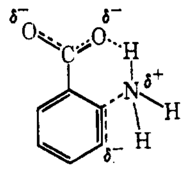
*ortho* position may be aided by means of an intramolecular hydrogen bonded transition state represented by **21**. Nevertheless, that more *meta* than *ortho* addition occurs even in low amide concentration indicates that induction and resonance effects of the carboxylate group predominate over the field effect in neutral additions.



**21**

**Registry No.**—3,4′-Iminodibenzoic acid, 18908-52-6; 3,3′-iminodibenzoic acid, 19,039-48-6; α-cyano-*m*-toluic acid, 5689-33-8; α-cyano-α-phenyl-*m*-toluic acid, 18908-55-9; α-cyano-α-phenyl-*p*-toluic acid, 18908-56-0; *m*-(1-cyano-*n*-butyl)benzoic acid, 5485-72-3; *p*-(1-cyano-*n*-butyl)benzoic acid, 18908-58-2; *p*-(1-cyanoethyl)benzoic acid, 18908-59-3; *p*-chlorobenzoic acid, 74-11-3.

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# Synthesis and Ionization Constants of *meta*- and *para*-Substituted 1-Phenyl-2-methylcyclopropene-3-carboxylic Acids

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1-Phenyl-2-methylcyclopropene-3-carboxylic acid and the $p$-OCH$_3$, $m$-CH$_3$, $p$-F, $p$-Cl, and $m$-Cl derivatives were prepared by the addition of ethyl diazoacetate to the appropriately substituted 1-phenylpropyne with subsequent hydrolysis. The ionization constants in 50% ethanol at 25° give $\rho = 0.57$ ($-\log K_0 = 6.45$) using $\sigma^0$ values. The cyclopropene ring appears to transmit resonance effects about as well as does the cyclopropane ring.

A number of investigators have attempted to evaluate the factors involved in the transmission of substituent effects to a functional group.[2] The relative transmission by various groups interposed between an aromatic ring and a functional group have been assessed by a comparison of Hammett $\rho$ values for a given reaction of the several series. On this basis, the cyclopropyl group exhibits enhanced transmission relative to the dimethylene group (but less than an ethylenic linkage[3,4]), which is consistent with the proposed conjugative ability of the three-membered ring.[5]

Another point of view expressed by Bowden[4] is that the relative abilities to transmit electronic influences within similar series may not necessarily be a function of conjugative or inductive effects but rather of an electrostatic interaction between the reaction site and the substituent. This electrostatic effect is a function of the distance and the direction of the substituent dipole relative to the reaction center.

The conjugative effect attributed to cyclopropane may be the result of *p*-orbital overlap with the C–C bond orbitals of cyclopropane,[6] which also have a large fraction of p-orbital character.[5] This introduces the possibility that other highly strained systems might also exhibit an enhancement in the transmission of electronic effects relative to an ordinary C–C $\sigma$ bond.

The C–C single bond in cyclopropene may provide another such model. The structure of cyclopropene has been considered by several investigators, and the results have been reviewed.[7] The external methylene bonds in cyclopropene are considered to be $sp^{2.5}$ hybridized indicating that the C–C single bonds have increased p-orbital character. The strain energy of cyclopropene is about 27 kcal/mol greater than that of cyclopropane, based on the heats of formation.[8]

The cyclopropene group will also serve for an additional examination of the electrostatic theory of substituent effects as discussed by Bowden.[4] Since this theory considers the distance and direction of the substituent dipole, conformational factors are important. In this regard, the rigidity of the cyclopropene system removes conformational factors as a variable.

This study is concerned with the ease with which electronic effects are transmitted from a substituent to a reaction site joined by means of the C–C single bond in cyclopropene. The compounds used in this study were a series of *meta*- and *para*-substituted 1-phenyl-2-methylcyclopropene-3-carboxylic acids.

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[1] Author to whom correspondence should be directed. Support of this work by The Robert A. Welch Foundation Grant E-136 is gratefully acknowledged. Based on the Ph.D. Dissertation of A. B. T., University of Houston, June 1968. Presented in part at the 2nd Conference on Linear Free Energy Relationships, University of California at Irvine, Irvine, Calif., March 29, 1968.

[2] J. A. Caputo and R. Fuchs, *J. Org. Chem.*, **33**, 1959 (1968), and references therein.

[3] R. Fuchs and J. J. Bloomfield, *ibid.*, **31**, 3423 (1966).

[4] K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963).

[5] See references cited by R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

[6] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967), and references therein.

[7] F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

[8] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

## Results

Table I shows the ionization constants of the 1-aryl-2-methylcyclopropene-3-carboxylic acids in 50% aqueous ethanol at 25° and the $\sigma^0$ [9] values for the substituents. A least squares treatment of $-\log K_i$ *vs.* $\sigma^0$ gives a $\rho$ value of 0.57 and a correlation coefficient of 0.98.

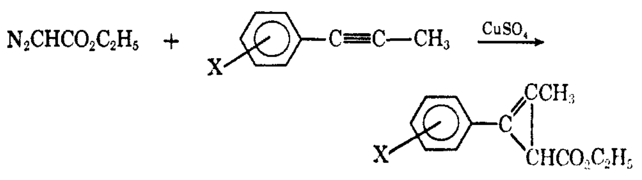
Table I

Apparent Dissociation Constants of *meta-* and *para-*Substituted 1-Phenyl-2-methylcyclopropene-3-carboxylic Acids in 50% Ethanol at 25°

| Substituent | $\sigma^0$ | p$K_a$ |
|---|---|---|
| *m*-Cl | 0.37 | 6.25, 6.27 |
| *p*-Cl | 0.27 | 6.29, 6.27 |
| *p*-F | 0.17 | 6.31, 6.33 |
| H | 0 | 6.44, 6.46 |
| *m*-$CH_3$ | −0.07 | 6.52, 6.51 |
| *p*-$OCH_3$ | −0.16 | 6.52, 6.53 |

## Discussion

The acids were synthesized by the addition of ethyl diazoacetate to the appropriately substituted propyne to form the corresponding ethyl esters, which were hydrolyzed to give the acids. The synthetic procedure was adapted from a previous preparation[10] of the unsubstituted acid, I (X = H).



Since the unsubstituted compound had been characterized, it was possible to characterize the substituted acids by a comparison of certain properties with those of the unsubstituted acid. The ultraviolet (uv) spectra of the substituted acids were quite similar to the spectrum of the acid (X = H). The substituted acids showed an absorption in the range 260–269 mμ ($\epsilon$ 15,000–27,000); the unsubstituted acid absorbed at 260 mμ ($\epsilon$ 17,000). All of the acids showed strong absorption increasing about 230 mμ and reaching a maximum below 210 mμ with shoulders appearing over the range 214–228 mμ ($\epsilon$ 12,000 to 28,300). The pnmr spectra of all the acids had striking similarities. The aromatic protons in each of the acids were typical, absorbing about $\delta$ 7.3; the acidic hydrogens appeared downfield about $\delta$ 11–12. The methyl protons and the single proton on the cyclopropene ring appeared as singlets about $\delta$ 2.3–2.4.

From the Bowden viewpoint[4] the electrostatic contribution to the relative transmission of substituent effects within similar series is determined by the factor $\cos\theta/r^2$ where $\theta$ is the angle between the line joining the reaction center and the center of the dipole, and the axis of the dipole.[11] Using a set of Framework Molecular Models with interatomic distances either taken or estimated from available data,[12] direct measurements were made to determine $r$ and $\theta$. The distance $r$ was taken from the *para* carbon atom (the assumed center of the dipole) to 0.89 Å beyond the carbonyl carbon atom.[4] The results are given in Table II. To assure that these measurements were consistent with those previously reported by Bowden,[4] some of his parameters were recalculated (Table II). In doing so there was reasonable agreement, excepting $\theta$ for the *trans*-2-phenylcyclopropanecarboxylic acid, which was reported[4] to be 32°, with $r$ = 6.19 Å; in this work $\theta$ was measured as 14° with $r$ = 7.1 Å. Dividing $\rho$ by $10^2 \cos\theta/r^2$ for related acid series (phenylacetic, $\beta$-phenylpropionic, *cis*-cinnamic, and *cis*-1,3-cyclobutanecarboxylic acid) lacking direct resonance interaction between aryl and carboxyl groups gives values 0.18–0.23. For *trans*-cinnamic, benzoic, and phenylpropiolic acids values of 0.35–0.37 are obtained, indicating that substituent effects are transmitted to an extent larger than would be predicted solely on the basis of an electrostatic effect. Direct resonance effects are possible in these series. The measurements of $r$ and $\theta$ in this work give a value of 0.28 for *trans*-2-phenylcyclopropanecarboxylic acid, which is clearly between that of groups incapable of resonance interaction and those capable of strong resonance effects. This suggests that the *trans*-cyclopropyl group may be capable of some resonance interaction. The cyclopropene-3-carboxylic acids with a value of 0.28 also appear to have some resonance interaction between the substituent and the reaction site. The value of $\rho/10^2 \cos\theta/r^2$ for the *cis*-2-phenylcyclopropanecarboxylic acid series is 0.16, meaning that $\rho$ is smaller than would be predicted on the electrostatic basis. This may result from slight defects in the electrostatic model, or from errors in $\theta$ and $r$ due to repulsions between the phenyl and carboxyl groups.

The various transmitting groups are placed in more sharply defined groupings on the basis of $\rho/10^2 \cos\theta/r^2$ for ester hydrolysis. As noted in Table II the nonconjugating phenylacetates and $\beta$-phenylpropionates have a value of 0.33 for $\rho/10^2 \cos\theta/r^2$. Also included in this group are the *cis*-cinnamates and *cis*-2-phenylcyclopropylcarboxylates. The series with conjugative interactions (*trans*-cinnamates, benzoates, and phenylpropiolates) have values 0.64 to 0.66. Here again, the *trans*-2-phenylcyclopropylcarboxylates are clearly intermediate with a value of 0.44 for $\rho/10^2 \cos\theta/r^2$; as mentioned previously, this suggests some conjugative interaction.

The above results indicate that substituent effects are transmitted nearly equally by the cyclopropene and *trans*-cyclopropane rings. The values are 0.57 and 0.54, respectively, with $\rho/10^2 \cos\theta/r^2$ being 0.28 in both systems. This suggests that in both groups there is some conjugative transmission of substituent effects, but the more highly strained cyclopropene system transmits no better considering its geometry than does the *trans*-cyclopropane ring.

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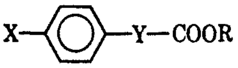
(9) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(10) I. A. D'yakonov, M. I. Komendantov, and S. P. Korshunov, *J. Gen. Chem. USSR*, **32**, 912 (1962).

(11) For discussion on this point, see ref 2 and 4 and J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(12) Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement 1956–1959; Special Publication No. 18, London, The Chemical Society, Burlington House, W.1, 1965.

TABLE II
CALCULATION OF ELECTROSTATIC INTERACTIONS



| Y | $\theta$ | r, Å | $10^2 \cos \theta/r^2$ | Acids | | Ethyl esters | |
|---|---|---|---|---|---|---|---|
| | | | | $\rho^a$ | $\rho/10^2 \cos \theta/r^2$ | $\rho^{b,c}$ | $\rho/10^2 \cos \theta/r^2$ |
| | 0 | 5.1 | 3.84 | 1.42[d] | 0.37 | 2.54 | 0.66 |
| $CH_2$ | 24 | 5.4 | 3.14 | 0.74 | 0.23 | 1.03 | 0.33 |
| $CH_2CH_2$ (*anti*) | 11 | 7.1 | 1.95 | 0.417[e] | 0.21 | 0.64 | 0.33 |
| *cis*-C=C | 41 | 4.8 | 3.28 | 0.63[e,f] | 0.19 | 1.09 | 0.33 |
| *trans*-C=C | 5 | 7.2 | 1.92 | 0.68[e,f] | 0.35 | 1.26 | 0.66 |
| C≡C | 0 | 7.6 | 1.73 | 0.625[e] | 0.36 | 1.1[g] | 0.64 |
| *cis*  | 43 | 4.7 | 3.31 | 0.517[e] | 0.16 | 1.10 | 0.33 |
| *trans*  | 14 | 7.1 | 1.92 | 0.542[e] | 0.28 | 0.85 | 0.44 |
| *cis*  | 26 | 7.9[h] | 1.44 | 0.256[i] | 0.18 | | |
|  | 20 | 6.8 | 2.04 | 0.57 | 0.28 | | |

[a] Based on ionization constants in 50% (v/v) aqueous ethanol at 25°. [b] Based on rates of ester hydrolysis in 87.8% (v/v) aqueous ethanol at 30°. [c] Values of $\rho$ taken from ref 4. [d] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [e] Reference 4. [f] Reference 5. [g] R. Fuchs, *J. Org. Chem.*, **28**, 3209 (1963). [h] The cyclobutane ring is assumed to deviate from planarity by an angle of 37°. [i] Reference 2.

## Experimental Section

**Ethyl 1-methyl-2-phenylcyclopropene-3-carboxylate** was prepared by an adaptation of the method of D'yakonov, *et al.*[10] **Procedure A.**—Freshly prepared, undistilled ethyl diazoacetate,[13] 15.0 g (0.13 mol), was added dropwise, over 15 min, to 30.0 g of 1-phenylpropyne (0.26 mol) at 115° in the presence of 0.025 g of anhydrous copper sulfate, under a nitrogen atmosphere. The reaction mixture was cooled and then distilled. The forerun, 15 g, was collected at 27–90° (0.4–0.5 mm). A second fraction of 5 g, collected at 90–100° (0.4 mm), was redistilled. A center cut of 3 g was taken at 80–81° (0.3 mm) [lit.[10] bp 86–87° (0.3 mm)]. Analysis of the distillate by gc showed a single component.

**1-Phenyl-2-methylcyclopropene-3-carboxylic acid** was prepared by the hydrolysis of 3.0 g (0.015 mol) of the ester at room temperature using 5.0 g (0.09 mol) of potassium hydroxide in 200 ml of 90% ethanol for 48 hr. **Procedure B.**—The ethanol was evaporated under vacuum, the residue was acidified with excess 0.1 *M* sulfuric acid and extracted with dichloromethane, and the solvent was then vacuum evaporated. The residue was recrystallized three times from 95% ethanol yielding 0.4 g (2% based on ethyl diazoacetate) of white crystals: mp 137.2–137.9° (lit.[10] mp 139°); nmr ($CCl_4$) $\delta$ 7.37 (m, 5, aromatic), 2.34 (s, 4, C–H, $CH_3$), 11.7 (s, 1, COOH); ir (hexachloro-1,3-butadiene mull) 2950 (s, br, 1895, 1689, 1490, 1430, 1370, 1330, 1310, 1285, 1270, 1240, 1105, and 1070 cm$^{-1}$; other ir (Nujol mull) 960, 805, 760, and 680 cm$^{-1}$; uv absorbance ($1.5 \times 10^{-5}$ *M* in absolute ethanol) at 260 m$\mu$ ($\epsilon$ 17,700) with a shoulder at 214 (17,000) on maximum <210.

*Anal.* Calcd for $C_{11}H_{10}O_2$: neut equiv, 174.2. Found: neut equiv, 173.8, 172.9.

**1-(*p*-Chlorophenyl)propyne. Procedure C.**—4-Chloropropiophenone (50.0 g, 0.30 mol), and 40 ml of dry benzene were cooled in an ice bath and with stirring 68.0 g (0.33 mol) of phosphorus pentachloride was added. The mixture was stirred overnight with gradual warming to room temperature. The mixture was again cooled and ice was slowly added until the mixture had been diluted to about 200 ml. The mixture was extracted with dichloromethane. The extracts were washed with water and with dilute aqueous sodium carbonate until the aqueous wash showed no acidity. The organic layer was dried with magnesium sulfate and the solvent was removed under vacuum. The residue was then added, dropwise and with stirring, to a slurry of 56.0 g (0.85 mol) of potassium hydroxide pellets and 70 ml of ethanol at an oil-bath temperature of 150°. After 4 hr the mixture was cooled in ice, diluted with 200 ml of water, and added slowly to 1 l. of 5% sulfuric acid mixed with crushed ice. The mixture was extracted with chloroform; the extracts were dried with magnesium sulfate and distilled. At 54–57° (0.7 mm) 18 g was collected (40%) [lit.[14] bp 125° (25 mm)]: ir 2240 and 2200 cm$^{-1}$ (acetylenic).

**1-(*p*-Chlorophenyl)-2-methylcyclopropene-3-carboxylic Acid.**—Using procedure A, 1-(*p*-chlorophenyl)propyne (18.0 g, 0.12 mol), 0.01 g of anhydrous copper sulfate, and 10.0 g (0.09 mol) of ethyl diazoacetate were allowed to react. Distillation of the reaction mixture gave two fractions: 12.3 g at 55–75° (0.7 mm) and 3.3 g at 80–130° (0.7 mm). The 3.3-g fraction was hydrolyzed according to procedure B. The crude acid thus obtained was recrystallized five times using benzene–heptane. Crystals (0.5 g) were obtained (4%): mp 134.2–134.8°; nmr ($CCl_4$) $\delta$ 7.37 (s, 4, aromatic), 2.32 (s, 4, C–H, $CH_3$), and 11.7 (s, 1, COOH); ir (hexachloro-1,3-butadiene mull) 2950, 1895, 1685, 1485, 1430, 1370, 1330, 1290, 1240, 1110, and 1090 cm$^{-1}$; other ir (Nujol mull) 1000, 930, 830, 810, 750, and 680 cm$^{-1}$; uv absorbance ($1.5 \times 10^{-5}$ *M* in absolute ethanol) at 268 m$\mu$ ($\epsilon$ 23,000) with shoulders at 228 (21,700) and 218 (23,600) on uv maximum <210.

*Anal.* Calcd for $C_{11}H_9O_2Cl$: C, 63.32; H, 4.35; Cl, 16.99; neut equiv, 208.6. Found: C, 63.23; H, 4.27; Cl, 17.14; neut equiv, 208.1, 209.9.

**1-(*p*-Methoxyphenyl)propyne.**—Using procedure C, 10.0 g (0.06 mol) of 1-(*p*-methoxyphenyl)-2-propanone[15] in 20 ml of benzene and 13.8 g (0.07 mol) of phosphorus pentachloride were allowed to react. In this experiment the crude product was extracted with petroleum ether and the wash was with aqueous sodium bicarbonate. The crude residue was added dropwise,

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(13) N. E. Searle, *Org. Syn.*, **36**, 25 (1956).

(14) D. Hamer and W. R. Magee, *J. Chem. Soc.*, 1847 (1964).

(15) Synthesized by a modification of the procedure for the *o*-methoxy isomer: R. V. Heinzelman, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 573.

with stirring, to a heated slurry (bath temperature 115°) of 15 g (0.4 mol) of sodium hydroxide in 30 ml of absolute ethanol. After 18 hr the reaction mixture was cooled by the addition of ice, and just enough water was added to salt out the organic phase which was extracted with petroleum ether. The extracts were dried with magnesium sulfate and distilled. A single fraction of 4.0 g (43%) was collected at 94–95° (3.6 mm) [115–117° (9 mm)[16]]. Gc showed a single component in the distillate. The ir showed absorption at 2280 $\text{cm}^{-1}$ characteristic of an acetylenic bond.

**1-(*p*-Methoxyphenyl)-2-methylcyclopropene-3-carboxylic Acid.**—Using procedure A, 48.8 g (0.33 mol) of 1-(*p*-methoxyphenyl)propyne, 0.032 g of anhydrous copper sulfate, and 18.3 g (0.16 mol) of ethyl diazoacetate were allowed to react. The dropwise addition of ethyl diazoacetate was extended to 1 hr. It was necessary to heat the reaction mixture to about 160° initially to start the evolution of nitrogen. The reaction mixture was cooled and added to 40 g of sodium hydroxide in 300 ml of 80% ethanol; the mixture was stirred overnight at 25°. The ethanol was removed under vacuum and 750 ml of water was added. After four extractions with ether the aqueous layer was acidified with excess 25% sulfuric acid and extracted six times with ether. The ether was evaporated, the residue was dissolved in 75 ml of benzene, and the solution was passed over a column of silica gel. The column was eluted with 750 ml of benzene, which was then evaporated. The residue was crystallized from ether plus pentane at −78° and then recrystallized six times from benzene–heptane, giving 4.0 g (12%) of material, mp 113.8–114.8°. One additional recrystallization from ethanol–ether–pentane and two from 2-butanone–pentane gave mp 116.2–117.4°; nmr ($CCl_4$) $\delta$ 7.14 (two d, 4, aromatic), 3.80 (s, 3, $OCH_3$), 2.33 and 2.31 (two s, 4, C–H, $CH_3$), and 12.0 (s, 1, $CO_2H$); ir (hexachloro-1,3-butadiene mull) 2950, 1895, 1680, 1500, 1460, 1430, 1370, 1330, 1235, 1100, and 1020 $\text{cm}^{-1}$; other ir (Nujol mull) 1605, 1570, 1175, 1165, 995, 950, 825, 790, 735, 690, and 635 $\text{cm}^{-1}$; uv absorbance ($1.5 \times 10^{-5}$ *M* in absolute ethanol) at 269 m$\mu$ ($\epsilon$ 27,000), shoulder at 228 (28,300), maximum at <210.

*Anal.* Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; neut equiv, 204.2. Found: C, 70.58; H, 6.05; neut equiv, 203.3, 204.0.

***m*-Chlorophenylacetylene.**—Following procedure C, 111.6 g (0.72 mol) of *m*-chloroacetophenone in 100 ml of dry benzene was treated with 168.0 g (0.81 mol) of phosphorus pentachloride. The extraction was with petroleum ether and the wash was with aqueous sodium bicarbonate. The crude reaction mixture was added to 160.0 g (4.0 mol) of sodium hydroxide in 400 ml of absolute ethanol at 110° with 10-hr contact. At 53–65° (5.5 mm), 32.7 g (33%) of distillate was obtained [bp 64–65° (12 mm)[17]]: ir 3300 $\text{cm}^{-1}$ (acetylenic C–H). Analysis by gc showed less than about 2% impurity.

**1-(*m*-Chlorophenyl)propyne.**—About 500 ml of liquid ammonia was condensed in a flask protected by a drying tube. With stirring, 1 g of sodium was added. After it dissolved, 0.2 g of ferric nitrate was added, and stirring was continued for 5 min. Additional sodium was added, in pieces of about 0.5 g, until a total of 6.9 g (0.30 g-atom) had been added. When the formation of $NaNH_2$ appeared to be complete, as evidenced by a change in color to gray, 32.7 g (0.24 mol) of *m*-chlorophenylacetylene was added dropwise over 15 min with an additional 15-min stirring. Next, 111 g (0.78 mol) of methyl iodide was added dropwise over 30 min; the mixture was stirred an additional 30 min. Additional ammonia was added, as necessary, to maintain volume. The ammonia was allowed to evaporate, water was added, and the resulting mixture was extracted with dichloromethane. The extracts were dried with magnesium sulfate and distilled. A single fraction of 32.3 g (90%) was collected at 74–76° (3.7 mm) [lit.[14] bp 118° (25 mm)]: ir 2260 and 2250 $\text{cm}^{-1}$ (acetylenic).

**(*m*-Chlorophenyl)-2-methylcyclopropene-3-carboxylic Acid.**—1-(*m*-Chlorophenyl)propyne (13.5 g, 0.09 mol), 0.009 g of anhydrous copper sulfate, and 5.4 g (0.005 mol) of ethyl diazoacetate were allowed to react by procedure A. The addition of ethyl diazoacetate was extended to 1 hr, and the reaction mixture was heated to 150° initially to start the evolution of nitrogen. The product was hydrolyzed, using 25 g (0.62 mol) of sodium hydroxide in 500 ml of 80% ethanol. Work-up and recrystallization of the solid residue four times from benzene–heptane yielded 1.3 g (14%) of product: mp 155.2–156.0°; nmr ($CDCl_3$) $\delta$ 7.37 (m, 4, aromatic), 2.37 (s, 1, C–H), 2.28 (s, 3, $CH_3$), and 10.7 (s, 3, $CH_3$); ir (hexachloro-1,3-butadiene mull) 2900, 1960, 1900, 1800, 1680, 1480, 1470, 1415, 1370, 1330, 1310, 1285, 1235, 1115, 1070, 1020, and 1010 $\text{cm}^{-1}$; other ir (Nujol mull) 1595, 1565, 975, 945, 900, 880, 805, 785, 715, 680, and 660 $\text{cm}^{-1}$; uv absorbance ($1.5 \times 10^{-5}$ *M* in absolute ethanol) at 264 m$\mu$ ($\epsilon$ 15,000) with shoulders at 222 (13,000) and 216 (15,700) on maximum at <210.

*Anal.* Calcd for $C_{11}H_9O_2Cl$: C, 63.32; H, 4.35; Cl, 16.99; neut equiv, 208.6. Found: C, 63.71; H, 4.39; Cl, 16.98; neut equiv, 208.4 and 207.4.

**1-(*p*-Fluorophenyl)propyne.**—By procedure C, 75.0 g (0.49 mol) of *p*-fluoropropiophenone in 60 ml of benzene was treated with 113.0 g (0.54 mol) of phosphorus pentachloride. The crude product was washed with aqueous sodium bicarbonate and then was added to a slurry of 70 g (1.75 mol) of sodium hydroxide in 125 ml of absolute ethanol at 115°. After 3 hr gc showed a single main new peak, contaminated with *p*-fluoropropiophenone and trace amounts of other components. The reaction mixture was cooled, diluted with water, neutralized with dilute sulfuric acid, and extracted with dichloromethane. The extracts were dried over $MgSO_4$ and distilled. At 58–61° (2 mm) 62.3 g were collected, ir 1630 $\text{cm}^{-1}$, suggesting a propene.

A 56-g portion of the above distillate was added, dropwise and with stirring, to a mixture of 95 g (1.16 mol) of sodium isopropoxide in 300 ml of dimethyl sulfoxide. After 18 hr at 25° the mixture was diluted with about 6 l. of water. The aqueous mixture was extracted with ether; the extracts were dried with magnesium sulfate and distilled. A single distillation fraction weighing 25.0 g (38%) was collected at 99–104° (49–59 mm): ir 2250 and 2200 $\text{cm}^{-1}$ (acetylenic). Gc showed a single component with only trace impurities.

*Anal.* Calcd for $C_9H_7F$ (doubly redistilled sample): C, 80.58; H, 5.26. Found: C, 80.68; H, 5.35.

**1-(*p*-Fluorophenyl)-2-methylcyclopropene-3-carboxylic Acid.**—1-(*p*-Fluorophenyl)propyne (25.0 g, 0.19 mol), 0.019 g of anhydrous copper sulfate, and 10.6 g (0.09 mol) of ethyl diazoacetate were allowed to react by procedure A. The addition of ethyl diazoacetate was extended to 1.5 hr; initially the reaction mixture was heated to about 150° but the temperature was quickly lowered to 100–105° when the evolution of nitrogen began. The mixture was hydrolyzed using 40 g of sodium hydroxide in 500 ml of 85% ethanol. Work-up gave a heavy oil which was passed through silica gel using benzene as the eluent. Vacuum evaporation of benzene left an oil which was crystallized, and recrystallized four times from benzene–heptane to give 0.6 g (3%) of white crystals: mp 112.0–112.5°; nmr ($CCl_4$) $\delta$ 7.21 (doublet of triplets, 4, aromatic), 2.31 (s, 4, C–H and $CH_3$), 11.2 (s, 1, COOH); ir (hexachloro-1,3-butadiene mull) 2050, 1890, 1690, 1500, 1430, 1410, 1365, 1325, 1305, 1275, 1240, 1220, 1155, 1125, 1090, 1025, and 1005 $\text{cm}^{-1}$; other ir (Nujol mull) 1605, 965, 945, 840, 815, 805, 720, 690, 670, 630, and 620 $\text{cm}^{-1}$; uv absorbance ($1.5 \times 10^{-5}$ *M* in absolute ethanol) 260 m$\mu$ ($\epsilon$ 16,300) with shoulder at 215 (12,700) on maximum <210.

*Anal.* Calcd for $C_{11}H_9O_2F$: C, 68.74; H, 4.72; F, 9.88; neut equiv, 192.2. Found: C, 68.59; H, 4.81; F, 9.86; neut equiv, 189.3, 190.6.

**1-(*m*-Methylphenyl)-2-propanone.**[15]—*m*-Tolualdehyde (150 g, 1.25 mol) was allowed to react with 113 g (1.50 mol) of nitroethane in the presence of 20 ml of *n*-butylamine in 200 ml of toluene. Reduction was effected with 625 ml of water, 250 g of iron powder, 9 g of $FeCl_3 \cdot 6H_2O$, and 450 ml of concentrated hydrochloric acid. Work-up afforded 100 g (59%) of distillate: bp 83–90° (4.4 mm); gc <5% impurities; nmr $\delta$ 1.98 (s, 3, $COCH_3$), 2.28 (s, 3, $ArCH_3$), 3.47 (s, 2, $CH_2$), and 7.2 (m, 4, aromatic); ir (neat) 3020, 2920, 2870, 2730, 1720, 1610, 1590, 1490, 1460, 1425, 1380, 1360, 1325, 1290, 1245, 1225, 1155, 1140, 1090, 1025, 905, 880, 770, 735, 695, 680, and 650 $\text{cm}^{-1}$. An analytical sample was purified by preparative gc.

*Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.21; H, 8.23.

**1-(*m*-Methylphenyl)propyne.**—Following procedure C, 20.0 g (0.14 mol) of 1-(*m*-methylphenyl)-2-propanone in 40 ml of benzene was treated with 31.0 g (0.15 mol) of phosphorus pentachloride. The crude mixture was taken up in ether and washed with aqueous sodium bicarbonate and dried. The ether was evaporated and the residue was added to mixture of 44 g (0.54 mol) of sodium isopropoxide in 150 ml of dimethyl sulfoxide. After 30 min the product was isolated by the procedure previously described for 1-(*p*-fluorophenyl)propyne. Distillation gave a

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single fraction at 96–101° (20 mm) weighing 13.6 g (77%): ir 2230 $cm^{-1}$ (acetylenic). An analytical sample was purified by preparative gc.

*Anal.* Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.70.

**1-(*m*-Methylphenyl)-2-methylcyclopropene-3-carboxylic Acid.**—Using procedure A, 16.4 g (0.14 mol) of ethyl diazoacetate was added to 37.5 g (0.29 mol) of 1-(*m*-methylphenyl)propyne in the presence of 0.029 g of anhydrous $CuSO_4$ over 2 hr. The reaction was started at 135° and then quickly lowered to 110–115°. The reaction mixture was hydrolyzed, using 40 g of NaOH in 500 ml of 90% ethanol. Work-up gave a heavy oil which was dissolved in 100 ml of benzene and passed through silica gel using benzene as the eluent. Vacuum evaporation left a heavy oil which was crystallized from ether–pentane at −78°. Recrystallization twice from benzene–heptane and twice from acetone–heptane gave 0.7 g of white crystals (3%): mp 125.6–126.4°; nmr ($CCl_4$) $\delta$ 7.35 (m, 4, aromatic), 2.32, 2.36, 2.38 (3 s, 7, C–H, $ArCH_3$, cyclopropene $CH_3$); ir (hexachloro-1,3-butadiene mull) 2950, 1895, 1845, 1675, 1480, 1415, 1370, 1125, 1110, 1285, 1270, 1240, 1105, and 1025 $cm^{-1}$; other ir (Nujol mull) 1180, 950, 900, 880, 850, 780, 725, and 680 $cm^{-1}$; uv absorbance ($1.5 \times 10^{-5}$ *M* in absolute ethanol at 261 m$\mu$ ($\epsilon$ 19,000) with shoulders at 227 (21,000) and 219 (25,300) on uv maximum <210.

*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; neut equiv, 188.2. Found: C, 76.80; H, 6.41; neut equiv, 187.3, 186.8.

**Instrumentation.**—p$K_a$ determinations in 50.0% (v/v) aqueous ethanol were carried out as previously reported.[3] Proton nmr were run at 100 MHz.

**Registry No.**—1-Phenyl-2-methylcyclopropene-3-carboxylic acid, 18826-56-7; 1-(*p*-chlorophenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-55-6; 1-(*p*-methoxyphenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-57-8; 1-(*m*-chlorophenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-58-9; 1-(*p*-fluorophenyl)propyne, 18826-59-0; 1-(*p*-fluorophenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-60-3; 1-(*m*-methylphenyl)-2-propanone, 18826-61-4; 1-(*m*-methylphenyl)propyne, 18826-62-5; 1-(*m*-methylphenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-63-6.

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# Photocycloaddition Reactions of Some 3-Substituted Cyclohexenones[1]

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The photochemical cyloaddition reactions of 3-methyl-, 3-phenyl-, and 3-acetoxycyclohexenones with the substrates cyclopentene, isobutene, 1,1-dimethoxyethylene, ethoxyethylene, *cis*- and *trans*-dichloroethylene, and acrylonitrile have been studied. These enones add to the various substrates bearing electron-donating substituents to give, sometimes accompanied by other products, bicyclo[4.2.0]octan-2-ones in which the orientation of the substituents is, in most cases, that predicted by the Corey rule of the oriented $\pi$ complex. Irradiation of 3-acetoxy- and 3-methylcyclohexenone with isobutylene yielded, in addition, significant quantities of the 8,8-dimethylbicyclo[4.2.0]octan-2-one derivatives, indicating that steric factors can sometimes outweight mild electronic demands in a substrate. The relative rates of addition of the various enones to each substrate were determined. These vary over one order of magnitude and are suggestive of processes involving diradical-like intermediates with a low degree of charge separation.

The photochemical cycloaddition of $\alpha,\beta$ unsaturated ketones to carbon–carbon double bonds has been the subject of much recent investigation.[2] Cyclic enones add to cyclic and acylic[3] olefins, alkynes,[3b] allenes,[3b,4] and to themselves to give cyclobutane derivatives. The cycloaddition reaction has been applied fruitfully to the preparation of key intermediates in total syntheses of natural products[5–7] and unusual cagelike molecules.[8–10]

A significant amount of evidence regarding the mechanism of the reaction has been gathered. Since the cycloaddition of enones proceeds when Pyrex-filtered light (> 2900 Å) is used, an initial n → $\pi$ excited singlet state must be formed. This initial excited state could give rise to either an n → $\pi^*$ triplet or $\pi$ → $\pi^*$ triplet. It is now generally agreed, on the basis of experiments involving sensitizers and quenchers and on studies of emission spectra, that the reactive excited states in dimerizations and crossed cycloadditions are n → $\pi^*$ triplets.[11–14] DeMayo has concluded that one or more triplet states other than that of lowest energy ($T_1$) are involved in the photocycloadditions of cyclopentenone.[14] Very recently Chapman has presented evidence that two different triplets are involved in photocycloadditions of isophorone and 4,4-dimethylcyclohexenone.[15] A considerable amount of the evidence so far available on the details of the mechanism of the cycloaddition process itself has been provided by Corey and coworkers, who studied the orientation and stereochemistry of the addition of cyclohexenone to several olefins.[4] Among

[1] Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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