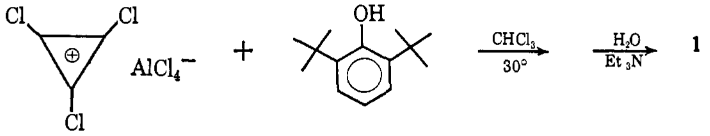
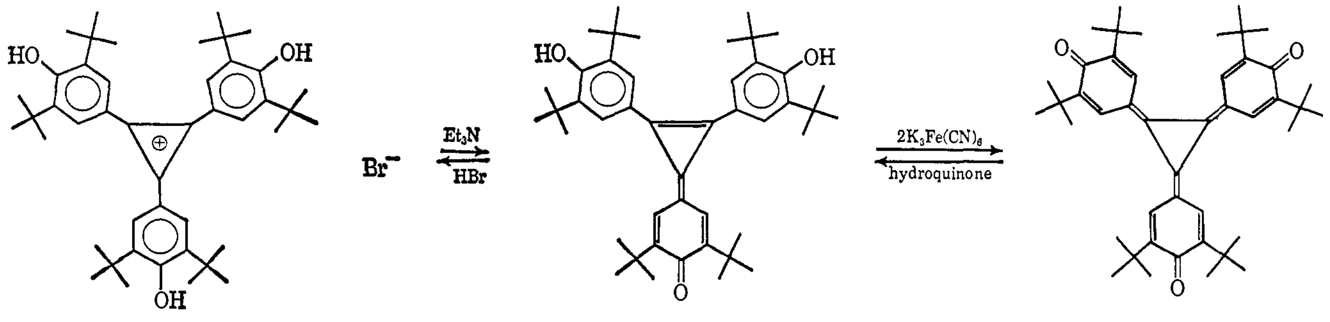
a trimethylenecyclopropane derivative of unprecedented stability. **2** was obtained by the oxidation of the quinocyclopropene **1**, which was in turn synthesized from trichlorocyclopropenium tetrachloroaluminate[2] and 2,6-di-*t*-butylphenol.





3 **1** **2**

Previous work from these laboratories showed that aryltrichlorocyclopropenes and diarylcyclopropenones could be obtained by the reaction of $C_3Cl_3^+AlCl_4^-$ with benzene and substituted benzenes.[2b] More recently we have found that triarylcyclopropenium ions are formed in this reaction when activated aromatic compounds react with $C_3Cl_3^+$ salts.[3] If one of the aromatic rings bears a *p*-hydroxyl group, deprotonation to a quinocyclopropene can often be effected.[3,4]

When 2,6-di-*t*-butylphenol in chloroform was allowed to react with $C_3Cl_3^+AlCl_4^-$, then hydrolyzed and treated with triethylamine, **1**[5] was formed in yields up to 70%. The quinocyclopropene **1**, an orange-red solid, showed the following ultraviolet-visible absorption maxima in acetonitrile solution: λ 310 mμ (log ϵ 4.40), 323 (4.42), 386 sh (4.56), and 406 (4.86). The infrared showed an absorption of medium strength at 1820 cm^{-1} and a strong band at 1595 cm^{-1}, both of which appear to be characteristic for the quinocyclopropene system.[3] **1** was quite insoluble in solvents commonly used for nmr spectra, but was soluble in trifluoroacetic acid. The proton nmr spectrum in this solvent showed singlets at τ 1.60 and 8.30 in a 1:9 ratio, as expected for the aromatic and *t*-butyl hydrogens in the protonated form of **1**.

Upon treatment with hydrogen bromide in ether, **1** was converted to the corresponding triarylcyclopropenium bromide, **3**. The infrared spectrum of **3** showed a strong band at 1590 cm^{-1} and a very strong, broad absorption at 1370 cm^{-1}, characteristic for carbon–carbon ring expansion in triarylcyclopropenium salts.[6] The ultraviolet spectrum in CH$_3$CN showed λ_{max} 241 mμ (log ϵ 4.50), 288 (4.14), 352 (4.73), and 370 (4.79); the spectrum is similar to that reported for trianisylcyclopropenium bromide.[7]

Oxidation of **1** in benzene with lead dioxide or aqueous basic potassium ferricyanide immediately gave an intense blue-green solution, which was evaporated to give crude **2**. Recrystallization from dichloromethane–acetonitrile afforded pure **2** as a dark blue powder, stable to above 250° in air, decomposing without melting at about 280°.

The ultraviolet-visible spectrum of **2** in benzene showed λ_{max} 307 mμ (log ϵ 4.13), 316 (4.15), 390 (4.62), 625 sh (4.43), and 685 (4.68). The infrared spectrum showed only six bands of strong or moderate intensity between 625 and 2500 cm^{-1}, at 1590, 1465, 1355, 1250, 1090, and 900 cm^{-1}, suggesting a highly symmetrical structure. Bands characteristic for hydroxyl or cyclopropene are absent. The nmr spectrum of **2** in CCl$_4$ consists of two singlets at τ 2.50 and 8.60 in 1:9 ratio. All of the spectral evidence is compatible with the assigned structure.

Upon treatment with hydroquinone, solutions of **2** are reduced to **1**. Spectroscopic studies indicate that the two-electron oxidation–reduction involving **1** and **2** is rapid in both directions and is essentially quantitative.

A diradical structure can be written for **2**, with two of the rings fully aromatic rather than quinonoid. Electron spin resonance measurements indicate that **2** does not contain unpaired electrons at 25°. The possibility that a diradical state may become populated at higher temperatures is under investigation.

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

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[2] (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964); (b) *ibid.*, **86**, 4215 (1964); (c) R. West, S. W. Tobey, and A. Sadô, *ibid.*, **88**, 2488 (1966).

[3] Unpublished work by R. West and D. C. Zecher.

[4] Two quinocyclopropenes have previously been reported. See A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963); B. Föhlisch and P. Bürgle, *Tetrahedron Letters*, 2661 (1965).

[5] All new compounds gave elemental analyses in good agreement with those calculated for the assigned structures.

[6] R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962); J. Chatt and R. G. Guy, *Chem. Ind.* (London), 212 (1963).

[7] R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

Robert West, David C. Zecher
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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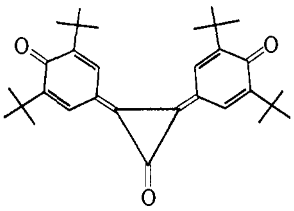
Synthesis of a Diquinocyclopropanone and a Diquinoethylene

Sir:

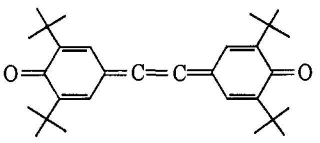
The reaction between trichlorocyclopropenium tetrachloroaluminate[1] and aromatic hydrocarbons leading

[1] (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 4215 (1964); (b) R. West, A. Sadô, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).

to diarylcyclopropenones has been reported earlier.[1a] When 2,6-di-*t*-butylphenol is added to $C_3Cl_3^+AlCl_4^-$ at room temperature or above, a triarylcyclopropenium ion is produced, as explained in the accompanying communication.[2] However, if the same reaction is carried out at 0°, bis(3,5-di-*t*-butyl-4-hydroxyphenyl)cyclopropenone (**1**) is produced as a colorless crystalline solid, mp 215° dec.[3] **1** is the precursor for two compounds with novel and interesting structures: the diquinocyclopropanone **2** and the diquinoethylene **3**.

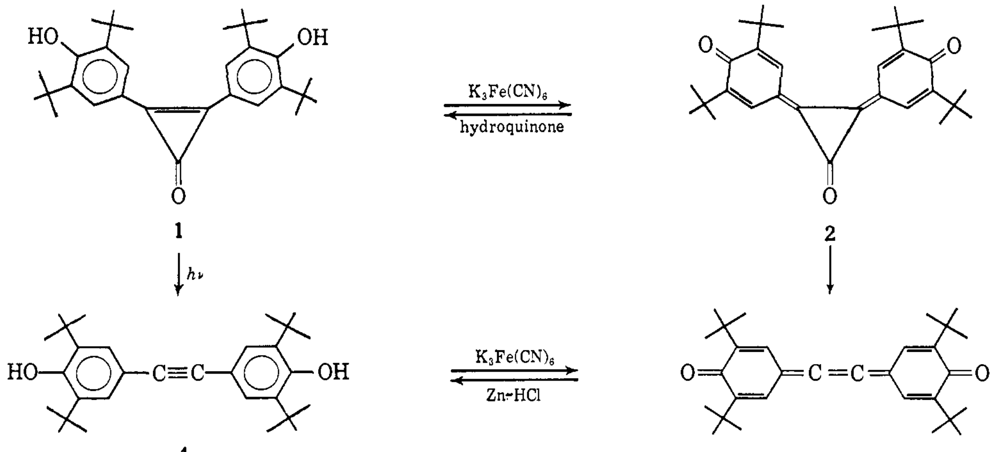


2



3

The infrared spectrum of **1** shows strong bands at 1840 and 1590 cm^{-1}, characteristic for cyclopropenones.[1a,4] The ultraviolet spectrum is similar to those of related cyclopropenones,[5] showing $\lambda_{max}^{CH_3CN}$ 236 mμ (log ϵ 4.26), 326 (4.40), and 344 (4.36), and the nmr spectrum is also consistent with the assigned structure.



1 2 4 3

Treatment of a benzene solution of **1** with lead dioxide or aqueous basic potassium ferricyanide gives an intensely purple solution with λ_{max} 542 mμ, from which **2** can be isolated as a purple solid. Two equivalents of $K_3Fe(CN)_6$ is required to convert **1** completely to **2**. If the solution of **2** is promptly treated with excess hydroquinone, essentially complete reduction back to **1** takes place. Solutions of **2**, however, are unstable and within a few hours change from purple to yellow-orange (λ_{max} 486 mμ). After this change no reaction takes place with hydroquinone.

Because of its instability **2** was not obtained absolutely pure,[3] but there is good evidence for the diquinocyclopropanone structure shown. The infrared spectrum contains a medium-strong band at 1810 cm^{-1} and an extremely strong band at 1590 cm^{-1}. Other cyclopropanones absorb in the region 1800–1840 cm^{-1},[6] and the triquinocyclopropane related to **2** has a similar strong band at 1590 cm^{-1}.[2] The structural assignment for **2** is further supported by identification of its decomposition product as the diquinoethylene, **3**, as explained below.

Photolysis[7] of a benzene solution of **1** gave excellent yields of bis(3,5-di-*t*-butyl-4-hydroxyphenyl)acetylene (**4**), as colorless crystals, mp 256–259° dec. The infrared spectrum of **4** lacked the strong absorption bands at 1840 and 1590 cm^{-1} present for **1**. The ultraviolet spectrum showed $\lambda_{max}^{CH_3CN}$ 295 mμ (log ϵ 4.56), 314 mμ (log ϵ 4.53); this spectrum is very similar to that recorded for *p,p'*-dimethoxytolan.[8] The nmr spectrum in CCl_4 contained singlets at τ 2.80 (aromatic), 4.87 (OH), and 8.55 (*t*-butyl).

Oxidation of a benzene solution of the acetylene **4** with excess $K_3Fe(CN)_6$ solution gave an orange-yellow solution of the diquinoethylene **3**. Evaporation of the solvent gave **3** as a red-purple solid, recrystallized from acetonitrile–dichloromethane, mp 250° dec. **3** *was identical in all respects with the product of decomposition of* **2**, as shown in the reaction scheme below. All spectral data support the structure shown for **3**. The infrared spectra of **3** and **2** are very similar, but **3** lacks the 1810-cm^{-1} carbonyl band of **2**. The electronic spectrum of **3** had $\lambda_{max}^{C_6H_6}$ 486 mμ (log ϵ 5.08). The nmr spectrum showed only singlets at τ 3.00 and 8.67 in the expected 1:9 intensity ratio.

As indicated above, hydroquinone does not effect reduction of solutions of **3**, but **3** can be reduced with powdered zinc and hydrochloric acid to **4**.

Apparently, the strained diquinocyclopropanone **2** readily undergoes decarbonylation in solution to give the more stable diquinoethylene **3**. The reactions of these substances are under study, and attempts to make other compounds of these new types are under way.

---

(2) R. West and D. C. Zecher, *J. Am. Chem. Soc.*, **89**, 152 (1967).

(3) Compounds **1**, **3**, and **4** gave elemental analyses in good agreement with those calculated for the assigned structures. **2** could not be purified because of its rapid decomposition in solution. Crude **2** gave the following. *Anal.* Calcd for $C_{31}H_{40}O_3$: C, 80.86; H, 8.70; O, 10.44. Found: C, 78.60; H, 8.69; O, 9.95; residue 1.9%. Corrected for residue: C, 80.12; H, 8.66; O, 10.14.

(4) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965); R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965); R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966).

(5) Unpublished work by R. West and D. C. Zecher.

(6) I. Haller and R. Srinivasan, *J. Am. Chem. Soc.*, **87**, 1144 (1965); W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966); N. J. Turro and W. B. Hammond, *ibid.*, **88**, 3672 (1966).

(7) Photolysis of diphenylcyclopropenone to tolan was reported by G. Quinkert, K. Opitz, W. Wiersdorff, and J. Weinlich, *Tetrahedron Letters*, 1863 (1963).

(8) Sadtler Ultraviolet Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1964, Spectrum No. 16128.

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David C. Zecher, Robert West
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received November 5, 1966

Nonplanar Cyclobutane. I. The 3-Isopropylcyclobutyl System. Nuclear Magnetic Resonance Spectra of Alcohols and Amines[1]

Sir:

During the past 15 years, a good deal of physical information has accumulated which supports a nonplanar structure for cyclobutane.[2-6] Recently, chemical evidence for a folded conformation for the cyclobutane system has been adduced from equilibration data.[7]

Cyclobutane is quite flexible and exhibits a dynamic ring-bending equilibrium which has been termed "pseudo-rotation.[8] In a pair of conformers representing the extremes of such flexion, equatorial and axial configurations may be assigned to substituents.[9] We have attempted to utilize a bulky group in a 1,3-disubstituted cyclobutane to retard this equilibrium to delineate these positions better in a manner analogous to the effect of "holding" groups in the cyclohexane system.[10] Thus, in Figure 1, favored conformations appear on the left. We hoped in this fashion to probe possible differences in behavior between axial and equatorial substituents, perhaps paralleling differences in cyclohexanes, and to provide better definition of the condition of nonplanarity. Accordingly, we have prepared and examined a series of 3-isopropylcyclobutane derivatives. In this communication, we wish to present the nmr spectra of the isomeric 3-isopropylcyclobutanols and 3-isopropylcyclobutylamines[11] (Figures 2 and 3), which provide convincing and dramatic evidence for the model depicted.

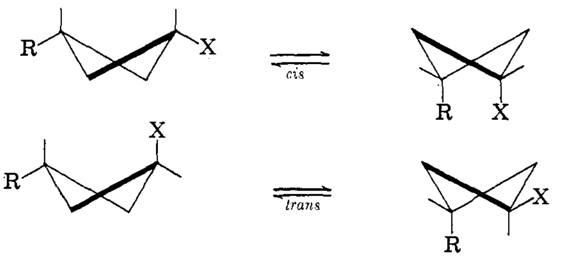

Figure 1.

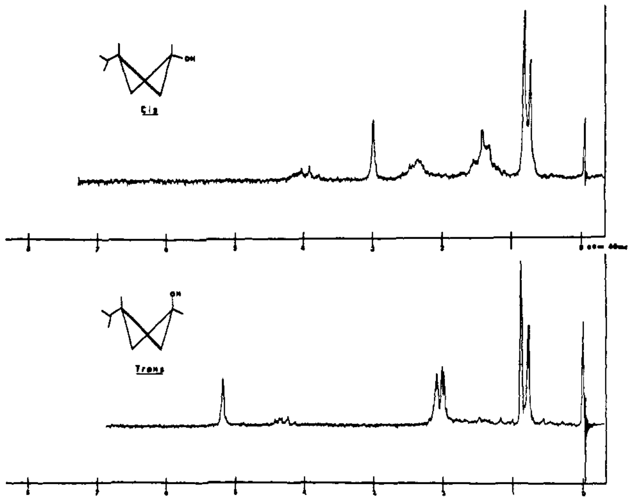

Figure 2.

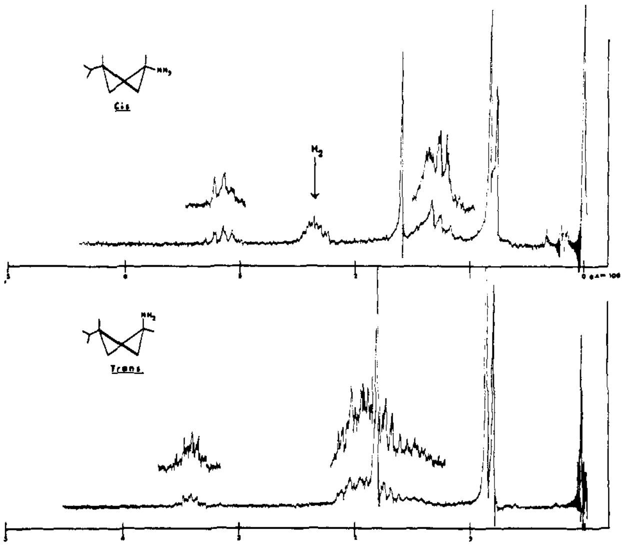

Figure 3.

The spectra were recorded for the amines at 100 Mc and the alcohols at 60 Mc. In both sets of spectra, the unsymmetrical doublet of the methyl protons appears similarly centered at *ca.* 0.8 ppm (relative to TMS). In the amines, the amino protons may be seen as a sharp resonance at about 1.6 ppm for the *cis* and 1.8 ppm for the *trans* isomer. The proton geminal to the amino group is located as a multiplet centered at 3.2 ppm for the *cis* and 3.4 ppm for the *trans* isomer. The latter assignment is reasonable since these protons are the most strongly deshielded by the amino group and should appear at lowest field. This conclusion was verified by a double resonance experiment which showed this resonance coupled to the resonances centered at 2.3 and 1.3 ppm in the *cis* and at 1.9 ppm in the *trans* isomer. The latter resonances are due to the ring methylene protons, and it is here that a pronounced distinction between the *cis* and *trans* isomers is seen.

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(1) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S167.

(2) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(3) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, 20, 1703 (1952).

(4) G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(5) R. C. Lord and I. Nakagawa, *J. Chem. Phys.*, **41**, 2951 (1963).

(6) W. G. Rothschild and B. P. Dailey, *ibid.*, **36**, 2931 (1962); L. C. Snyder and S. Meiboom, *Chem. Eng. News*, **44**, No. 17, 51 (1966).

(7) N. L. Allinger and L. A. Tushaus, *J. Org. Chem.*, **30**, 1945 (1965).

(8) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947); see also J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).

(9) For cases in which there is a single halogen substituent, recent work has indicated that the "axial" conformer may be relatively planar; see J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3884, 3891 (1965); H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **44**, 865 (1966); W. G. Rothschild, *ibid.*, **45**, 1214 (1966).

(10) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5592 (1955).

(11) Full details of the synthesis and configurational assignments of the alcohols and amines will be published in a forthcoming paper concerned with deamination of the amines.