Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Styrene. Compound **1** (9.3 g, 0.10 mole), freshly distilled styrene (10.4 g, 0.10 mole), and a trace of hydroquinone were heated at 150 ± 5° for 4 hr. Fractionation of the product through a semimicro, spinning-band column gave 9.3 g (48%) of 2-phenyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**32**) as a colorless oil, bp 106–109° (1 mm), $n^{25}\text{D}$ 1.5350–1.5360. Infrared and ultraviolet spectra of the product showed a small amount of hydroquinone. The product displayed infrared absorption (neat) at 2230, 1380, 745, and 695 cm^{-1}, and nmr absorption (CCl_4) at τ 2.58 (4.9 H, narrow multiplet), 6.38 (0.9 H, multiplet), 7.5–8.5 (6.6 H, multiplets), and 8.81 (3.0 H, singlet). *Anal.*[18] Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 84.33; H, 7.52; N, 7.38.

2-Phenyl-4-methylbicyclo[2.1.1]hexanecarboxylic Acid (34). A mixture of 2-phenyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**32**) (3.8 g, 19.3 mmoles), 25 ml of alcohol, and 25 ml of 6 *N* NaOH was heated at reflux for 72 hr. The alcohol was evaporated. The aqueous phase was extracted with ether, acidified, and extracted with ether. The second ether extract was dried over $MgSO_4$, filtered, and concentrated. The residue was recrystallized from hexane, giving 2.45 g (57%) of **34** as colorless needles, mp 103–105°. The acid displayed nmr absorption ($CDCl_3$) at τ −2.01 (1.02 H, singlet), 2.71 (5.03 H, singlet), 6.29 (0.90 H, multiplet), 7.6–8.5 (5.88 H, multiplets), and 8.81 (3.00 H, singlet). *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.73, 77.64; H, 7.36, 7.34.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and *p*-Methoxystyrene. Compound **1** (9.3 g, 0.10 mole), *p*-methoxystyrene (13.4 g, 0.10 mole), and a trace of hydroquinone were heated at 150 ± 5° for 20 hr. Distillation of the product gave 10.8 g (48%) of 2-(*p*-methoxyphenyl)-4-methylbicyclo[2.1.1]hexanecarbonitrile (**33**) as a viscous oil, bp (superheating) 125–135° (1 mm), $n^{25}\text{D}$ 1.5387. The product had infrared absorption (neat) at 2230, 1380, and 832 cm^{-1}, and nmr absorption (CCl_4) at τ 2.83 (4.0 H, AB pattern), 6.23 (4.0 H, large singlet over small multiplet), 7.5–8.5 (7.0 H, multiplet), and 8.79 (3.0 H, singlet). *Anal.*[18] Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.54, 79.57; H, 7.61, 7.62; N, 7.73, 7.88.

2-(*p*-Methoxyphenyl)-4-methylbicyclo[2.1.1]hexanecarboxylic Acid (35). A mixture of 2-(*p*-methoxyphenyl)-4-methylbicyclo[2.1.1]hexanecarbonitrile (**33**) (4.54 g, 20 mmoles), 25 ml of alcohol, and 25 ml of 6 *N* NaOH was heated at reflux for 9 days. Work-up as described before for **34** gave 2.84 g (60%) of **35** as pale yellow microcrystals, mp 106–108°. The product had nmr absorption ($CDCl_3$) at τ −2.00 (0.99 H, singlet), 2.94 (4.00 H, AB pattern), 6.25 (4.02 H, large singlet over a multiplet), 7.6–8.5 (6.00 H, multiplets), and 8.79 (3.10 H, singlet). *Anal.* Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.13, 73.20; H, 7.37, 7.40.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and 1-(N,N-Dimethylamino)cyclopentene. **1** (9.3 g, 0.10 mole) and 1-(N,N-dimethylamino)cyclopentene (11.1 g, 0.10 mole) were heated starting at 110° to finally 170° over 5 hr. Distillation gave 13.3 g of product, bp 85–120° (2 mm). This crude product was added to a solution of picric acid (20 g) in alcohol (400 ml). The precipitate was filtered, recrystallized from alcohol, filtered, rinsed with alcohol and ether, and air dried, giving material, mp 199–200°. To the picrate and water (100 ml) were added ether (100 ml) and 6 *N* NaOH (20 ml). The aqueous layer was extracted with ether, and the combined ether phases were extracted with 0.6 *N* NaOH, dried over $MgSO_4$, filtered, and concentrated. The residue was distilled twice through a short-path still (1 mm) to give 7.21 g of colorless oil, $n^{25}\text{D}$ 1.4968, bp 285° (micro). The product was characterized as 2-(N,N-dimethylamino)-2,3-trimethylene-4-methylbicyclo[2.1.1]hexanecarbonitrile (**36**) by infrared absorption (neat) at 2230 and 1380 cm^{-1}, and nmr absorption (CCl_4) at τ 7.57 (5.9 H, singlet), 7.1–8.5 (12.0 H, multiplets), and 8.87 (3.0 H, singlet). *Anal.* Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.22, 76.14; H, 9.93, 9.96; N, 13.32, 13.29.

Thermolysis of *exo*- and *endo*-2,3-Dimethylbicyclo[1.1.0]butanecarbonitrile (46). Mixtures of *exo*- and *endo*-2,3-dimethylbicyclo[1.1.0]butanecarbonitrile (**46**) were dissolved in nitrobenzene, sealed in nmr tubes under vacuum, analyzed for initial concentrations by nmr, heated at 160 ± 1° in a constant temperature oil bath, quenched in ice periodically, and analyzed directly by nmr. The concentrations of both isomers diminished throughout. The broad nmr absorption of the products did not include much in the vinyl region.

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[18] The presence of thermal dimers of 3-methylbicyclo[1.1.0]butanecarbonitrile, which are not separated by this distillation, cause high nitrogen and low carbon values.

Methylcyclopropenone and Related Compounds[1]

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.
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Abstract: Reaction of lithium trichloromethide at −100° with various acetylenes produces substituted cyclopropenones after hydrolysis. Using this procedure, methyl-, propyl-, dimethyl-, and (previously known) dipropylcyclopropenone have been prepared in moderate yields; attempts to produce cyclopropenone from the reaction with acetylene failed. A facile base-catalyzed exchange of the ring hydrogen in propylcyclopropenone has been observed; the acidity of this proton can be related in part to hybridization effects, as reflected in the nmr chemical shift and C^{13} coupling constant. The basicities of methyl- and dimethylcyclopropenones were measured, H_0 at half-protonation being −5.0 and −1.5, respectively. Methylcyclopropenone is slowly cleaved by sodium hydroxide to a mixture of methacrylic and crotonic acids. Pyrolysis of methylcyclopropenone at 200° affords propyne and carbon monoxide, but heating at 100° produces a dimeric lactone.

In the years since the synthesis of diphenylcyclopropenone[2] a number of other substituted cyclopropenones have been prepared.[3] However, to date neither the parent compound nor a monosubstituted derivative has been reported, although such compounds would be of considerable interest. In our laboratory a number of attempts to synthesize such compounds

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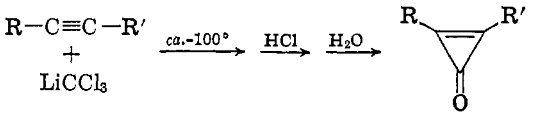
[1] Support of this work by the Petroleum Research Fund and the National Science Foundation is gratefully acknowledged.

[2] (a) R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); (b) M. E. Vol'pin, Y. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR*, 506 (1959).

[3] (a) R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960); (b) R. Breslow, J. Posner, and A. Krebs, *ibid.*, **85**, 234 (1963); (c) R. Breslow, T. Eicher, A. Krebs, R. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965); (d) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965); (e) D. Farnum and P. Thurston, *ibid.*, **86**, 4206 (1964); (f) R. R. Kostikov and I. A. D'yakonov, *Zh. Obshch. Khim.*, **34**, 3845 (1964).

from HBr eliminations (the "modified Favorskii reaction" which successfully produces disubstituted cyclopropenones[3b–d]) have failed. The other general approach to cyclopropenones, dihalocarbene addition to acetylenes,[2b,3a,d] is experimentally unattractive in its usual forms if the acetylene is a gas. However, the recently reported observation by Miller and Whalen[4] that lithium trichloromethide can be prepared at −115° and that it reacts as a dichlorocarbene donor at −100° was of interest, since at such temperatures all acetylenes are liquid or solid, and concentrated solutions of acetylene itself are easily prepared.

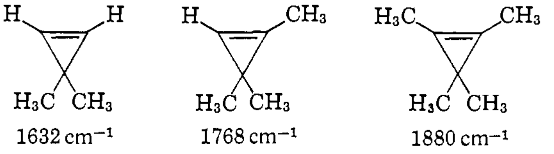
Syntheses of Cyclopropenones. Reaction of lithium trichloromethide with 4-octyne at −95°, followed by low-temperature acidification and then a normal aqueous work-up, caused complete reaction of the lithium salt (addition of cyclohexene before quenching yielded no detectable dichloronorcarane) and formation of a 19% yield of di-*n*-propylcyclopropenone (Ia), identical with an authentic sample.[3a] Similar reactions with 1-pentyne, propyne, and 2-butyne afforded *n*-propylcyclopropenone (Ib), methylcyclopropenone (Ic), and dimethylcyclopropenone (Id). These compounds were fully characterized by analytical and spectroscopic methods. Several unsuccessful attempts were made to synthesize unsubstituted cyclopropenone from acetylene by the same procedure. The desired ketone could not be detected in the infrared spectrum of the methylene chloride extract from aqueous work-up (nor isolated by distillation of the extract). On the chance that the ketone might be so water soluble as to resist extraction, one reaction mixture was worked up with D_2O. Examination of the heavy water solution in the infrared showed no bands in the cyclopropenone region; the nmr spectrum showed no protons in the expected (δ 8.6) region for cyclopropenone ring protons. Control experiments showed that acetylene reacts with lithium trichloromethide, since subsequent addition of cyclohexene yields only small amounts of dichloronorcarane (after treatment with fourfold excess of acetylene, only a 3.5% yield of dichloronorcarane is produced under conditions in which 35% is formed in the control). However, the yield of chloroform on quenching the acetylene reaction was almost as high as that in the control, suggesting that proton transfer occurs between acetylene and the chloroform anion.

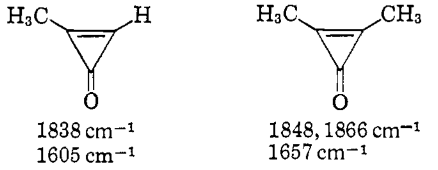


Ia, R = R′ = n-C_3H_7
b, R = n-C_3H_7; R′ = H
c, R = CH_3; R′ = H
d, R = R′ = CH_3

Physical Properties. The properties of the new cyclopropenones were more or less as expected from previous experience. Thus the high polarity of these ketones is reflected in quite high boiling points; methylcyclopropenone has bp 57° at 2 mm, while 2-butanone has bp 79.6° at 760 mm.

All the compounds show in the infrared the two characteristic bands in the 1800–1870- and 1600–1660-cm^{-1} regions which have been observed previously. Krebs[5] has assigned the lower energy transition to the carbonyl stretch on the basis of solvent shifts, but O^{18} substitution in some cyclopropenones affects the high-energy transition most strongly[6] and on this basis the assignment is reversed. Most likely the two modes (carbonyl stretch and olefin stretch) are so strongly coupled that the two infrared bands cannot be uniquely assigned to them. Since the "double bond stretching vibration" of cyclopropenes is strongly affected by substitution,[7] a comparison of methyl- and dimethylcyclopropenone might indicate which is the "cyclopropene" band. Both bands of the cyclopropenone are shifted on methylation, the low-energy one somewhat more. Thus the most reasonable conclusion is again that simple pure assignments cannot be made.





The nmr spectra show some interesting features. The propyl nmr spectra of Ia and Ib show that the cyclopropenone ring is more deshielding than is a cyclopropene, but less than a cyclopropenyl cation ring, as has been discussed previously for Ia.[3d] The shifts of the methyls in Ic and Id confirm this. In addition, both Ib and Ic have their signal for the ring proton at very low field, δ 8.68 and 8.66, respectively. These shifts should be compared with δ 6.66 for the proton of 1,1,2-trimethylcyclopropene[7] and δ 10.42 for that of dipropylcyclopropenyl cation.[8] The shift in the cyclopropenones may in part reflect some positive charge delocalization, and a small ring current,[8] but magnetic anisotropy of the carbonyl group is also a major factor. Thus the observed chemical shifts cannot safely be used for a simple interpolation to the amount of "cyclopropenyl cation" character in the ketones. The C^{13}–H coupling constant in methylcyclopropenone (213 cps) is of the same order of magnitude as the 218 cps of 1,1,2-trimethylcyclopropene[7] and the 228 cps of diethylcyclopropenyl cation.[9] All of them reflect a large s contribution to the carbon hybrid orbital.

Reactions. The basicities of some cyclopropenones have been determined previously.[3c,d] The availability of methyl- and dimethylcyclopropenone present further opportunity to evaluate the effect of alkyl groups on this basicity. In principle this can be done by measuring the nmr chemical shift of the methyls of Ic and Id in solutions of various acidity as was done for Ia,[3d] since protonation of the ketones shifts the methyls to lower field. The results of such a measurement, rela-

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[4] W. T. Miller, Jr., and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964).

[5] A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

[6] A. Krebs, private communication.

[7] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99, 3796 (1963).

[8] R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

[9] G. L. Closs, private communication.

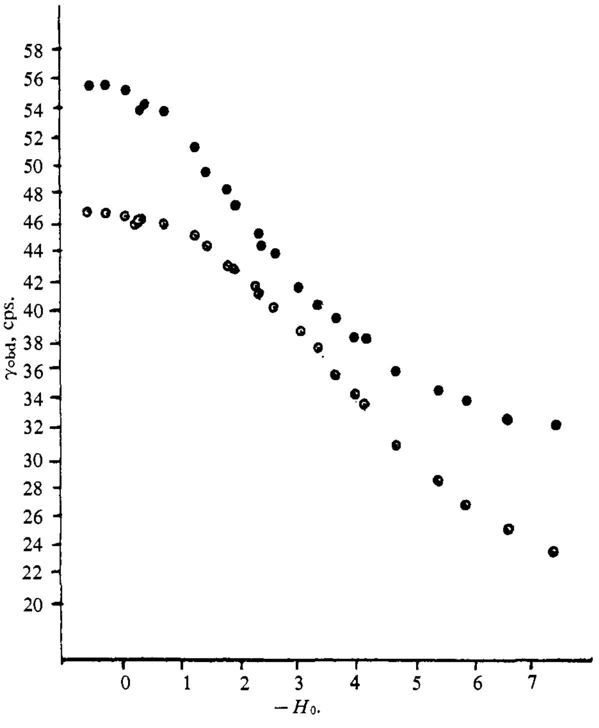

Figure 1. Chemical shift of: ⊙, methylcyclopropenone (Ic); and ●, dimethylcyclopropenone (Id) *vs.* H_0 (*cf.* Table I).

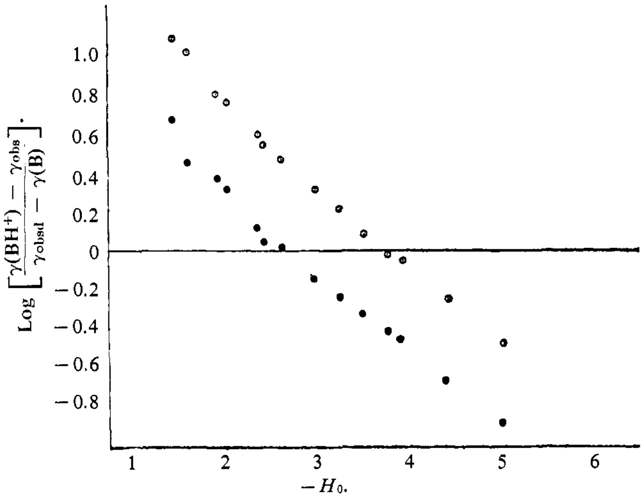

Figure 2. Standard logarithmic plot of the data in Figure 1 (and Table I) for Ic (⊙) and Id (●). The ordinate is the log of the ratio: (chemical shift of protonated ketone minus the actual shift in an acid solution)/(actual shift minus the chemical shift of free ketone). At half-protonation this term should be zero.

tive to internal tetramethylammonium chloride, are shown in Figure 1. It is apparent that the relative chemical shifts are changing over a wide range of H_0, so wide that simple protonation of the ketones cannot alone be responsible for the nmr shifts. Obviously the methyl shifts are also being affected by the change in medium, and this change is not reflected to the same extent in the signal of the internal tetramethylammonium standard.[10] Figure 2 is a standard logarithmic plot of these data. From these plots half-protonation occurs at H_0 of −2.3 for dimethylcyclopropenone (Id) and −3.5 for methylcyclopropenone (Ic). However, such a treatment ignores the clear curvature of the lines in Figure 2, which is probably due to the fact that the relative chemical shift keeps changing in acids of increasing strength even after the ketones are completely protonated. Accordingly we examined the possibility of using each ketone as an internal standard for the other. Assuming that the basicities of Ic and Id are rather different, one would expect the methyl signal of Id to move down relative to that of Ic as Id becomes protonated, and the trend should reverse as the less basic Ic then protonates as well. Presumably each protonated ketone would be subject to more or less the same nmr solvent effects in strong acid, so the tailing of Figure 1 should not be a problem with this method. The results of this comparison are shown in Figure 3; a standard logarithmic plot of the data is presented in Figure 4.[11] The experimentally derived equations of Figure 4, assuming that the relative nmr changes observed do correspond to protonation, are

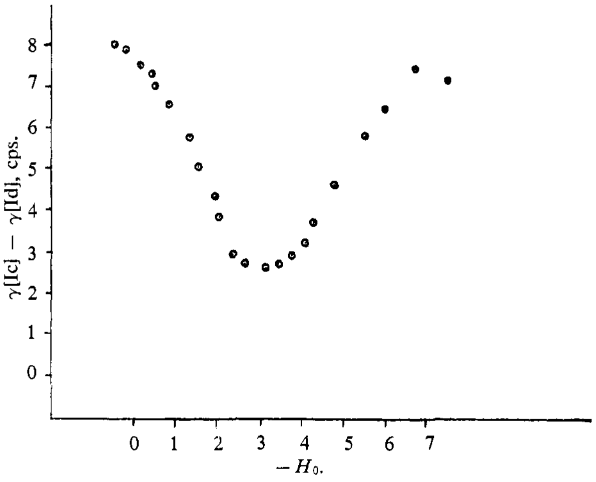

Figure 3. Difference in chemical shift between Ic and Id as a function of acidity (*cf.* Table I).

$$(-1.22 \pm 0.05)H_0 = (6.12 \pm 0.23) - \log \frac{[\text{Ic}]}{[\text{IcH}^+]}$$

and

$$(-1.64 \pm 0.05)H_0 = (2.48 \pm 0.08) - \log \frac{[\text{Id}]}{[\text{IdH}^+]}$$

From this it is apparent that the ketones are not behaving as Hammett bases, since the slopes are 1.22 and 1.64 rather than 1.00. The half-protonation points from this treatment are calculated as H_0 = −5.0 for methylcyclopropenone (Ic) and H_0 = −1.5 for dimethylcyclopropenone (Id). These values are rather different from those derived from Figure 2. It is not really clear which, if either, of these treatments is correct, but we prefer the method of Figure 4 since it is more likely to minimize nmr effects extraneous to the protonation of interest.

Hydrogens on cyclopropene double bonds are acidified,[7,12] apparently because of the same increased s

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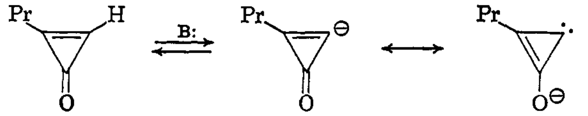
(10) Similar problems with this method are cited by E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(11) Since Ic might begin to protonate before Id was finished, the difference in chemical shift between IdH^+ and Ic was taken as an unknown in this calculation. Best fit came with a difference of 2.0 cps; the experimental minimum shift difference, at H_0 = −3 in Figure 3, is 2.7 cps.

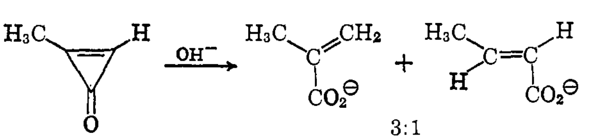
(12) K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957).

character in the carbon orbital which causes a large C^{13}–H coupling constant relative to that in unstrained olefins. The acidity is still much less than that of acetylenic protons,[9] but we felt that cyclopropenones might have some special factors contributing to their acidity. Thus proximity of the anion to the carbonyl dipole is stabilizing, and as well perhaps a carbene resonance form may contribute. These are related to the



sorts of factors which have been invoked to explain the stability of the thiamine anion.[13] These considerations are borne out by the finding that propylcyclopropenone (Ib) exchanges its ring proton in D_2O containing 4% sodium bicarbonate with a half-life of 40 min at room temperature; under the same conditions the half-time for exchange of the acetylenic proton of propargyl alcohol is 70 min. Thus by this kinetic criterion the cyclopropenone is even more acidic than an acetylene.

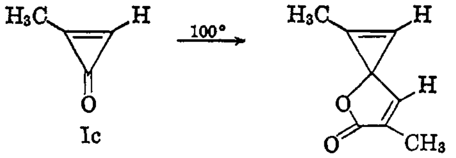
With stronger bases the cyclopropenones may cleave, as noted earlier.[3] Treatment of methylcyclopropenone (Ic) with excess 0.05 *N* aqueous sodium hydroxide results in cleavage to a mixture of methacrylic and crotonic acids, the reaction half-time being approximately 2 days at room temperature. The preferential cleavage to methacrylic acid is as expected from the relative stabilities of the two possible intermediate carbanions.



Ic

3:1

Pyrolysis of methylcyclopropenone (Ic) at 205° produces propyne and carbon monoxide, as expected based on previous experience.[3] However, on heating at 100°, Ic produces a dimer (II). The structure of this dimer is



Ic

II

related to that proposed[3c] for the dimer of diphenylcyclopropenone, but in the present case the structural evidence is stronger. Thus II has a vinyl proton at δ 6.60 which is weakly coupled to the methyl and has a C^{13} coupling constant of only 174 cps as expected for the lactone vinyl proton. On the other hand, a vinyl proton at δ 7.25 has a C^{13} coupling of 232 cps, so it must be a cyclopropene ring proton. The other spectral data are also as expected for II,[14] and the mass spectrum shows the parent (*m*/*e* 136) and principal fragments at *m*/*e* 108 (loss of CO), 96 (loss of propyne), and 68 (methylcyclopropenone). It is interesting that the ultraviolet spectrum of II has λ_{max} 241 mμ, while that of 3,4-dimethylcrotonolactone is only at 213 mμ.[15] Apparently the cyclopropene ring is part of the chromophore.

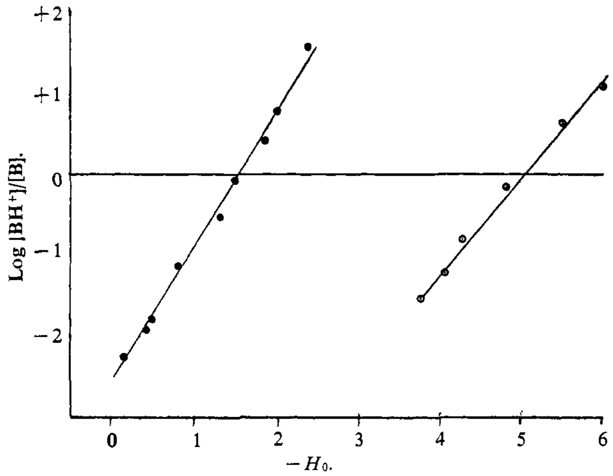


Figure 4. A logarithmic plot of the data in Figure 3. The ordinate is the log of the ratio protonated ketone/unprotonated ketone, derived from the observed difference in chemical shift of Ic and Id in acids of different strength, including weak acid where both are free and strong acid where both are protonated, and the calculated difference in chemical shift between fully protonated Id and free Ic. This value for best fit (2.0 cps) is somewhat different from the observed minimum shift difference of 2.7 cps at H_0 = −3.10. The difference is expected if the titration curves of Ic and Id overlap somewhat.

Experimental Section

Reaction of Lithium Trichloromethide with Acetylenes. Di-*n*-Propylcyclopropenone. Bromotrichloromethane (4.1 g, 0.0206 mole) was added dropwise over a 1-hr period to a mechanically stirred suspension of methyllithium (10 ml of a 1.92 *N* solution in ether prepared from lithium wire and methyl bromide, 0.0192 mole) in anhydrous ether (75 ml) held at −115° (ether-frozen ether slurry).[4] After the addition was complete, 4-octyne (8.0 ml, 0.058 mole) was added dropwise over 25 min to the stirred suspension held at −115°. The reaction mixture was then warmed to −95° (methylene chloride–frozen methylene chloride slurry) for 2 hr. Cyclohexene (4.0 ml, 0.04 mole) was added dropwise over 20 min and the reaction mixture was held at −95° for 1 additional hr. Any remaining base then was destroyed by addition of a solution of anhydrous hydrogen chloride in ether (6 ml of an approximately 4 *N* solution). The reaction mixture was warmed to room temperature and chlorobenzene (0.764 g) was added as an internal standard. The mixture was extracted with water (40 ml) and dried over anhydrous sodium sulfate. Analysis by vpc (10-ft column, 20% Ucon polar on 60–80 mesh firebrick, held at 126°) showed there to be less than 0.5% of 7,7-dichloronorcarane.[16] The ether was removed under reduced pressure and methylene chloride was added (50 ml). The organic phase was extracted with 65% sulfuric acid (three 10-ml portions). The combined acid extracts were diluted with water (60 ml) and extracted with methylene chloride (two 30-ml portions). The combined organic extracts were dried over anhydrous sodium sulfate and distilled yielding 0.52 g of **di-*n*-propylcyclopropenone** (19% yield based on methyllithium), identical with an authentic sample.[3a]

***n*-Propylcyclopropenone.** Bromotrichloromethane (1.75 g, 0.034 mole) was added dropwise over a 1-hr period to a mechanically stirred suspension of methyllithium (19 ml of a 1.68 *N* solution in ether, 0.032 mole) in anhydrous ether (75 ml) held at −115°

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(13) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

(14) The position of the methyl on the lactone double bond is established by the finding that dimethylcyclopropenone (Id) does not dimerize under these conditions, but it gives a mixed dimer with Ic in which the lactone ring is derived from Ic. These data are explainable in terms of steric hindrance to opening a cyclopropenone ring on the alkylated side. On this basis II has the less hindered structure, as shown.

(15) D. E. Ames, R. E. Bowman, and T. F. Grey, *J. Chem. Soc.*, 375 (1954).

(16) Prepared by the procedure of W. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

under an argon atmosphere. After 45 min of additional stirring, 1-pentyne (10 ml, approximately 0.1 mole; distilled from calcium hydride immediately before use) was added dropwise over a 10-min period. The reaction mixture was then warmed to −100° (methylene chloride, approximately 1% ether slurry) and stirred for 2 hr. Anhydrous hydrogen chloride in ether (10 ml of an approximately 4 *N* solution) was added at −100°. The reaction mixture then was warmed to room temperature, extracted with water (50 ml), and dried over anhydrous sodium sulfate, and the volume of the solution was reduced to approximately 10 ml under reduced pressure. Methylene chloride (80 ml) was added and the resulting solution was extracted with 65% sulfuric acid (three 10-ml portions). The combined aqueous extracts were diluted with water (80 ml) and extracted with methylene chloride (two 20-ml portions). The combined organic extracts were dried over anhydrous sodium sulfate and distilled (bp approximately 40°, oil bath temperature, at 2 mm) yielding *ca.* 0.5 g of ***n*-propylcyclopropenone.**

The infrared spectrum (neat film) showed strong absorptions at 1600 (double bond) and 1835 (carbonyl) and a medium absorption at 3030 cm^{-1} (ring hydrogen). The nmr spectrum (carbon tetrachloride solution) showed a triplet at δ 1.06 (methyl, 3.22 protons, J = 7 cps), a sextuplet at 1.78 (β-methylene, 2.06 protons, J = 7 cps), a triplet at 2.72 (α-methylene, 2.02 protons, J = 7 cps), and a singlet at 8.68 (ring proton, 1.00 proton). The mass spectrum showed a parent ion at *m/e* 96, and a major fragment at 68. *Anal.* Calcd for C_6H_8O: C, 74.97; H, 8.39. Found: C, 75.38; H, 8.53.

Methylcyclopropenone. As in the previous experiment bromotrichloromethane (44 ml, 0.44 mole) was added dropwise over 2 hr to a stirred suspension of methyllithium (260 ml of a 1.7 *M* solution in ether, 0.44 mole) in ether (250 ml) held at −115° under an argon atmosphere after which the reaction mixture was stirred for an additional 30 min. Propyne (approximately 50 ml at −78°, approximately 0.8 mole) was then added dropwise over 20 min. After 2 hr of additional stirring at −96°, concentrated hydrochloric acid (50 ml) was added dropwise over 10 min.[17] Water (75 ml) was added to the warmed reaction mixture (room temperature) and the volume of the organic phase was reduced to 70 ml by distillation of ether under reduced pressure keeping the temperature below 50°. The phases were separated and the organic phase was extracted with water (25 ml). The combined aqueous extracts then were extracted continuously with methylene chloride for 24 hr yielding (after distillation of the methylene chloride under reduced pressure) crude methylcyclopropenone (15.9 g of a mixture shown to contain 37%, by weight, of methylcyclopropenone, 20% yield based on methyllithium, 11% of dimethylcyclopropenone, and 50% of methylene chloride by integration of the nmr spectrum). The crude material was distilled (bp 57° at 2 mm) yielding **methylcyclopropenone** contaminated with approximately 5 mole % **dimethylcyclopropenone** (from a small contaminant of 2-butyne in the starting propyne).

The infrared spectrum (carbon tetrachloride solution) showed very strong absorptions at 1838 (carbonyl) and 1605 cm^{-1} (double bond). The nmr spectrum (carbon tetrachloride solution) showed a singlet at δ 2.40 (methyl, 3.0 protons) and a singlet at 8.66 (ring proton, 1.0 proton, $J_{C^{13}H} = 213 \pm 4$ cps) as well as a small singlet at 2.25 (dimethylcyclopropenone). The mass spectrum showed a parent ion at *m/e* 68. *Anal.* Calcd for C_4H_4O: C, 70.58; H, 5.92. Found: C, 70.91; H, 6.14.

Dimethylcyclopropenone. Dimethylcyclopropenone (bp 54–58° at 0.7 mm) was prepared similarly from bromotrichloromethane (43 ml, 0.425 mole), methyllithium (250 ml of a 1.7 *N* solution in ether), ether (250 ml), and 2-butyne (58 g, 1.05 moles; distilled from calcium hydride immediately before use) in 12% yield (based on methyllithium).

The infrared spectrum (carbon tetrachloride solution) showed a very strong doublet at 1848 and 1866 (carbonyl) as well as a very strong absorption at 1657 cm^{-1} (double bond). The nmr spectrum (carbon tetrachloride solution) showed only one singlet at δ 2.25. The mass spectrum showed a parent ion at *m/e* 82. *Anal.* Calcd for C_5H_6O: C, 73.15; H, 7.37. Found: C, 72.97; H, 7.54.

Attempted Preparation of Cyclopropenone. As in the previous experiment, a suspension of lithium trichloromethide in ether at −115° was prepared from methyllithium (35 ml of a 2.04 *N* solution in ether) and bromotrichloromethane (14.1 g, 0.71 mole). Acetylene (*ca.* 0.17 mole; washed three times with concentrated sulfuric acid, potassium hydroxide, and Drierite) then was trap-to-trap distilled (through a trap at −78°) into the reaction flask (held at −115°). The reaction was then stirred at −100° for 2 hr, after which a solution of anhydrous hydrogen chloride in ether was added (15 ml of a *ca.* 2 *N* solution). Water (25 ml) then was added, and the reaction mixture was warmed to room temperature and extracted with water (three 25-ml portions). The combined aqueous extracts were saturated with sodium chloride and continuously extracted with methylene chloride for at least 7 days. No cyclopropenone could be detected by examining the infrared spectrum of the methylene chloride or by further attempts at isolation.

Table I. Chemical Shifts of Methyl- and Dimethylcyclopropenone in Aqueous Sulfuric Acid Solutions ($Me_4N^+Cl^-$ as Internal Standard)

Normality of acid	$-H_0$[18]	Separation of methyl from standard, cps	Separation of dimethyl from standard, cps	Separation of methyl from dimethyl, cps
0.465	−0.50	46.6	55.6	8.0
0.916	−0.20	46.6	55.7	7.9
1.895	0.14	46.3	55.2	7.5
2.461	0.40	46.1	53.8	7.3
2.722	0.48	46.2	54.4	7.0
3.862	0.80	45.7	53.8	6.6
5.80	1.32	45.0	51.4	5.8
6.57	1.51	44.4	49.6	5.1
8.14	1.87	43.2	48.5	4.4
8.80	2.02	43.1	47.5	3.9
10.44	2.39	41.5	45.4	3.0
10.82	2.46	41.1	44.7	3.0
11.72	2.68	40.1	44.1	2.8
13.26	3.10	38.5	41.8	2.7
14.40	3.43	37.2	40.6	2.8
15.51	3.72	35.5	39.7	3.0
16.59	4.02	34.3	38.5	3.3
17.38	4.22	33.5	38.3	3.8
19.53	4.76	30.8	36.2	4.7
21.84	5.45	28.3	34.9	5.9
23.44	5.93	26.8	34.1	6.5
25.80	6.63	25.1	33.0	7.5
28.46	7.42	23.4	32.2	7.2

In a similar experiment, the remaining base was destroyed by addition of a solution of deuterium chloride (prepared from phosphorus pentachloride and deuterium oxide) in ether followed by extraction with deuterium oxide (three 10-ml portions). Each of the aqueous extracts was examined in the infrared (1700–2000 cm^{-1}) and in the nmr (δ 6.6–10.0). No cyclopropenone could be detected.

Base-Catalyzed Exchange of the Cyclopropenone Ring Hydrogen. A. Control Experiment. A solution of *n*-propylcyclopropenone (0.1 ml) in deuterium oxide (0.25 ml) did not exchange hydrogens over a 3-hr period at room temperature as determined by integration of the nmr spectrum. A saturated solution (0.10 ml) of sodium carbonate in deuterium oxide then was added and the nmr spectrum after 11 min showed that the cyclopropenone hydrogen had already exchanged, whereas the methylene hydrogens next to the cyclopropenone ring had not. Water (0.30 ml) was added after 1 hr and integration of the nmr spectrum showed that the ratio of the area of the cyclopropenone singlet to the α-methylene triplet was 0.49:1.94 demonstrating that the exchange was reversible.

B. Rate Determination. A stock solution of sodium bicarbonate (0.103 g) in deuterium oxide (2.280 g) was prepared. A solution of *n*-propylcyclopropenone (0.183 g, 0.00191 mole) in this stock solution (0.642 g) was prepared, and the exchange of the cyclopropenone hydrogen was observed at ambient temperature as a function of time by following the ratio of the cyclopropenone hydrogen to the α-methylene hydrogens in the nmr; under these conditions $t_{1/2} = 40 \pm 10$ min. A solution of propargyl alcohol (0.107 g, 0.00191 mole) in the stock solution (0.644 g) was prepared and the exchange of the acetylenic hydrogen was observed as a function of time by following the ratio of the acetylenic hydrogen to the methylene hydrogens in the nmr; $t_{1/2}$ was 75 ± 10 min.

Basicities of Methyl- and Dimethylcyclopropenone. Various sulfuric acid–water solutions were prepared and standardized by

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[17] The yield suffers unless this neutralization–hydrolysis is initiated at −100°.

titration against standard base.[18] Solutions of approximately 1% of either methylcyclopropenone or dimethylcyclopropenone and 1% of tetramethylammonium chloride in each of the aforementioned solutions were examined in the nmr. The separation between the methyl peak of the cyclopropenone and the center peak of the methyl triplet of tetramethylammonium chloride was measured. A mixture of approximately equal amounts of methylcyclopropenone and dimethylcyclopropenone was prepared and solutions of approximately 1% of this mixture were prepared. The separation between the two methyl peaks was measured. The data are summarized in Table I and presented in Figures 1–4.

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Macro Rings. XXXII. Photochemistry of [2.2]Paracyclophane[1]

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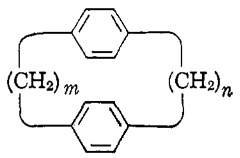
Abstract: Irradiation of [2.2]paracyclophane in methanol in a quartz vessel with a 200-w medium-pressure lamp produced *p*-methyl-*p'*-methoxymethylenebibenzyl (IV), *p*-ethylbibenzyl (V), *p,p'*-dimethylbibenzyl (VI), *p*-methyl-*p'*-β-hydroxyethylbibenzyl (VII), and β-*p*-methylphenylethyl alcohol (VIII). When carried out in methanol-O-*d* one atom of deuterium was observed in the *p*-methyl group of IV. Similar products were observed when the irradiation was carried out in ethyl alcohol. Use of a low-pressure mercury lamp (90% of its emission is at 2537 A) and ethanol as solvent in a quartz vessel produced only *p*-methyl-*p*-ethoxymethylenebibenzyl (IX) as product. Use of the medium-pressure lamp in methanol or ethanol as solvent and a Corex filter produced only *p*-ethylbibenzyl (V). The rate of photolysis of [2.2]paracyclophane to give hydrocarbon V was found to correlate roughly with the relative ease with which these solvents provide hydrogen atoms to radicals (2-propanol $\geq$ ethanol $\geq$ methanol > cyclohexane in rate). Use of acetone as a photosensitizer and solvent produced only hydrocarbon V. Photolysis in ethanol with a Vycor filter produced a 21% yield of hydrocarbon V and a 16% yield of ether IX. In an identical experiment, except that the solution was 0.01 *M* in naphthalene (quencher), only ether IX was produced. These experiments suggest that ethers IV and IX arise by solvolysis of a zwitterion produced from a charge-transfer excited singlet state which is generated when [2.2]paracyclophane absorbs light in the 2500-A region. Hydrocarbon V appears to arise from a low-energy triplet–singlet–triplet intersystem crossover that involves an absorption of light in the 2800–3000-A region, or is produced by triplet–triplet energy transfer from triplet acetone. Hydrocarbon VI and alcohols VII and VIII seem to arise from a biradical produced by cleavage of a high-energy singlet associated with light absorption in the region below 2400 A. These conclusions are in harmony with interpretations of the ultraviolet absorption and the fluorescence and phosphorescence spectra of [2.2]paracyclophane.

Previous studies of the [*m.n*]paracyclophanes (I) have demonstrated the presence of transannular effects in their ultraviolet,[2a] infrared,[2b] and nuclear magnetic resonance[2c] (nmr) spectra, in their π-base strength,[2c,3] in their electrophilic substitution reactions,[4] and in their molecular geometries.[5] These examples of transannular effects suggested that the photochemistry of the smallest homolog, [2.2]paracyclophane, might involve transannular bond formation. This type of phenomenon has been encountered in the dianthracene analog of [2.2]paracyclophane.[6] Specifically it was anticipated that [2.2]paracyclophane might undergo a multiple Diels–Alder reaction under the influence of light to give the polycyclic substance II.



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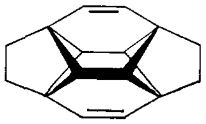

II

Results

Light Sources. Direct irradiation, photosensitization, and quenching techniques were all employed. Most of the irradiations were carried out in an immersion-well apparatus with a Hanovia 200-w medium-pressure mercury lamp as light source, and under an atmosphere of purified nitrogen. The wavelength of absorbed light was varied through use of commercial filter sleeves placed around the light source. Without these filters, the quartz vessel transmitted all of the ultraviolet light. The Vycor filter transmitted light only above 230 mμ, and the Corex filter transmitted light only above 270 mμ. In one experiment (see below), a low-pressure mercury lamp was used, 90% of whose emission is at 253.7 mμ. The very insoluble starting material went into solution as reaction occurred in all experiments.

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