

the expected height.⁹ The function $G = \sigma(\rho)/\rho_H$, where ρ_H is the hydrogen electron density, exhibits a shallow minimum of approximately 0.21 at $t_0 = 0.25 \text{ \AA}^{-1}$ (460 independent reflections); here the Rh-H distance is 1.72 \text{ \AA}. At $t_0 = 0.30 \text{ \AA}^{-1}$ (761 independent reflections) G is 0.23 and the Rh-H distance is 1.66 \text{ \AA}. At lower values of t_0 , G is substantially higher. The standard deviation in the hydride position at $t_0 = 0.25 \text{ \AA}^{-1}$, as estimated by Cruickshank's method,¹⁰ is 0.15 \text{ \AA}, about 7 times that estimated for the carbonyl C. On the basis of these calculations we feel confident that the Rh-H distance is $1.72 \pm 0.15 \text{ \AA}$.

Figure 1 is a perspective view of the molecule. It has the bipyramidal configuration surmised by Vaska.⁵ The Rh atom lies approximately 0.36 \text{ \AA} below the phosphorus plane toward the carbonyl, and so the CRhP₃ segment is neither tetrahedral nor part of a regular trigonal bipyramid. The Rh-CO distance is normal, and there appears to be no *trans* effect as in HPtX(PR₃)₂ (X = Br,¹¹ Cl¹²) where the Pt-X distance is abnormally long. Table I lists some of the more important distances and angles.

TABLE I

SELECTED DISTANCES AND ANGLES IN HRh(CO)(P(C₆H₅)₃)₃

	Distance, \text{ \AA}		Angle
Rh-H	1.72(15) ^a	Rh-C-O	179(2) ^o
Rh-P	2.337(8)	OC-Rh-H	170(5)
	2.314(7)		
	2.317(7)	P-Rh-CO	94.8(9)
			103.8(8)
Rh-CO	1.81(2)		98.0(9)
C-O	1.18(3)	P-Rh-P	115.8(3)
			120.6(3)
P-phenyl	1.83(2) ^b		116.6(3)
		Phenyl-P-phenyl	101.3(2.1) ^b

^a The numbers in parentheses are estimated standard deviations. ^b Average of the nine phenyl rings.

(9) The experimental heights of the hydride peak are 0.40, 0.34, and 0.20 e/\text{ \AA}^3 at t_0 values of 0.30, 0.25, and 0.20 \text{ \AA}^{-1}. The theoretical heights for a hydride ion undergoing no thermal motion are 0.42, 0.32, and 0.21 e/\text{ \AA}^3. Different assumptions about the charge on the H and about thermal motion do not seriously affect this remarkable agreement.

(10) D. W. J. Cruickshank, *Acta Cryst.*, **7**, 519 (1954), and earlier papers.

(11) P. G. Owston, J. M. Partridge, and J. M. Rowe, *ibid.*, **13**, 246 (1960).

(12) R. Eisenberg and J. A. Ibers, unpublished results.

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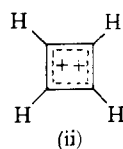
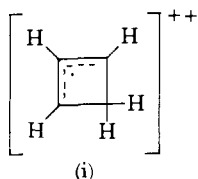
RECEIVED AUGUST 29, 1963

Formation of the Stable 1,3-Dihydroxy-2,4-diphenylcyclobutadiene Dication by Ionization of an α -Bromoketone

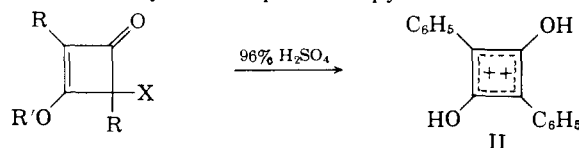
Sir:

Routes to analogs of the cyclobutadiene dication¹ seem to be under active investigation by several groups.²⁻⁴ We wish to report the ionization of the α -

(1) Systematic nomenclature of such dicarbonium ions presents a problem.²⁻⁴ It seems to us that the name "cyclobutenyl dication" implies structure (i), in which two electrons have been removed from the cyclobutenyl radical, rather than (ii), while the name "cyclobutadiene dication" implies structure (ii), in which two electrons have been removed from cyclobutadiene. The latter name is in accord with the current practice for naming radical anions and dianions derived from conjugated cycles.



bromoketone 2-bromo-3-hydroxy-2,4-diphenylcyclobutenone (I) in 96% sulfuric acid to give stable solutions of a carbonium ion, most probably the 1,3-dihydroxy-2,4-diphenylcyclobutadiene dication (II),⁵ as demonstrated by n.m.r. spectroscopy.



I, R = C₆H₅; R' = H; X = Br
 III, R = C₆H₅; R' = C₆H₅CH₂CO, X = H
 IV, R = C₆H₅; R' = X = H
 V, R = C₆H₅; R' = H; X = OH
 VII, R = CH₃; R' = H; X = Br

Bromoketone I, m.p. 175-177^o [*Anal.* Calcd. for C₁₆H₁₁BrO₂: C, 60.95; H, 3.49; Br, 25.39. Found: C, 61.01; H, 3.67; Br, 25.23; infrared $\lambda_{\text{max}}^{\text{Nujol}}$ 5.71 μ ; ultraviolet $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ 262 m μ , ϵ 2.29 $\times 10^4$. Methyl ether from I and diazomethane, m.p. 115-116^o. *Anal.* Calcd. for C₁₇H₁₃O₂Br: C, 62.06; H, 3.95; Br, 24.32. Found: C, 62.24; H, 4.24; Br, 24.10; $\lambda_{\text{max}}^{\text{Nujol}}$ 5.67-6.15 μ (*cf.* ref. 6a).] was obtained by the following sequence of reactions. Phenylacetyl chloride in boiling ether was treated dropwise with triethylamine to give a 67% yield of 2,4-diphenyl-3-phenylacetoxycyclobutenone (III), m.p. 120-122^o, $\lambda_{\text{max}}^{\text{Nujol}}$ 5.60, 5.70 μ , according to the procedure described by Johnson and Marshall.^{6b} Hydrolysis with sodium hydroxide in aqueous methanol gave 2,4-diphenyl-3-hydroxycyclobutenone (IV), m.p. 155-157^o (*lit.*⁷ 160^o). The methyl ether from (IV) and diazomethane had m.p. 134-135^o. *Anal.* Calcd. for C₁₇H₁₄O₂: C, 81.60; H, 5.60. Found: C, 81.86; H, 5.88; infrared $\lambda_{\text{max}}^{\text{Nujol}}$ 5.71, 6.12 μ . Bromination of IV or III with bromine in chloroform afforded I in 96% and 84% yields, respectively.

The α -bromoketone I gave an immediate precipitate with silver perchlorate in ethanol or dry acetonitrile. It dissolved in aqueous sodium bicarbonate with the formation of a transient pink color. Acidification of the cold bicarbonate solution immediately after dissolution afforded the unstable hydroxyketone, 2,3-dihydroxy-2,4-diphenylcyclobutenone (V), m.p. 188-190^o. *Anal.* Calcd. for C₁₆H₁₂O₃: C, 76.18; H, 4.80. Found: C, 76.19; H, 4.63; $\lambda_{\text{max}}^{\text{Nujol}}$ 3.0, 5.82 μ . V regenerated bromoketone I upon treatment with anhydrous hydrogen bromide in dry ether.

Bromoketone I dissolved in 96% sulfuric acid to give a deep red solution, λ_{max} 487 m μ , ϵ 1.44 $\times 10^5$. When diluted with ice-water this solution gave a precipitate of the hydroxy ketone V in near quantitative yield. The n.m.r. spectrum of the sulfuric acid solution is reproduced in Fig. 1. A comparison with that of diphenylcyclopropenium hexafluorophosphate⁸ in the same solvent and that of benzhydrol in a 1:1 mixture of thionyl chloride and 15% fuming sulfuric acid⁹ (see

(2) T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

(3) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

(4) H. Hart and R. W. Fish, *ibid.*, **82**, 5419 (1960).

(5) The extent of protonation of the oxygen atoms is in no way established in the present investigation. It seems reasonable that both will be protonated in the strongly acidic medium.

(6) (a) H. H. Wasserman and E. V. Dehmow, *J. Am. Chem. Soc.*, **84**, 3786 (1962); (b) T. B. Marshall, Ph.D. Thesis, Cornell University, 1950.

(7) H. Staudinger and S. Bereza, *Ber.*, **44**, 533 (1911).

(8) (a) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960), and unpublished results; (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(9) The n.m.r. spectrum of the deep yellow-orange solutions of benzhydrol (10%) in 1:1 thionyl chloride and 15% fuming sulfuric acid was unchanged over several hours at about 10^o. Benzhydrol could be recovered in 60% yield by dropwise addition of the aged solution to excess ice-cold aqueous sodium hydroxide with vigorous stirring.

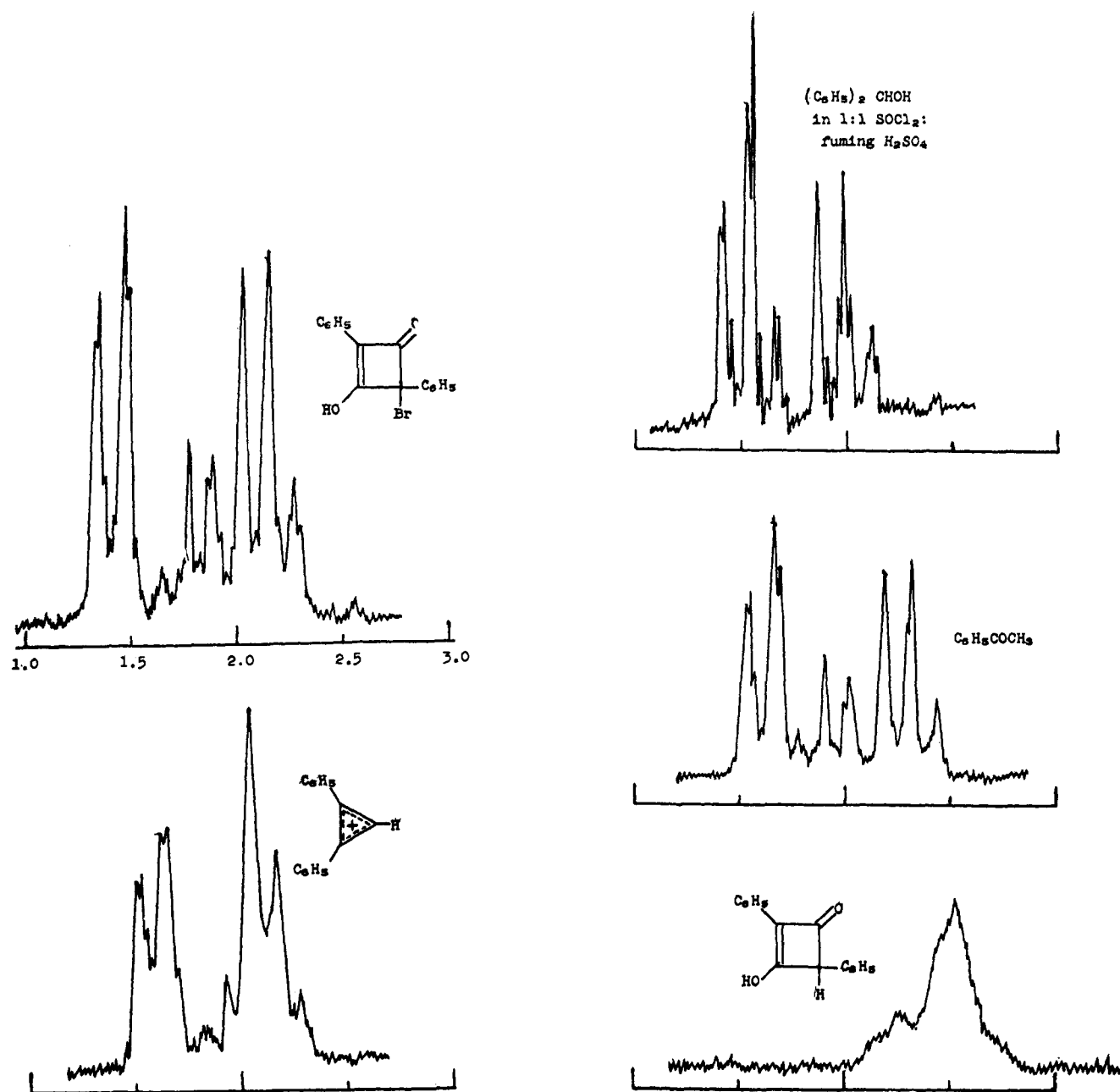


Fig. 1.—N.m.r. spectra of some aryl carbonium ions in sulfuric acid. Solutions were made up at 0° to a concentration of 10% of solute. Spectra were determined within 30 min. of preparation.

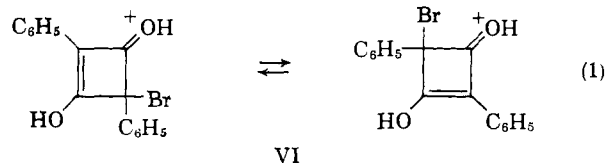
Fig. 1) demonstrates the presence of benzylic type carbonium ions. Thus, in each case multiplets are observed for the aromatic protons near $\tau = 1.5$ and 2.0 p.p.m.^{10,11} in approximate area ratios of 2 to 3. A similar spectrum, though at higher τ -values, is exhibited by solutions of acetophenone in 96% sulfuric acid. These observations seem best explained by the formation of a carbonium ion such as II upon solution of I in 96% sulfuric acid. A less acceptable alternative, the formation of a carbonium ion such as VI, perhaps in rapid equilibrium¹² as depicted in eq. 1, is conclusively ruled out by the appearance of the n.m.r. spectrum of a solution of ketone IV in 96% sulfuric acid (see Fig. 1).^{12b}

(10) Proton n.m.r. spectra are reported on the τ -scale with tetramethylsilane defined as $\tau = 10$ p.p.m.

(11) Tetramethylammonium tetrafluoroborate ($\tau = 6.87$) was used as an internal standard.¹²

(12) (a) D. G. Farnum, M. A. T. Heybey and B. Webster *Tetrahedron Letters*, No. 5, 307 (1963); (b) The broadened spectrum of ketone IV may be the result of equilibration of the two enols, as also suggested by the broadening of the methine hydrogen resonance at $\tau = 4.80$ p.p.m.

Such solutions exhibit complex n.m.r. absorption at $\tau = 2.1$ – 2.7 p.p.m. and, therefore, a species such as carbonium ion VI could not be expected to exhibit n.m.r. absorption below $\tau = 2$ p.p.m.



It should be noted that, in contrast to the striking situation with cyclopropenium ions, where alkyl substituents on the double bond favor ionization more than similarly placed phenyl substituents,^{8b} the phenyl groups seem essential to the ionization of bromoketone I. Thus, 2-bromo-3-hydroxy-2,4-dimethylcyclobuten-1-one (VII)^{12,13} is completely resistant to solvolysis in

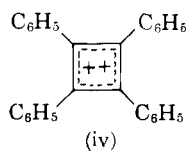
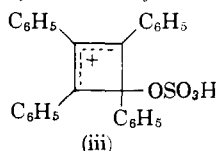
(13) R. B. Woodward and G. Small, Jr., *J. Am. Chem. Soc.*, **72**, 1297 (1950).

96% sulfuric acid over several days at room temperature as evidenced by the unchanged doublet in its n.m.r. spectrum,¹⁴ although it is solvolyzed in aqueous solution under similar conditions. The comparison is not rigorous, since in the case of I a phenyl group not previously conjugated with the double bond is brought into conjugation with the carbonium ion. However, the vast difference in the reactivities of bromoketones I and VII leaves no doubt that the phenyl groups of dicarbonium ion II are exerting a major stabilizing influence. The close similarity in the appearance of the n.m.r. spectra of sulfuric acid solutions of carbonium ion II, acetophenone, benzhydrol, and the diphenylcyclopropenium ion, in spite of evident differences in the importance of phenyl delocalization of the positive charge, suggests that the extent of phenyl delocalization of the positive charge may not be the dominant factor in reversing the order of the chemical shifts in triaryl-carbonium ions.¹⁵⁻¹⁷

Acknowledgment.—We thank the National Science Foundation for support under NSF Grant G-14454.

(14) The n.m.r. spectrum of the corresponding alcohol in 96% sulfuric acid exhibits a singlet at $\tau = 8.02$ p.p.m. and would easily have been detected.

(15) This point is further brought home by an examination of the spectroscopic properties of sulfuric acid solutions of 3,4-dibromo-1,2,3,4-tetra-phenylcyclobutene.¹⁶ The visible spectrum exhibits a maximum at 482 $m\mu$,² similar to that of 11, but with an extinction coefficient of 50,000, less than one-half that of 11. The n.m.r. spectrum in 1:1 thionyl chloride and fuming sulfuric acid exhibits a multiplet extending from $\tau = 1.90$ to 2.55 of an entirely different appearance from those shown in Fig. 1. These differences can be explained either in terms of a rapidly rearranging monocation (iii) or a dication (iv) in which the phenyl groups are hindered from coplanarity as in the trityl carbonium ion.¹⁷



(16) We are grateful to Dr. Freedman for a sample of the dibromide.

(17) R. Dehl, W. R. Vaughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); *J. Chem. Phys.*, **34**, 1460 (1961).

(18) Fellow of the Alfred P. Sloan Foundation.

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BRIAN WEBSTER

RECEIVED AUGUST 29, 1963

Improved Bond Angle Calculations¹

Sir:

Recently one of us published a calculation of the bond angles in some six-membered aromatic ring systems containing carbon and nitrogen atoms.² The bond angles were obtained by evaluating and minimizing the molecular energy as a function of the internal bond angles with the additional restraint that the sum of the six angles be 720°. Apparently we did not impose any conditions relating the bond angles and distances. It was pointed out to us by Coulson³ that we might obtain a better agreement with experiment if we restrict the bond angles to those values only that are compatible with hexagons whose sides are equal to the experimental bond distances. This means that we have to impose a second geometrical constraint on the angles in order to ensure that the six vectors having the experimental bond distances as magnitudes and connecting the adjacent nuclei form a closed hexagon. In order to illustrate this geometrical

constraint we consider pyridine, following the notation of Fig. 2 of ref. 2 and calling the carbon atoms C_β , C_γ , C_δ , etc. We have to impose the condition that C_δ lies directly under N, or, according to Coulson³

$$(\text{NC}_\beta) \sin \frac{1}{2} \alpha - (C_\beta C_\gamma) \sin \left(\frac{1}{2} \alpha + \beta \right) - (C_\gamma C_\delta) \sin \frac{1}{2} \delta = 0 \quad (1)$$

where $(C_\beta C_\gamma)$ is the experimental distance between C_β and C_γ and (NC_β) and $(C_\gamma C_\delta)$ are similarly defined. For pyrimidine and pyridazine we have to impose similar restrictions on the bond angles; for pyrazine, *s*-triazine, and *s*-tetrazine they are automatically fulfilled because of the molecular symmetry. The experimental bond distances in pyridazine are not available so that we took (CC) and (CN) equal to the average values for the other molecules and we chose (NN) in such a way that (CN) is the geometrical average of (CC) and (NN).

The results of the bond angle calculations according to the method of ref. 1 with the inclusion of the geometrical restraint (1) are shown in the last column of Table I. In the first column we have listed the experimental values, insofar as they are available, the second column contains the old results of ref. 2, and the third column shows Coulson's values. The definitions of the angles and the sources of the experimental results may be found in ref. 2.

TABLE I

EXPERIMENTAL AND VARIOUS CALCULATED BOND ANGLES

Molecule	Angle	Exptl. ^a	Kilm-Hameka ^a	Coulson ^b	Present
Pyridine	α	117°	110°	115.0°	114.9°
	β	124	121	124.4	125.0
	γ	118.5	122	119.4	119.0
	δ	118	123	117.0	117.0
Pyrimidine	α	115	111	115.0	114.0
	β	128	124	128.7	130.4
	γ	123	125	121.3	121.2
	δ	116	124	118.6	119.1
Pyridazine	α		113	120.1	119.7
	β		124	124.0	124.1
	γ		123	116.9	116.2
Pyrazine	α	115	112	112.6	112.6
	β	122.5	124	123.7	123.7
<i>s</i> -Triazine	α	113	114	114.4	113.8
	β	127	126	125.6	126.2
<i>s</i> -Tetrazine	α	116	115	116.3	115.0
	β	127	130	127.5	130.0

^a See ref. 2. ^b See ref. 3.

It follows that the inclusion of the geometrical constraint (1) in our calculations improves the agreement between theory and experiment considerably, the mean deviation is reduced from 3.4° to 1.6°. It is interesting to note that this quantity is 1.2° for Coulson's calculations³ and that the mean deviation between our present results and Coulson's values is only 0.7°.

One is automatically drawn to a comparison between Coulson's method and ours since his results agree about equally well with experiment. It may be argued that Coulson's method is the simpler of the two whereas ours gives more insight into the nature of the various effects determining the bond angles. However, we believe that the two methods should rather be considered as supplementary to one another instead of competing. Coulson's approach shows a very convenient simple way to calculate bond angles and our more detailed considerations seem to justify the various assumptions that were made by Coulson.

(1) This work was supported by a grant from the U. S. Army Research Office (Durham) to the University of Pennsylvania.

(2) H. Kim and H. F. Hameka, *J. Am. Chem. Soc.*, **85**, 1398 (1963).

(3) C. A. Coulson, private communication; see also C. A. Coulson, *J. Chem. Soc.*, in press.