Attempts to Generate Diphenylcyclopropenylidene. III. Hydride Abstraction–Decarboxylation of 1,2-Diphenylcyclopropenecarboxylic Acid

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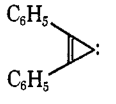
Abstract: Triphenylmethyl perchlorate in acetonitrile efficiently abstracts the hydrogen α to the carboxyl group of 1,2-diphenylcyclopropene-3-carboxylic acid to give the perchloric acid salt of the oxazolone **10**. This salt is readily converted with triethylamine to the free oxazolone which, in turn, undergoes typical ring-opening reactions with water or ethanol to give the corresponding amides **11** and **12**. In chloroform in the presence of ethanol and excess lithium carbonate, the salt of the oxazalone adds ethanol and decarboxylates to give **13**. Hydride abstraction occurs in methylene chloride in the presence of lithium carbonate to give 1,2-diphenyl-3-triphenylmethylcyclopropenium perchlorate **15**. Formation of this material indicates that both hydride abstraction and decarboxylation have occurred. A mechanism involving the diphenylcyclopropenylidene is suggested to explain formation of **15**.

For some time we have been interested in singlet carbenes in which the electrophilicity of the carbene has been suppressed by incorporation of its vacant p orbital in an unsaturated ring in such a way as to make it an integral part of an aromatic system.[2] In particular, we have attempted to generate diphenylcyclopropenylidene[4–6] (**1**) and cycloheptatrienylidene[3] (**2**). Whereas the latter of these two species has apparently yielded to at least one standard method for generating carbenes, generation of the diphenylcyclopropenylidene has turned out to be a much more difficult problem. In fact, to date, the only type of reaction that we have found that gives products that even suggest a carbene intermediate is the rather unorthodox α elimination of carboxylic acids from diphenylcyclopropenol esters.[4,5,7] For example, reaction of the cyclopropenyl carbamate **3** with base in the presence of dimethyl fumarate gives the anticipated carbene adduct, spiropentene **4**. Our current thought on this reaction is that it does, indeed, actually involve the diphenylcyclopropenylidene.



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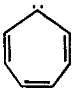

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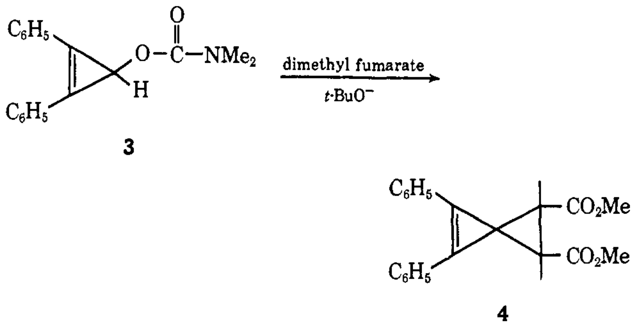

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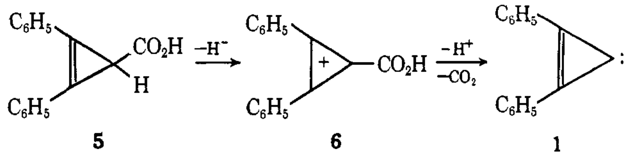
As another possible source of this interesting intermediate, we have now explored the hydride abstraction–decarboxylation sequence pictured in Scheme I.[8] The results of this study will be presented and discussed in this paper.

Scheme I



5 **6** **1**

Results and Discussion

Although hydride abstraction has been effectively used as a method to generate a variety of stable cations,[9,10] including some cyclopropenyl systems,[10] to the best of our knowledge, there is no report of hydride abstraction α to a carboxyl group. In view of the electron-withdrawing properties of this type of group, it was anticipated that hydride abstraction from acid **5** might be considerably more difficult than from simple alkyl- or aryl-substituted cyclopropenes. It was therefore encouraging when it was found that equimolar quantities of triphenylmethyl perchlorate and diphenylcyclopropenecarboxylic acid (**5**) in acetonitrile gave a high yield of triphenylmethane and a white perchlorate salt. Spectral data on the perchlorate salt clearly showed preservation of the diphenylcyclopropenyl moiety (cyclopropene absorption at 5.41 μ (1850 cm^{-1}), ultraviolet radiation typical of the diphenylcyclopro-

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[1] Alfred P. Sloan Fellow, 1963–1967.

[2] Carbene electrophilicity can also be suppressed by delocalization of nonbonded electrons of heteroatoms into the vacant p orbital of the carbene. For a summary of recent references on this subject, see D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 528 (1966), and ref 3 of this paper.

[3] W. M. Jones and C. L. Ennis, *ibid.*, **89**, 3069 (1967).

[4] W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964).

[5] W. M. Jones and M. E. Stowe, *Tetrahedron Letters*, 3459 (1964).

[6] See R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966), for an example of a cyclopropenylidene as a possible contributing resonance form to the hybrid of a cyclopropenone anion.

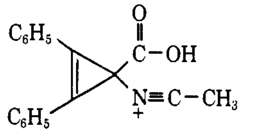
[7] M. E. Stowe, unpublished results.

[8] For at least one example of decarboxylation from a zwitterion that is believed to lead to a nucleophilic carbene, see H. Quast and E. Frankenfeld, *Angew. Chem. Intern. Ed. Engl.*, **4**, 691 (1965).

[9] *Cf.* H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4558 (1957); D. J. Bertelli, C. Golino, and D. J. Dreyer, *ibid.*, **86**, 3329 (1964).

[10] *Cf.* H. D. Prinzbach and D. Seip, *Angew. Chem.*, **73**, 169 (1961); H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, 1217 (1963); W. M. Jones and R. S. Pyron, *J. Am. Chem. Soc.*, **87**, 1608 (1965); W. M. Jones and R. S. Pyron, *Tetrahedron Letters*, 479 (1965).

enyl chromophore),[11] loss of the cyclopropenyl hydrogen (nmr), and presence of the perchlorate ion (infrared). However, the nmr spectrum showed that a molecule of the solvent, acetonitrile, had also been incorporated in the molecule. These results and the method of synthesis suggested two possible structures for this salt, the Ritter type of intermediate[12] **7** or the protonated oxazolone **8**.



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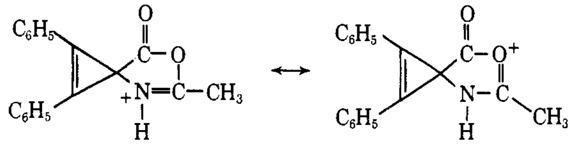
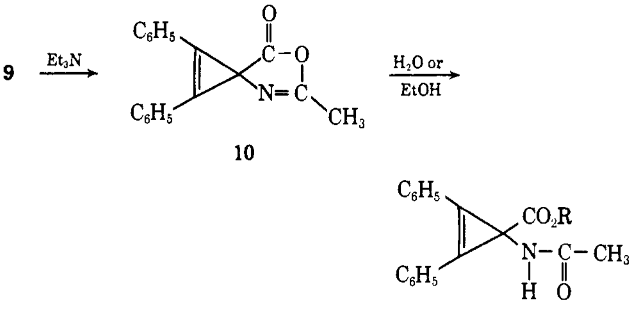


8 **9**

The infrared spectrum argues strongly for the protonated oxazolone alternative in that it shows intense absorptions at 5.36 μ (1865 cm^{-1}) and 6.01 μ (1665 cm^{-1}). To make the ring-opened structure **7** consistent with these results would require assignment of the low wavelength absorption to the $C{\equiv}N^{+}$– and the long wavelength absorption to the acid carbonyl. Although the former may be reasonable, the latter certainly would not be since any effect of the electronegative $-N^{+}{\equiv}C-$ group should cause a shift of the acid carbonyl to a wavelength shorter than its normal 5.85 μ (1710 cm^{-1}).[13] In the protonated oxazolone structure, the low wavelength absorption can be reasonably assigned to the carbonyl stretch and the 6.01-μ (1665 cm^{-1}) absorption to the C=N.[14] The effect of the positively charged nitrogen on the position of the carbonyl absorption is probably a result of a significant contribution of resonance form **9** to the hybrid of the salt.

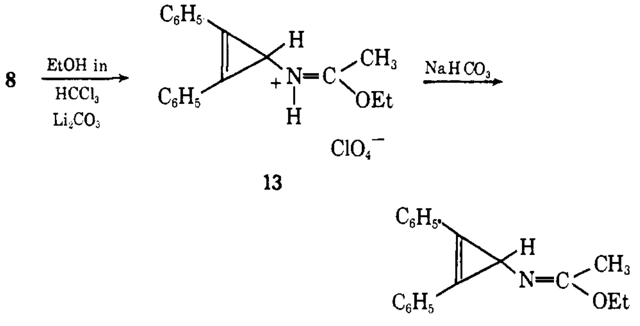
Further support for incorporation of the acetonitrile α to the carboxyl was obtained by neutralizing the salt with triethylamine to give the neutral oxazolone **10**. Not only were spectra reasonable for this structure (infrared absorptions at 5.39, 5.58 and 6.01 μ (1885, 1792, and 1665 cm^{-1});[14] nmr resonances at δ 2.35 (CH_3–), 7.54 (phenyl, multiplet)) but treatment of the oxazolone with water or ethanol under acidic or basic conditions gave the expected acid[15] and ester[15] **11** and **12**.



10

11, R = H
12, R = Et

Although the oxazolone itself could not be used as a precursor to the desired cyclopropenylidene, its formation not only demonstrated the feasibility of the hydride abstraction step of our suggested Scheme I but the chemistry of its salt **8** alluded to the potential feasibility of the second step—decarboxylation of the cation. Thus when a solution of **8** in chloroform containing a small amount of ethanol and a large excess of lithium carbonate (as a suspension) was refluxed, decarboxylation occurred to give **13** which, upon treatment with aqueous sodium bicarbonate, gave the free base **14**. Structural assignments of these rather surprising products rest on correct analyses, ultraviolet and infrared absorptions which leave no doubt about the presence of the diphenylcyclopropenyl moiety (see Experimental Section) and the following data. Presence of the methyl group and incorporation of an ethoxy group into **13** was clearly demonstrated by the nmr spectrum which showed a three-hydrogen singlet at δ 2.70 and the triplet and quartet of an ethyl group centered at δ 1.56 and 4.98, respectively. That the ethoxy was carried over to the free base was not as clearly shown by the nmr due to poor resolution when only a small amount of material was available for examination. Nonetheless, elemental analysis leaves no doubt but that this group is still present and the nmr shows broad absorptions centered at about δ 1.2 and 4.1 in addition to the other anticipated resonances. Presence of the C=N group in both **13** and **14** is indicated by infrared absorptions around 1660 cm^{-1}. In addition, **13** shows the complex absorption in the infrared region about 3200 cm^{-1} that is typical of the N^{+}–H (stretch) as well as an absorption at 1530 cm^{-1} (N–H bending) and a very intense absorption at 1060 cm^{-1} (ClO_4^-). All of these absorptions were cleanly removed upon conversion to **14**. Presence of a cyclopropenyl hydrogen was indicated by the nmr spectra of both compounds as well as the ultraviolet spectrum of **14** in the presence of fluoroboric acid which went cleanly to the typical spectrum of diphenylcyclopropenyl cation.[11] The mass spectrum of **14** also supports the assigned decarboxylated structure in that it shows a rather intense peak (most intense peak in the spectrum at *m/e* greater than 43) at *m/e* 191 which corresponds to the diphenylcyclopropenyl cation. Finally additional evidence for the decarboxylated structure was obtained by hydrolyzing a small amount of **14** with aqueous fluoroboric acid followed by tlc analysis of the product. With the exception of a small spot at the



13

14

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[11] For example, see R. Breslow, J. Lockhart, and W. W. Chang, *J. Am. Chem. Soc.*, **83**, 2375 (1961).

[12] *Cf.* J. J. Ritter, *et al.*, *J. Am. Chem. Soc.*, 70, 4045, 4048 (1948).

[13] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, p 222.

[14] See ref 13, p 459. The shift of the carbonyl (and, possibly, the small shift of the C=N) frequency probably results from the strain imposed on the oxazolone ring by the spirocyclopropene.

[15] *Cf.* J. W. Cornforth in "Heterocyclic Compounds," Vol. 5, R. E. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp 354–357.

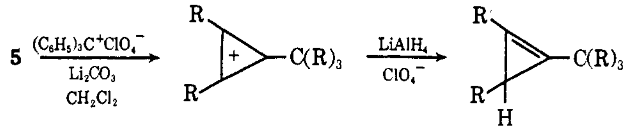
origin, the chromatogram was superimposable with that of bisdiphenylcyclopropenyl ether. There was not enough material to isolate and characterize further.

The mechanism of formation of **13** is unknown. However, the structure of the product suggests attack of a nucleophile (ethanol or ethoxide) on the carbon of the C=N followed by decarboxylation, etc. Furthermore, since ethanol under basic conditions reacts with the carbonyl carbon of the free oxazolone to simply give the ring-opened ester, the reaction of ethanol with the salt probably involves attack on the protonated molecule. This is under further investigation.

To obviate attack of the solvent on the cation **6**, the reaction solvent was changed from acetonitrile to methylene chloride. In the absence of base, most of the results of this study were relatively unsatisfactory. In the first place it was found that an equimolar mixture of trityl cation and the acid gave very limited reaction as evidenced by a low yield of triphenylmethane and good recovery of starting material. This contrast with the reaction in acetonitrile is probably due simply to the fact that formation of the salt **8** shifts an inherently unfavorable equilibrium. When the reaction was run in the presence of a large excess of the trityl cation, inseparable mixtures of unstable products were obtained. In one case, however, there was isolated in 61% yield a rather interesting (albeit irrelevant to the current problem) white crystalline material that is probably a perchloric acid salt of the starting diphenylcyclopropenecarboxylic acid. This material, which has a typical diphenylcyclopropene ultraviolet spectrum, showed an interesting nmr spectrum in that, in addition to phenyl resonances and a cyclopropene ring singlet, the spectrum showed two broad single hydrogen absorptions centered at δ 8.16 and 6.6. The presence of these two peaks, both of which were readily washed out with D_2O, indicated nonequivalent hydrogens and are rather difficult to justify. One possibility is a diprotonated (on oxygen) acid dimer although we have no strong evidence to support this. This salt showed one other interesting property in that simple solution in acetic anhydride led to rapid carbon monoxide evolution.[16] Dilution of the resulting solution with ether gave a high yield of the expected diphenylcyclopropenium perchlorate.[16]

Although the results of attempted hydride abstractions in methylene chloride in the absence of base tended to be ambiguous, in the presence of added lithium carbonate the reaction appeared surprisingly straightforward. Thus, when a solution of the acid in methylene chloride was slowly added to an excess of trityl perchlorate and lithium carbonate in refluxing methylene chloride and the resulting mixture worked up, there was isolated in 50% yield (based on unrecovered acid) the perchloric acid salt of 1,2-diphenyl-3-triphenylmethylcyclopropenium perchlorate (**15**), whose structure was confirmed by reduction to the cyclopropene **16** (Scheme II). Formation of this compound is remarkable in that it represents precisely what is outlined in Scheme I: loss of both the cyclopropene hydrogen and the carboxyl group. Furthermore, in view of the nature of the reactants, about the only reasonable mechanism that can be written to explain formation of this material is *via* the hoped-for diphenylcyclopropenylidene (**1**). However, despite the fact that this reaction probably does involve formation of the carbene, it is unlikely that it will develop into a very useful method for studying this species since the trityl cation is electrophilic enough to dominate trapping of this nucleophilic intermediate. Support for this presumption rests on the fact that in preliminary experiments, neither dimethyl fumarate nor *p*-toluenesulfonylazide (even employing inverse addition) succeeded in competing with the trityl cation for the intermediate. Further work along these lines is in progress.

Scheme II



15 **16**, 100%

R = C_6H_5

Experimental Section

General. Except where indicated, infrared spectra were obtained with a Beckman IR10 spectrometer. Nmr spectra were obtained on a Varian Model A-60-A spectrometer and ultraviolet spectra were obtained on a Cary Model 15 spectrometer. Microanalyses are by Galbraith Laboratories. Melting points were taken in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Diphenylcyclopropenecarboxylic acid was synthesized by the method of Breslow, Winter, and Battiste[17] and triphenylmethyl perchlorate was prepared by the method of Dauben, *et al.*[18] Commercial reagent grade solvents were generally dried by adsorptive filtration through a column of Woelm alumina (activity 1) according to the instructions given in Woelm Publication AL 7.

2-Methyl-4-(spiro-1,2-diphenylcyclopropenyl)-2-oxazolinium-5-one Perchlorate (8). A mixture of 1,2-diphenylcyclopropenecarboxylic acid (5.0 g, 21.2 mmoles), triphenylmethyl perchlorate (7.25 g, 21.2 mmoles), and 300 ml of dry acetonitrile was stirred at room temperature in the dark for about 24 hr, protected from atmospheric moisture. Most of the solvent was removed under reduced pressure (bath temperature 60–65°). The concentrated solution was then added very slowly (at least 10 min) to about 1.5 l. of rapidly stirred anhydrous ether. This gave a flocculent precipitate which on further stirring crystallized and settled to the bottom. Collection of the solid by filtration under nitrogen followed by several ether washings gave 6.0 g (75%) of white solid.

Recrystallization from tetrahydrofuran–ethyl acetate gave a white crystalline solid that was too unstable for analysis. Attempted melting point determination on this solid led to considerable darkening as low as 70°; at about 135° the black mass was melted and considerable bubbling occurred.

The infrared spectrum (KBr) had bands (cm^{-1}) at 3400–2400 (broad), 1867, 1850, 1663, 1445, 1405, 1310, 1290, 1043, 885, 758, 688, 620. The ultraviolet spectrum (CH_3CN) was identical with that of **11**.

2-Methyl-4-(spiro-1,2-diphenylcyclopropenyl)-2-oxazolin-5-one (10). The perchlorate (**8**) (1 g, 2.6 mmoles) was suspended in 20 ml of dichloromethane and triethylamine (0.4 ml, 2.7 mmoles) was added dropwise with stirring. When the addition of the base was complete the solution was a clear yellow; addition of about 50 ml of 1:1 ether–pentane served to separate the triethylammonium perchlorate as an oil. The solution was separated from the oil by decantation and the remaining oil, which made the solution appear cloudy, was removed by swirling with anhydrous magnesium sulfate. Evaporation of the ether gave 0.625 g (89%) of a light yellow solid that was readily purified by recrystallization from hot hexane to give the white oxazolone, mp 132–134°. The analytical sample

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[16] D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960); R. Breslow and H. Hover, *ibid.*, **82**, 2644 (1960); R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

[17] R. Breslow, R. Winter, and M. A. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

[18] H. J. Dauben, L. Honnen, and K. Harmon, *ibid.*, **25**, 1442 (1960).

was prepared by sublimation, mp 134–135°. The infrared spectrum (KBr) had bands (cm^{-1}) at 1858, 1790, 1665, 1443, 1305, 1240, 1126, 1035, 981, 750, 682. The ultraviolet spectrum (CH_3CN) showed absorptions at 315 mμ (ε 4.50), 299 (4.56), 227 (4.32), 221 (4.43). The ultraviolet spectrum (CH_3CN–HBF_4) showed absorptions at 312 (4.47), 297 (4.54), 277 (4.34), 220 (4.36). The nmr spectrum ($CDCl_3$, TMS internal standard) showed resonances at δ 2.35 (singlet, methyl), 7.54 ppm (narrow multiplet, phenyls).

Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.37; H, 4.68; N, 4.93.

N-(1,2-Diphenyl-3-carboxycyclopropenyl)acetamide (11). Acidic or basic hydrolysis of the neutral **10** leads to amide **11** in good yield. Compound **8** is also rapidly hydrolyzed to **11** by water. Recrystallized three times from absolute ethanol the extremely fine needles melted at 197–198°. The infrared spectrum (KBr) had bands (cm^{-1}) at 3235, 3030, 1845, 1690, 1640, 1525, 1290, 1165, 990, 766, and 688. The ultraviolet spectrum (CH_3CN) showed absorptions at 317 mμ (ε 4.40), 301 (4.48), 229 (4.24), 223 (4.30); the ultraviolet spectrum (CH_3CN/HBF_4) showed absorptions at 314 mμ (4.42), 298 (4.50), 228 (4.26), 221 (4.30). The nmr spectrum (DMSO-d_6, TMS internal standard) showed resonances at δ 1.86 (singlet, methyl), 7.53, and 7.93 ppm (multiplets, phenyls).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.55; H, 5.30; N, 4.93.

N-(1,2-Diphenyl-3-ethoxycarbonylcyclopropenyl)acetamide (12). Treatment of 2-oxazolin-5-one (**10**) with anhydrous ethanolic HCl for 2 days at room temperature led to a high yield of the ester **12**. The perchlorate salt (**8**) of **10** with ethanol also gives the ester in good yield. From neutral ethanol at room temperature or refluxing chloroform containing excess ethanol, **10** was recovered unchanged. In the presence of excess ethoxide both **8** and **10** were converted into ester **12**, but not as cleanly as under acidic conditions.

The ester, recrystallized from chloroform–ether, melted at 170–172°. The infrared spectrum (KBr) had bands (cm^{-1}) at 3240, 3040, 1832, 1724, 1635, 1535, 1300, 1250, 1100, 760, and 690. The ultraviolet spectrum (CH_3CN) showed absorptions at 316 mμ (ε 4.45), 301 (4.53), 229 (4.30), 222 (4.35); the ultraviolet spectrum (CH_3CN–HBF_4) showed absorptions at 312 (4.46), 297 (4.55), 227 (4.32), 220 (4.36). The nmr spectrum ($CDCl_3$, TMS internal standard) showed resonances at δ 1.13 and 4.16 (triplet and quartet, ethyl, J = 7.0 cps), 1.97 (singlet, methyl), 6.47 (broad, NH), 7.5 and 7.85 ppm (aromatic multiplets).

Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.48; H, 5.93; N, 4.32.

Decarboxylation of 8 to Give 13. The perchlorate **8** and lithium carbonate (1 g of each) were added to 60 ml of chloroform (technical grade, passed through Woelm basic alumina) and the mixture was allowed to reflux for 2 hr. The solid was removed from the mixture by filtration and the solution was concentrated to about 5 ml. Addition of pentane and ether led to a gummy precipitate that could not be induced to solidify. Water was added and enough methylene chloride was added to dissolve all of the residue. The organic layer was then rapidly washed with water and saturated sodium chloride solution and dried over sodium sulfate. Concentration of the solution followed by addition of pentane gave 0.11 g of near white solid **13**, mp 150–154° dec. Recrystallization was achieved by dissolving the solid in tetrahydrofuran and adding ether; this gave white needles, mp 154–155° dec. The following spectral data were obtained for this compound: the infrared spectrum (KBr cm^{-1}) had bands at 3300–3000 (multiplet) 1830, 1650, 1530, 1430, 1345, 1110, 1060, 770, and 690; the nmr spectrum (acetone-d_6, TMS internal standard) showed resonances at δ 1.56 and 4.08 (triplet and quartet, J = 7.0 cps, ethyl) 2.70 (singlet, methyl), 4.43 (singlet, cyclopropenyl hydrogen), and 7.52 and 7.82 ppm (multiples, phenyls).

Anal. Calcd for $C_{19}H_{20}NO_5Cl$: C, 60.39; H, 5.34; N, 3.71; Cl, 9.39. Found: C, 60.22; H, 5.37; N, 3.87; Cl, 9.63.

When the above compound was stirred with a mixture of aqueous sodium bicarbonate and ether, the white solid slowly disappeared. Separation of the layers followed by washing the ether layer with water, drying, and evaporating gave a yellowish solid. This solid was purified by sublimation at 70° (0.1 mm) followed by recrystallization from hot heptane. The infrared spectrum of this material showed significant absorptions (KBr, cm^{-1}) at 3090–2900 (multiplet), 1820, 1802 (shoulder), 1660 (strong C=N), 1595, 1490 1480, 1445, 1375, 1350, 1250, 1170, 1130, 1060, 1020, 905, 840, 770, 760, 720, 690, 620. The ultraviolet spectrum (CH_3CN) showed absorptions at 322 mμ (ε 21,000), 308 (35,800), 232 (16,500), and 225 (21,000). In the presence of a drop of fluoroboric acid, the spectrum showed absorptions at 305 (31,900) 292 (31,600), and 245 (10,800). The nmr spectrum was poorly resolved owing to insufficient material. It showed absorptions centered about δ 1.1, 2.3, 3.6, 4.1, and 7.4. These show areas that are roughly consistent with CH_3 of ethyl, CH_3, cyclopropenyl hydrogen, CH_2 of ethyl, and aromatic protons, respectively.

Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.58, 82.33; H, 6.81, 6.96; N, 4.87, 4.93.

1,2-Diphenyl-3-triphenylmethylcyclopropenium Perchlorate (15). Triphenylmethyl perchlorate (3.7 g, 10.8 mmoles) and lithium carbonate (*ca.* 1 g) were placed in a dry flask equipped with a nitrogen inlet, a dropping funnel, a reflux condenser with a drying tube, and a stirrer. About 150 ml of dried dichloromethane was added and the reaction flask was wrapped with aluminum foil to protect the triphenylmethyl perchlorate solution from light. The flask was then immersed in an oil bath and the solvent brought to reflux. 1,2-Diphenylcyclopropenecarboxylic acid (0.77 g, 3.26 mmoles) dissolved in 50 ml of dichloromethane was placed in the dropping funnel and added to the reaction mixture dropwise over a period of 7 hr. The resulting green reaction mixture was then allowed to stir at room temperature overnight; the solid salts were removed by filtration and the solution was concentrated on a rotary evaporator. The concentrated solution was then added slowly to about 1 l. of rapidly stirred anhydrous ether and the solid that was found was collected by vacuum filtration under a stream of nitrogen. This solid (0.584 g) was recrystallized from acetonitrile–ether to give white crystals, mp 215° dec. This material did not give a satisfactory analysis; its structure was confirmed by reduction to the hydrocarbon (see below).

The infrared spectrum (KBr) had bands (cm^{-1}) at 1832, 1594, 1496, 1417, 1392, 1096, 763, 706, 680, 623. The ultraviolet spectrum (CH_3CN) showed absorptions at 260 mμ (ε 4.28); the ultraviolet spectrum (CH_3CN–HBF_4) showed absorptions at 300 (4.38), 253 (4.25), 230 (4.17). The nmr spectrum (CH_3CO_2H, benzene internal standard) showed resonances (parts per million downfield from benzene) at δ 0.17 (singlet, triphenylmethyl) and 0.58 (multiplet, cyclopropene phenyls).

1-Triphenylmethyl-2,3-diphenylcyclopropene (16). The cyclopropenium perchlorate (69 mg, 0.13 mmole) was suspended in ethyl ether (5 ml) and a solution of lithium aluminum hydride (11 mg, 0.42 mmole) in ether (10 ml) was added during about 5 min. After stirring for 5 additional min water was cautiously added to the solution. The solution was washed two more times with water, once with brine, and dried over sodium sulfate. Evaporation of the ether gave 56 mg (99%) of a white solid which after recrystallization from hexane melted at 146–148°. The ultraviolet spectrum (CH_3CN) showed absorptions at 267 mμ (ε 4.26) with a slight shoulder at *ca.* 283. The nmr showed the aliphatic singlet at δ 3.22 while the aromatic region had two major peaks at δ 7.10 and 7.19. The infrared spectrum (KBr) had bands (cm^{-1}) at 3015, 3055, 1832, 1595, 1485, 1433, 1022, 1008, 775, 758, and 701.

Anal. Calcd for $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 93.83; H, 6.04.

Isolation of the Perchloric Acid Salt of 1,2-Diphenylcyclopropenecarboxylic Acid. The acid **5** (2.0 g, 8.5 mmoles) and triphenylmethyl perchlorate (5.9 g, 17.2 mmoles) were stirred in 350 ml of dry methylene chloride at −10 to 0° for *ca.* 20 hr. Concentration of the solution to about 30 ml led to the separation of 0.915 g of an off-white solid (solid A). Dilution of the filtrate with 600 ml of anhydrous ether led to recovery of 4.6 g of triphenylmethyl perchlorate. After concentrating the yellow ether filtrate to about 100 ml, it was extracted with potassium carbonate solution. This was neutralized and 0.95 g of starting acid was collected by extraction with sodium bicarbonate; this left 0.331 g of a dark orange, carbonate-soluble, bicarbonate-insoluble solid which could not be characterized.

Solid A from above was recrystallized by dissolving in tetrahydrofuran and adding pentane; after two such recrystallizations a white solid was obtained, mp 147–148° dec. The infrared, nmr, and ultraviolet spectra of this solid were identical with those for the starting acid except that the infrared (KBr) contained additional peaks at 2.98, 9.0, and 9.2 μ and the nmr ($CDCl_3$, TMS) had two new broad absorptions at δ 6.6 and 8.16. The two new nmr peaks could be washed out with D_2O to give an HOD peak integrating for 2.3–2.5 protons.

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