Aryltrichlorocyclopropenes and Arylhydroxycyclopropenones

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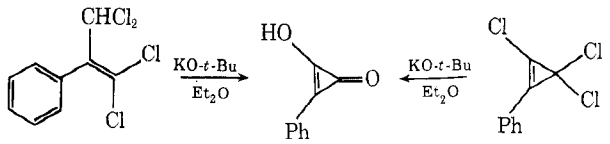
By the reaction of aromatic hydrocarbons with tetrachlorocyclopropene and aluminum chloride, five new aryltrichlorocyclopropenes have been prepared; ^{35}Cl nuclear quadrupole resonance (nqr) data for these compounds are reported. With aluminum chloride these products give aryldichlorocyclopropenium salts. Hydrolysis of the latter in aqueous acetone at 0° provides arylhydroxycyclopropenones in yields of 40–80%, much higher than by previous methods. The pK_a values of the arylhydroxycyclopropenes have been determined; transmission of electronic effects takes place through the cyclopropenone ring.

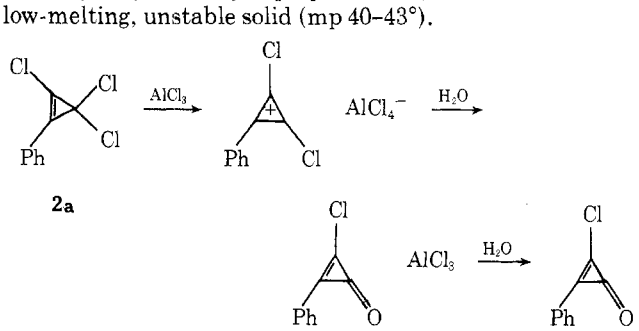
Synthesis of Substituted Phenylhydroxycyclopropenones. Phenylhydroxycyclopropenone (1) was first synthesized by Farnum and Thurston in 1964[1] utilizing the vinyl carbene to cyclopropene rearrangement.[2] The lengthy synthetic sequence necessary, in conjunction with low overall yields (4%), discouraged attempts to prepared other arylhydroxycyclopropenones by this method. The preparation of phenyltrichlorocyclopropene (**2a**) and other aryltrichlorocyclopropenes in high yield (80%) from commercially available tetrachlorocyclopropene[3] afforded an alternative route to these interesting compounds. Successful conversion of **2a** to **1a** was realized in potassium *tert*-butoxide–ether, but again this reaction suffered from low yields (0–12%) and unaccountably varying results.[4,5]



1a **2a**

The unpredictability of this reaction prompted us to investigate other methods of converting **2a** to **1a**. Our attention was specifically directed toward the preparation of phenylchlorocyclopropenone (**3**), the "acid chloride" of **1a**, as a possible precursor to **1a**. Impetus for this work was generated by the successful transformation of tetrachlorocyclopropene to dichlorocyclopropenone by hydrolysis of an aluminum chloride complex.[6]

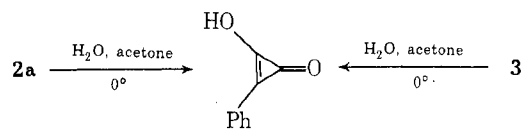
Phenyldichlorocyclopropenium tetrachloroaluminate, prepared by dissolving equal molar amounts of **2a** and aluminum chloride in methylene chloride, was slowly converted upon standing in moist air to a phenylchlorocyclopropenone–aluminum chloride complex with the liberation of hydrogen chloride. When this complex was hydrolyzed, phenylchlorocyclopropenone (**3**) was isolated as a low-melting, unstable solid (mp 40–43°).



3

Upon exposure to moist air, **3** slowly underwent ring opening to phenylchloroacrylic acid. (A similar reaction has been observed for **2a**.)[5] However, when dissolved in an acetone–water mixture at about 0°, **3** was converted to **1a** in about 40% yield. The success of this reaction encouraged us to reinvestigate the solvolysis of **2a** under these same conditions. Phenylhydroxycyclopropenone could be obtained consistently in yields ranging from 50 to 70% by simply treating **2a** with cold aqueous acetone solution.

Interception of the reaction before completion indicated the presence of substantial amounts of **3**. In fact, **3** could probably be prepared on a preparative scale by monitoring the reaction and by more careful temperature control.

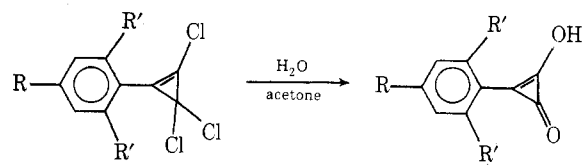


1a

The successful conversion of **2a** to **1a** prompted us to prepare other aryltrichlorocyclopropenes and transform them to arylhydroxycyclopropenones. The method has some limitations, however, because of difficulties in preparing pure aryltrichlorocyclopropenes. Strongly deactivated aromatics such as trifluoromethylbenzene and benzonitrile were unreactive toward trichlorocyclopropenium ion under the Friedel–Crafts conditions. Monosubstituted aromatics such as chlorobenzene, toluene, and anisole reacted smoothly, but generally gave mixtures of isomers which generally could not easily be separated.

In the case where a single isomer was obtained (*tert*-butyl) or where separation of isomers could be achieved (anisyl), the substituent was assigned to the para position of the aromatic ring. This assignment is based on the A_2B_2 type spectrum[7] which was observed for the aromatic protons in the nmr. In addition to the known compounds **2a** and its *p*-fluoro analog **2c**, four new aryltrichlorocyclopropenes were prepared (**2b, 2d–f**), all colorless, crystalline solids readily soluble in organic solvents.

Compounds **2a–f** were converted to the corresponding arylhydroxycyclopropenes (**1a–f**) by the method described, in yields ranging from 40 to 80%. **1b–f** are also new substances, isolated as white powders.



2a,	R = R′ = H	→	**1a**
b,	R = *t*-C_4H_9; R′ = H	→	**1b**
c,	R = F; R′ = H	→	**1c**
d,	R = OCH_3; R′ = H	→	**1d**
e,	R = H; R′ = Br	→	**1e**
f,	R = R′ = CH_3	→	**1f**

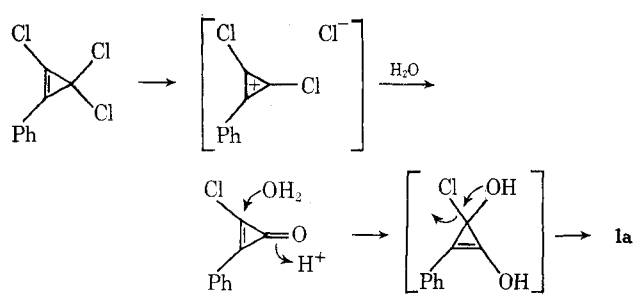
The formation of the arylhydroxycyclopropenones from the corresponding trichlorocyclopropenes presumably occurs initially by way of an intermediate cyclopropenium

Table I
Dissociation Constants and Substituent Effects in Arylhydroxycyclopropenones

pH	Log $\frac{D_{A^-} - D}{D - D_{HA}}$	$-\text{Log}\ \gamma_{A^-}$	pK	pK av	Log (K/K_0)
		Phenylhydroxycyclopropenone (**1a**)			
				2.01 ± 0.03	0.00[a]
1.09	+0.82	0.09	2.00		
1.63	+0.31	0.06	2.00		
1.97	−0.02	0.05	2.00		
2.53	−0.53	0.03	2.03		
		p-tert-Butylphenylhydroxycyclopropenone (**1b**)			
				2.21 ± 0.03	−0.20
1.79	+0.35	0.06	2.20		
1.88	+0.26	0.05	2.19		
2.16	+0.02	0.04	2.22		
2.44	−0.26	0.03	2.21		
3.07	−0.85	0.02	2.24		
		p-Fluorophenylhydroxycyclopropenone (**1c**)			
				2.07 ± 0.04	−0.06
1.77	+0.28	0.05	2.10		
2.00	0	0.05	2.05		
2.30	−0.28	0.04	2.06		
2.58	−0.54	0.03	2.07		
		p-Methoxyphenylhydroxycyclopropenone (**1d**)			
				2.33 ± 0.07	−0.32
1.68	+0.55	0.06	2.29		
2.26	−0.07	0.04	2.23		
2.57	−0.26	0.03	2.34		
2.96	−0.57	0.02	2.41		
		2,6-Dibromophenylhydroxycyclopropenone (**1e**)			
				1.38 ± 0.02	+0.63
0.82	+0.44	0.10	1.36		
1.14	+0.14	0.09	1.37		
1.39	−0.08	0.08	1.39		
1.56	−0.26	0.07	1.37		
1.97	−0.62	0.05	1.40		

[a] By definition.

ion, which is then rapidly converted to the corresponding cyclopropenone. The final hydrolysis probably occurs by way of a Michael-type addition across the α,β-unsaturated carbonyl group of the cyclopropenone, followed by elimination of hydrogen chloride.



Acid dissociation constants of the arylhydroxycyclopropenes were determined spectrophotometrically. The principal bands for the acid and anion forms overlap seriously, having maxima which differ by less than 10 nm. In order to obtain precise results for pK's, special precautions were used, as explained in the Experimental Section. The results are given in Table I. Also tabulated are values for log K/K_0, where K_0 is the dissociation constant for the hydrogen compound **1a**. These are plotted against the appropriate values of σ for the substituents in Figure 1.

Table II
Nqr Absorption Frequencies of Substituted Phenyltrichlorocyclopenones (77°K)

Compd	Absorption frequency, MHz: Vinylic	Allylic
2a	37.71	35.71, 35.17
2b	37.97	36.20, 34.55
2c	37.7	37.7, 37.5
2d	No signal	
2e	37.81	35.91, 35.59
2f	37.61	35.58, 35.22

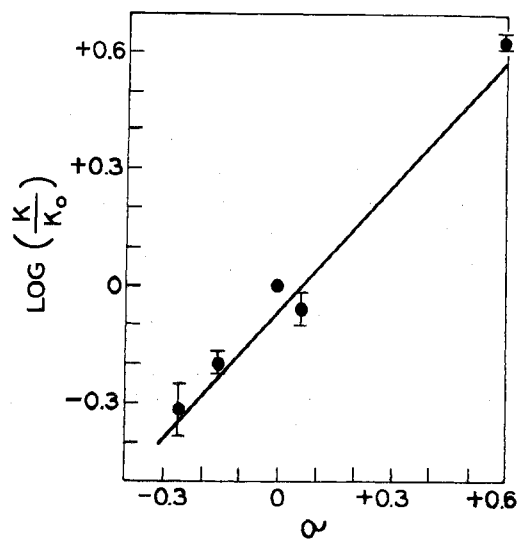


Figure 1. Plot of log K/K_0 *vs.* sum of σ constants for substituents for phenylhydroxycyclopropenes **1a–e**. K_0 is the dissociation constant for the unsubstituted compound, **1a**.

The linearity of the plot indicates that the electronic effects of the substituents contribute to the dissociation of **1a–e** even though these effects are insulated by a vinyl group. The slope of the line, ρ, is approximately equal to 1. The phenylhydroxycyclopropenes can be viewed as vinylogous phenols; ρ for ionization of phenols in water is 2.11.[8] Experiments with substituted cinnamic acids indicate that insertion of two additional sp^2 carbons between the carboxyl group and the substituted aromatic ring attenuates ρ by a factor of 0.47.[9] If this attenuation is taken into account the ρ value of 1 estimated for the phenylhydroxycyclopropenes is quite reasonable.

A linear relationship between σ constants on ^{35}Cl nuclear quadrupole resonance frequencies is found for chlorobenzenes.[10] Since a σ–ρ relationship was found for the dissociation constants of **1a–e**, it seemed worthwhile to search for a similar relationship involving the chlorine nqr frequencies of **2a** and **3e**. All of these compounds showed ^{35}Cl nqr lines at 77°K except *p*-MeOPhC$_3$Cl$_3$, which gives no nqr signals. The frequencies are listed in Table II. The vinylic chlorines in trichlorocyclopropenes have been shown to absorb at higher frequency than the allylic chlorines,[11] and our assignments have been made accordingly.

The results show small differences but no clearly discernible substituent effect appears. Intermolecular interaction in the solid state may influence the ^{35}Cl nqr frequencies, obscuring the small differences expected due to substituent affects. Moreover, the structures of **2a–e** may differ from those of the oxo carbons. The two rings in the oxo carbon anions are probably coplanar, whereas in the trichloro compounds the angles between the rings need not be coplanar and may be determined by crystal packing effects. If the rings are not coplanar, transmission of substituent effects would be reduced, and might vary depending on the interring angle.

Experimental Section

Synthesis. Phenyltrichlorocyclopropene (2a). Benzene (1.4 g, 18 mmol) in dichloromethane (50 ml) was added to a stirred suspension of trichlorocyclopropenium tetrachloroaluminate prepared from $AlCl_3$ (2.64 g, 19.7 mmol) and C_3Cl_4 (3.6 g, 20.2 mmol) in dichloromethane (50 ml) at room temperature. Hydrogen chloride was slowly evolved and a homogeneous solution resulted. Hydrolysis in ice water followed by extraction and drying ($MgSO_4$) gave after vacuum distillation (65–70°, 0.2 mm) phenyltrichlorocyclopropene (3.1 g, 79%): mp 37–39° (recrystallized from pentane, low temperatures); nmr (CCl_4, TMS) τ 2.45 (multiplet); ν_{max} (Nujol) 1810 (w), 1600 (w), 1250 (s), 1150 (s), 1100 (s), and 750 cm^{-1}.

Anal. Calcd for $C_9H_5Cl_3$: C, 49.40; H, 2.27; Cl, 48.47; mol wt, 219.5. Found: C, 49.53, H, 2.34; Cl, 48.42; *m/e* 218.

The following aryltrichlorocyclopropenes were prepared in the manner outlined above, recrystallized in the solvent indicated, and sublimed under high vacuum.

***p-tert*-Butylphenyltrichlorocyclopropene (2b)** (yield 75%) had mp 63–65° (pentane, low temperature); nmr (CCl_4, CH_2Cl_2) τ 2.36 (A_2B_2 type multiplet,[8] 3.92 H), 8.58 (singlet, 9 H); ν_{max} (CH_2Cl_2) 1600 (s), 1150 (s), 1020 (s), 1000 (s), and 830 cm^{-1} (s).

Anal. Calcd for $C_{13}H_{13}Cl_3$: C, 56.65; H, 4.75; Cl, 38.60. Found: C, 56.59; H, 4.77; Cl, 38.46.

***p*-Fluorophenyltrichlorocyclopropene (2c)** (yield 75%) had nmr (CCl_4, CH_2Cl_2) τ 2.63 (multiplet, A_2B_2X, identical with that previously reported); infrared spectrum identical with that of an authentic sample.[3,5]

***p*-Methoxyphenyltrichlorocyclopropene (2d).** Following the same procedure, an 84% yield of a mixture of the ortho (30%) and para (70%) isomers was isolated (mp 70–80°). Fractional recrystallization from hexane (0°) afforded the pure para isomer (15%): mp 85–88°; nmr (CCl_4, CH_2Cl_2) τ 2.6 (A_2B_2 multiplet,[7] 3.9 H), 6.2 (singlet, 3 H); ν_{max} (Nujol) 1600 (s), 1250 (s), 1160 (s), 830 (s), 720 cm^{-1} (s). Mass spectrum calcd for $C_{10}H_7Cl_3O$: mol wt *m/e* 249.53; P + 2, 98; P + 4, 31.9; P + 6, 3.47. Found: *m/e* 248; P + 2, 95; P + 4, 31; P + 6, 3.45.

Mesityltrichlorocyclopropene (2e) (yield 83%) had mp 70–74° (ether, low temperature); nmr (CCl_4, CH_2Cl_2) τ 3.03 (2.1 H, s), 7.35 (6 H, s), 7.61 (3 H, s).

Anal. Calcd for $C_{12}H_{11}Cl_3$: C, 55.10; H, 4.24; Cl, 40.66. Found: C, 55.05; H, 4.46; Cl, 40.52.

2,6-Dibromophenyltrichlorocyclopropene (2f). Trichlorocyclopropenium tetrachloroaluminate was prepared by mixing C_3Cl_4 (8.0 g, 45 mmol) with $AlCl_3$ (6.0 g, 45 mmol). To this salt was added 10.0 g (43 mmol) of *p*-dibromobenzene and the mixture was heated to 80° until hydrogen chloride was no longer evolved. Hydrolysis of the cooled reaction mixture gave 12.8 g (79%) of 2,6-dibromophenyltrichlorocyclopropene, which was recrystallized from hexane (cooled to 0°): mp 95–98°; nmr (CCl_4, CH_2Cl_2) τ 2.14 (multiplet, 1 H), 2.46 (multiplet, 2 H); ν_{max} (Nujol) 1800 (w), 1280 (s), 1240 (s), 1160 (s), 1060 (s), 830 (s), and 730 cm^{-1} (s).

Anal. Calcd for $C_9H_3Cl_3Br_2$: C, 28.65; H, 0.80; Cl, 28.19; Br, 42.36. Found: C, 28.52; H, 0.88; Cl, 27.90; Br, 42.30.

Phenylchlorocyclopropenone (3). An aluminum chloride complex of phenyltrichlorocyclopropenone was prepared by allowing a methylene chloride solution of phenyltrichlorocyclopropenium tetrachloroaluminate prepared from phenyltrichlorocyclopropene (5.0 g, 2.3 mmol) and aluminum chloride (3.0 g, 2.3 mmol) to stand for several days in air. This process could be hastened by slowly stirring the solution of the cyclopropenium ion in methylene chloride in a well-ventilated hood followed by grinding the resulting paste with a mortar and pestle until it was transformed into a powder. This process was repeated if necessary. The reaction was monitored by the appearance of bands in the infrared spectrum at 1865 and 1640 cm^{-1}. The resulting cyclopropenone complex (5.0 g) was redissolved in CH_2Cl_2 and hydrolyzed.

After drying, the solvent was removed under vacuum at low temperatures. Extraction of the red residue several times with petroleum ether followed by evaporation of the solvent and repeated recrystallization of the residual semisolid (1.35 g) from ether–pentane (−78°) afforded phenylchlorocyclopropenone as a low-melting, unstable solid (720 mg, 20%): mp 40–43° dec; ν_{max} 1865, 1640, 1220 cm^{-1}; *m/e* 164. Mass spectrum calcd for 1 Cl: P + 2, 32.6. Found: 34.2.

The pentane-insoluble residue still containing strong bands at 1865 and 1640 cm^{-1} and slowly crystallized upon standing (0.55 g). Chromatography of this material on silica gel (benzene–chloroform) afforded *cis*-2-phenyl-3-chloroacrylic acid (0.25 g), mp 117–119° (lit.[5] mp 113–115°), identical with a sample prepared from phenyltrichlorocyclopropene.

Conversion to Phenylhydroxycyclopropenone. Phenylchlorocyclopropenone–aluminum chloride complex (5.0 g) was hydrolyzed as reported above. The residual semisolid was then dissolved in acetone (50 ml) containing ice (15 g) and stirred at 0° for 3 hr and then at room temperature for approximately 1 hr. Evaporation of the acetone under vacuum afforded a semisolid, which was dried under vacuum and then slurried in anhydrous ether. Phenylhydroxycyclopropenone (1.2 g) was isolated (36% based on phenyltrichlorocyclopropene): neut equiv 144 (calcd, 146); mp 242–244° dec (lit.[4] mp 244–245°).

Anal. Calcd for $C_9H_6O_2$: C, 73.96; H, 4.14. Found: C, 73.78; H, 4.12.

Phenylhydroxycyclopropenone (1a). Phenyltrichlorocyclopropene (3.8 g, 17.3 mmol) was dissolved in acetone (75 ml, 0°), and ice (30 g) was added. After 4 hr at 0° the solution was allowed to warm for 60 min, and following evaporation of most of the acetone at reduced pressure and low temperature, the solid was filtered, dried, and washed with anhydrous ether to give 1.7 g (66%) of **1a**: λ_{max} (log ϵ) of acid 266 (10,300), 256 (17,500), 248 (18,000), 202 nm (18,800); of anion 275 (9240), 265 (18,000), 256 (18,000), 204 nm (13,800). The infrared and ultraviolet spectra were identical with those previously reported.[1,4,12] If the reaction was interrupted before completion, substantial amounts of phenylchlorocyclopropenone could be detected in the infrared spectrum.

The following arylhydroxycyclopropenones were prepared in the manner outlined above except where noted. No attempt was made to optimize the yields.

***tert*-Butylphenylhydroxycyclopropenone (1b)** (yield 50%) had mp 123°; ν_{max} (Nujol) broad band at 1880–900 with fine structure at 1600, 1400, 1190, 1130, 1070, 1015 cm^{-1}; ir bands at 850 (m), 835 (w), and 750 cm^{-1} (w); λ_{max} (rel ϵ)[15] of acid 275 (0.57), 262 (1.02), 255 (0.99), 205 nm (0.85); of anion 281 (0.99), 265 (1.00), 260 (1.00), 208 nm (0.63).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.81; H, 6.90.

***p*-Fluorophenylhydroxycyclopropenone (1c)** (yield 55%) had mp 115 dec; ν_{max} (Nujol) broad band at 1900–880 with fine structure at 1600, 1410, 1221, 1160, 1100, 1010 cm^{-1}; ir bands at 850 (m), 830 (w), 810 cm^{-1} (w); λ_{max} (rel ϵ)[15] of acid 253 (0.98), 270 (1.00), 210 nm (0.67); of anion 260 (0.97), 255 (1.00), 205 nm (0.75).

Anal. Calcd for $C_9H_5FO_2$: C, 65.85; H, 3.07. Found: C, 65.60; H, 3.01.

***p*-Methoxyphenylhydroxycyclopropenone (1d).** *p*-Methoxyphenyltrichlorocyclopropene (410 mg, 1.65 mmol) was dissolved in acetone–water (0°) and after 2 hr was allowed to stand at room temperature overnight. Evaporation of the solvent and trituration with anhydrous ether afforded **1d** (130 mg), which was purified by dissolving in dilute base containing some acetone and reprecipitating with dilute acid: yield 40%; mp 238–242° dec; ν_{max} (Nujol) broad band 1880–900 with fine structure at 1865, 1600, 1510, 1115, 1265, 1180, 1035, band at 848 cm^{-1}; neut equiv 177 (calcd, 176.16); λ_{max} (rel ϵ)[15] of acid 280 (0.86), 270 (1.00), 210 nm (0.67); of anion 286 (0.56), 268 (1.00), 208 nm (0.66).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 67.53; H, 4.36.

2,6-Dibromophenylhydroxycyclopropenone (1e). 2,6-Dibromophenyltrichlorocyclopropene (660 mg, 1.75 mmol) was dissolved in acetone–water and maintained at 0° overnight. Filtration afforded 320 mg of solid. Evaporation of the solvent followed by titration with anhydrous ether afforded **1e** (100 mg, 79%): mp >250°; ν_{max} (Nujol) broad band 1900–1200 with fine structure at 1860, 1612, 1078, 1048, 881, and 808 cm^{-1}; neut equiv 292 (calcd, 303.9); λ_{max} (rel ϵ)[15] of acid 270 (0.77), 260 (1.00), 236 (1.96), 228 nm (1.88); of anion 276 (0.92), 267 (1.00), 235 (1.48), 232 nm (1.48).

Anal. Calcd for $C_9H_4Br_2O_2$: C, 35.56; H, 1.32; Br, 52.58. Found: C, 35.42; H, 1.29; Br. 52.42.

Mesitylhydroxycyclopropenone (1f). Mesityltrichlorocyclopropene (2.0 g, 7.6 mmol) was dissolved in acetone, and water was added to cloudiness. After 2 days at room temperature the product was isolated by filtration (1.0 g, 70%): mp >270°; λ_{max} (Nujol) broad band 1900–880 with fine structure at 1600, 1180, 863, 855, and 743 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.90; H, 6.40.

Dissociation Constants. Values for pK were measured spectrophotometrically using the method for **1a** which was described in detail elsewhere.[16] The acid being studied was purified by slurrying in ether, filtered, and dried, then added to water. The solution was stirred for several minutes and then vacuum filtered

to remove undissolved sample. This stock solution was then stored in ice water to retard decomposition. The optical density of the stock solution was checked periodically to determine purity; experiments were never extended beyond about 4 hr. Stock solution was added to a volumetric flask by weight using a top loading analytical balance and diluted to volume with sulfuric acid solution (dilution of stock was generally about 1:100; so final temperature was ambient, 25°). Spectra were taken immediately, and then the pH was measured. The existence of isosbestic points indicated that there was no decomposition. For each of the compounds **1a-e**, the spectrum was determined at 5 or 6 sulfuric acid concentrations. Because of the problem of overlapping bands, the ratio of the acid to the anionic form was determined at about ten different wavelengths for each spectrum, and the average was used in determining pK.

Nqr Spectra. Compounds **2a-e** were repurified either by vacuum distillation or recrystallization before determination of the nqr spectra, which were run at 77°K using a Decca Radar Ltd. nqr spectrometer.

Acknowledgments. This work was partially supported by a grant from the National Science Foundation.

Registry No.—**1a**, 1600-39-1; **1b**, 51212-52-3; **1c**, 51212-53-4; **1d**, 51212-54-5; **1e**, 51212-55-6; **1f**, 51212-56-7; **2a**, 24648-07-5; **2b**, 51212-57-8; **2c**, 3854-79-3; **2d**, 51212-58-9; **2e**, 51212-59-0; **2f**, 51212-60-3; **3**, 20434-13-3; $AlCl_3$, 7446-70-0; C_3Cl_4, 6262-42-6; *p*-dibromobenzene, 106-37-6.

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(12) Additional proof of structure of **1a** is given by its conversion to a known four-membered ring compound (unpublished studies by J. Chickos). Reaction of **1a** with diazomethane gives phenylmethoxycyclopropene, which reacts with 2,6-dimethylphenylisonitrile[13] with ring expansion to give (2,6-dimethylphenylimino)phenylmethoxycyclobutenone; the latter upon hydrolysis yields phenylmethoxycyclobutenedione, identified by comparison with an authentic sample.[14]
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A General Synthetic Route to Cycloalkylidenecycloalkanes. Reactions of α Anions of Cycloalkanecarboxylic Acid Salts with Cycloalkanones

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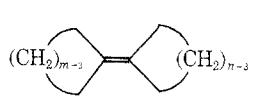
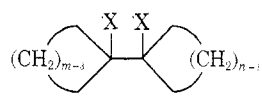
A versatile synthetic route leading to symmetrical and unsymmetrical cycloalkylidenecycloalkanes of general formula **1** has been developed. Treatment of α-lithiated cycloalkanecarboxylic acid salts **5** with cycloalkanones **6** leads to the β-hydroxy acids **7**. These acids are then converted into the corresponding β-lactones **8**. Thermolyses of **8** produce excellent yields of **1**. Symmetrical olefins **1** ($m = n$ = 4, 5, 6, 7, and 8) and unsymmetrical olefins **1** (m = 4, n = 5 or 6; m = 5, n = 6) have been prepared by application of this procedure. Other substituted cyclic ketones such as adamantanone have also been successfully utilized in this reaction scheme. The α-lithiated salt of 4-cycloheptene-1-carboxylic acid undergoes a facile reaction with **6** (n = 6) to yield the β-hydroxy acid, which can then readily be converted into the corresponding diene without any problem of double-bond isomerizations. Attempts to utilize cyclopropanecarboxylic acid were unsuccessful.

During the course of another research project being performed in our laboratories we had need of a number of cycloalkylidenecycloalkanes of general formula **1**. Although several useful synthetic routes to tetrasubstituted olefins of type **1** have been reported previously, an examination of each method indicates some limitation to general applicability.



1



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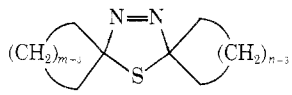

3

In only a few cases is the Wittig[2] procedure applicable to the synthesis of **1**. Cyclopropylidenetriphenylphosphorane, on treatment with cyclopentanone or cyclohexanone, leads to **1** (m = 3, n = 5) and **1** (m = 3, n = 6), respectively.[3] Other cycloalkylidenetriphenylphosphoranes have been prepared with four-, five-, six-, and seven-membered rings.[4] Cyclohexylidenetriphenylphosphorane, on treatment with cyclohexanone, leads to enolate formation.[4a]

Vicinal dinitro compounds such as **2** (X = NO_2) have been converted to **1** ($m = n$ = 5 or 6, and m = 6, n = 7).[5] The major limitation is the accessibility of the requisite nitrocycloalkane precursors for the preparation of **2** (X = NO_2, $m = n$) and the accessibility of 1,1-dinitrocycloalkanes required to prepare **2** (X = NO_2, $m \neq n$).

The zinc debromination of vicinal dibromides **2** (X = Br, $m = n$) leads to **1** ($m = n$ = 5, 6, or 7).[6] Unsymmetrical olefins **1** ($m \neq n$) would be difficult to prepare by this procedure because of the inaccessibility of pinacols of type **2** (X = OH, $m \neq n$).[7]

The preparation of several 2,5-dispiro-Δ^3-1,3,4-thiadiazolines **3** ($m = n$) have recently been reported.[8] Thermolysis of **3** ($m = n$ = 6) led to loss of nitrogen to form the episulfide, which afforded **1** ($m = n$ = 6) on treatment with *n*-butyllithium.[8a] However, thermolysis of **3** ($m = n$ = 7) did not yield the episulfide or **1** ($m = n$ = 7). Cyclobutylidenecyclobutane **1** ($m = n$ = 4) was prepared from **3** ($m = n$ = 4) when heated with triphenylphosphine.[8c] This