may form an azeotrope, but this has not been established. To overcome this difficulty, the above isolation procedure, utilizing the basic character of phosphines, was devised for IIa and then was applied to all P-methyl compounds. (The higher boiling P-aryl compounds were easily fractionated from THF).

B. Lithium Aluminum Hydride Reduction.—An 18.5-g. (0.10 mole) sample of Ia was dispersed in 100 ml. of ether and treated with 0.2 g. (0.053 mole) of lithium aluminum hydride. A gentle reaction occurred. After 2 hr., the mixture was hydrolyzed carefully and treated with dilute sodium hydroxide. Ether extraction was performed and the extracts then were distilled to give 3.2 g. (0.028 mole, 28% yield) of IIa, identical with that prepared by magnesium reduction.

Preparation of P-Aryl-3-phospholenes.—The reduction of adducts Id, e, and g was carried out in essentially the same manner used for Ia and b. However, it was usually necessary to heat the mixture after the first addition of magnesium to start the reaction. At reflux, however, consumption of magnesium proceeded briskly. The mixture was refluxed 1–2 hr. after the reaction had subsided. The temperature during reduction of If was held below 35°, and the mixture was stirred an additional 18 hr. after no further reaction was apparent.

About one-half of the solvent was removed by distillation, and then cold water was added slowly. The mixtures were made basic with 10 *N* sodium hydroxide, and the resulting slurries were extracted several times with benzene or ether. After drying over sodium sulfate, the extracts were stripped of solvent and distilled

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[12] A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 998 (1955).

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, (a) Chapter 3, (b) Chapter 18.

[14] B. Buchner and L. B. Lockhart, Jr., *Org. Syn.*, **31**, 88 (1951).

[15] Based on the weight of adduct when isolated, otherwise on the starting material in the adduct preparation. In the latter case, 100% yield of adduct was assumed; some excess magnesium was used therefore.

in vacuo. Thus were obtained **3-methyl-1-phenyl-3-phospholene** (IId), **3,4-dimethyl-1-phenyl-3-phospholene** (IIe), **3-chloro-1-phenyl-3-phospholene** (IIf), and **3-methyl-1-(*p*-tolyl)-3-phospholene** (IIg). Additional information is given in Table I.

Preparation of Quaternary Salts from 3-Phospholenes.—About 1 g. of the 3-phospholene was treated in ether with about 2 g. of benzyl bromide. The salt slowly deposited on standing as either a crystalline solid or an oil that later crystallized. All salts were recrystallized readily from a mixture of methanol and ethyl acetate. Melting point and analytical data appear in Table I.

The ethiodide of IId was prepared in the same manner. It developed a yellow color on standing, but gave a satisfactory analysis. Color formation occurred more rapidly with the ethiodide of IIa; ethiodides were concluded, therefore, to be less satisfactory derivatives than the benzyl bromide salts.

Spectra.—The infrared spectra of IIa, c, d, and e were taken on films of the liquids. A Perkin-Elmer Model 21 spectrophotometer was used. The n.m.r. spectrum of IIe was prepared on the neat liquid, with tetramethylsilane as internal reference. This spectrum was kindly prepared by Dr. James P. Collman, University of North Carolina, using a Varian A-60 spectrometer.

The Synthesis of Some 2,3-Diarylcyclopropane-1-carboxylic Acids

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Received July 10, 1963

The three possible stereoisomeric 2,3-diphenylcyclopropane-1-carboxylic acids were prepared and their structure assignments were corroborated by n.m.r. spectra and pK_a measurements. As expected, the all-*cis* isomer, prepared by the catalytic hydrogenation of 2,3-diphenylcyclopropene-1-carboxylic acid, was the weakest acid in the series. The three possible stereoisomeric bis(*p*-methoxyphenyl)- and the four 2-(*p*-methoxyphenyl)-3-phenylcyclopropane-1-carboxylic acids also were prepared (two as an inseparable mixture), and structure assignments were made.

There is considerable recent literature dealing with 2-aryl- and 2,2-diarylcyclopropane-1-carboxylic acids,[1] but little information is available concerning 2,3-diarylcyclopropane-1-carboxylic acids; in fact, only three such compounds have been reported.[2] The compounds were desired for contemplated studies of the cyclopropylcarbinyl rearrangements of 2,3-diarylcyclopropylmethanols[1] as a possible route to the synthesis of biologically active α,α'-disubstituted stilbenes. Since published procedures[2a–c] for the preparation of 2,3-diarylcyclopropanecarboxylic acids from stilbenes indicated disappointingly low yields, better preparative techniques were sought.

Of the three possible isomers of 2,3-diphenylcyclopropane-1-carboxylic acid,[3] only two have been prepared, namely, those derived from *cis*- and *trans*-stilbene. The third possible isomer in the series, the all-*cis* compound has not been isolated previously. Preparation of it by catalytic hydrogenation of the known 2,3-diphenyl-2-cyclopropene-1-carboxylic acid appeared feasible, because *cis* hydrogen addition should occur on the side opposite the carboxyl group.

Accordingly, syntheses of the 2,3-diarylcyclopropane-1-carboxylic acids were undertaken to provide all the stereoisomers in a given series both for structure and property characterization and as possible starting materials of interest for further transformations.

Results and Discussion

Repetition of previous work[2a,b] confirmed that the reaction of *cis*- and *trans*-stilbene with ethyl diazoacetate in the absence of solvent gave 2,3-diphenylcyclopropane-1-carboxylic acids in yields of only about 20%. The principal difficulty was that, at the temperature (125°) necessary for the thermal decomposition of ethyl diazoacetate, *trans*-stilbene sublimed to the upper surfaces of the reaction flask out of contact with the liquid diazo compound. However, when the reaction mixture was diluted with benzene, anhydrous copper sulfate was added, and the reaction was conducted at reflux temperature, the reaction proceeded smoothly and in high yield. A recent report[4] indicates that refluxing cyclohexane also achieves the improved results.

After considerable preliminary work, optimum conditions involving the use of freshly dehydrated copper sulfate as the catalyst and benzene as the solvent were achieved, whereby all the *cis*- and *trans*-stilbenes were converted to the corresponding 2,3-diarylcyclopropane-1-carboxylic acids in good yield. From the *cis*-stilbenes were obtained the *trans,trans* isomers, and from the *trans*-stilbenes the *cis,trans* isomers. Only where *trans*-4-methoxystilbene was the starting material, was a mixture of isomers obtained. Attempts to separate the two isomers, *cis*-2-(*p*-methoxyphenyl)-*trans*-3-phenylcyclopropane-1-carboxylic acid and *trans*-2-(*p*-methoxyphenyl)-*cis*-3-phenylcyclopropane-1-carboxylic acid as the free acids, or methyl esters, were unsuccessful. Thin layer chromatography of the methyl esters on a silica gel plate showed the two expected isomers as overlapping spots. In acetone and in carbon tetrachloride, the n.m.r. spectrum of the mixture showed splitting of the peaks due to the arylmethoxy group and the carbomethoxy group, indicating that these groups are in different environments and hence the two isomers are present.

Catalytic reduction of 2,3-diphenyl-2-cyclopropene-1-carboxylic acid gave a product, m.p. 170–172°, different

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(1) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026, 6396 (1955); F. J. Impastato, L. Barash, H. M. Walborsky, *ibid.*, **81**, 1516 (1959); H. M. Walborsky and J. F. Pendleton, *ibid.*, **82**, 1405 (1960); H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *ibid.*, **83**, 2517 (1961); F. J. Impastato and H. M. Walborsky, *ibid.*, **84**, 4839 (1962).

(2) (a) A. Burger, D. G. Markees, W. R. Nes, and W. L. Yost, *ibid.*, **71**, 3307 (1949); (b) G. P. Hager and C. I. Smith, *J. Am. Pharm. Assoc.*, **41**, 193 (1952); (c) W. M. Jones, *J. Am. Chem. Soc.*, **81**, 3776 (1959); (d) V. Biro, W. Voegtli, and P. Läuger, *Helv. Chim. Acta*, **37**, 2230 (1954).

(3) The designations of *cis* and *trans* isomers used in this paper are based on the relationships of the aryl groups to the carboxylic acid group. Thus *trans,trans*-2,3-diphenylcyclopropane-1-carboxylic acid refers to the isomer in which both phenyl groups, although *cis* to each other, are *trans* to the carboxyl.

(4) I. A. D'yakanov, M. I. Komendantev, Fu Gui-siya, and G. L. Korichev, *J. Gen. Chem. USSR*, **32**, 928 (1962); I. A. D'yakanov, Fu Gui-siya, G. L. Korichev, and M. I. Komendantev, *ibid.*, **31**, 681 (1961).