total of one proton had been incorporated, and was distributed equally between II and III. This result was reproducible, and the same equilibrium was obtained from the reverse order of addition of II and III, so a true equilibrium has been reached. These results show clearly that II and III have essentially the same acidity, so that the anion of III, which may be symbolized as I, has no special stability because of its cyclic conjugation, and is in that respect *not* an aromatic system.

This conclusion was confirmed by the synthesis of the esters IV and V, which were sufficiently acidic to be titratable against a glass electrode. The lithium salt of II was treated with diethyl carbonate and gave IV, b.p. (bath temp.) 190–200° (0.1 mm.).[7] This compound was soluble in 0.1 *N* NaOH, and recovered unchanged on acidification. The lithium salt of III similarly gave V, m.p. 81–83°.[7] Each of the compounds (IV) and (V) in aqueous acetonitrile solution (0.5 mmole in 9 ml. H_2O, 13.5 ml. CH_3CN) at 26° was titrated with 0.2*N* NaOH against a Beckman Model GS meter with E-2 electrode under nitrogen. The titration of IV was completely reversible with acid, and reproducibly indicated a pK_a[8] of 8.9 ± 0.1. Although V hydrolyzed more rapidly, it could be titrated reversibly over the entire curve and had pK_a[8] 11.1 ± 0.2. Thus again it is apparent that the cyclic anion has no special stability.

The anions from III and V are yellow (V with base gives a new λ_{max} at 370 mμ, $\epsilon \sim 2000$), so cyclic conjugation is spectroscopically detectable. However, it is clear that a system which would be strongly aromatically stabilized with a p-p double bond is not stabilized with a carbanion–sulfone double bond. The failure of such a double bond to complete the aromatic system probably is related to the theoretical arguments which previously have been advanced,[4] but our results demonstrate clearly that previous chemical experience with p-p double bonds cannot be extended unmodified to these new multiple bond systems.

[8] These pK_a's are not referred to pure water solution; *cf.* ref. 1.

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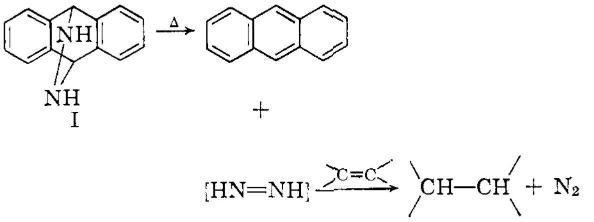
RECEIVED JANUARY 15, 1962

CHEMISTRY OF DIIMIDE. III. HYDROGEN TRANSFER TO MULTIPLE BONDS BY DISSOCIATION OF THE DIIMIDE-ANTHRACENE ADDUCT, ANTHRACENE-9,10-BIIMINE

Sir:

The stereospecific *cis* hydrogenation[1,2] of multiple bonds by a variety of species related to hydrazine can be interpreted most readily in terms of diimide [HN=NH] as the active reducing agent. The systems known to effect such reduction include (1) hydrazine in combination with various oxidizing agents,[2–4] (2) potassium azodiformate[3,5] and (3) p-toluenesulfonylhydrazine.[2,6] To this list may now be added anthracene-9,10-biimine (I) which appears to act according to the equation



As is the case with the previously described systems the diimide precursor I is an effective reductant for azo and mono- and disubstituted olefinic linkages. These examples are illustrative:

Azobenzene ⟶ Hydrazobenzene (2, 99%)
trans-Cinnamic acid ⟶ β-Phenylpropionic acid (3, 81%)
cis-4-Cyclohexene-1,2-dicarboxylic acid ⟶ *cis*-Cyclohexane-1,2-dicarboxylic acid (5, 45%)
Sclareol ⟶ Dihydrosclareol (6, 80%)[7]
3α-Hydroxy-$\Delta^{11,12}$-cholenic acid ⟶ Lithocholic acid (8, 79%)
cis-1,4-Dihydroxy-2-butene dibenzoate ⟶ 1,4-Dihydroxybutane dibenzoate (8, 38%)
Maleic acid ⟶ Succinic acid (3, 87%)
Fumaric acid ⟶ Succinic acid (3, 80%)

The figures in parentheses refer to the number of equivalents of I employed in the reaction and the yield of isolated product. Although no acetylenic substrates were tested, it seems quite likely that the triple bond can be reduced readily.

The reagent I was prepared by careful hydrolysis of the anthracene–diethyl azodiformate adduct[8] in excess 2 *M* sodium hydroxide in ethanol[9] under nitrogen at 25° for 20 hours, then concentration *in vacuo*, dilution with water, acidification with hydrochloric acid, filtration (to remove insoluble impurities) and basification to precipitate I (all operations must be carried out in the cold, yield 78%). The product was obtained as a fine white powder, found: C, 80.46; H, 5.69; N, 13.38, dec. *ca.* 100° with evolution of gas but without melting to give a solid residue of anthracene, identified by mixed m.p. and infrared absorption. In the temperature range of its thermal stability the diimide adduct I is ineffective as a reducing agent for multiple bonds, but at higher temperatures where the rate of dissociation is appreciable reduction of unsaturated linkages occurs. In general the reductions using I as a diimide precursor can be carried out at 50–90° in various solvents; use of ethanol at reflux has proven to be quite satisfactory as a standard technique.

Deuteriation of maleic and fumaric acids was accomplished using I in deuterium oxide–dioxane solution at *ca.* 85° to give stereospecifically *meso*- and *dl*-2,3-dideuteriosuccinic acids, respectively

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[1] E. J. Corey, D. J. Pasto and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

[2] S. Hünig, H. Müller and W. Thier, *Tetrahedron Letters*, **11**, 353 (1961).

[3] E. J. Corey, W. L. Mock and D. J. Pasto, *ibid.*, **11**, 347 (1961).

[4] F. Aylward and M. Sawistowska, *Chem. and Ind.*, 404, 433 (1961).

[5] E. E. van Tamelen, R. S. Dewey and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

[6] R. S. Dewey and E. E. van Tamelen, *ibid.*, **83**, 3729 (1961).

[7] M. M. Janot, *Compt. rend.*, **191**, 847 (1930); **192**, 845 (1931).

[8] O. Diels, S. Schmidt and W. Witte, *Chem. Ber.*, **71**, 1186 (1938).

[9] Prepared by addition of water to ethanolic sodium ethoxide.

(*cis* addition), in accord with the stereochemical results for diimide reduction in other systems.[1]

Thermal decomposition of I at 100° *in vacuo* at the inlet of a mass spectrometer (Consolidated 21-103C, ionizing voltage 13 v., ionizing current 74 μ a.) caused the appearance of peaks at m/e 28, 29 and 30 (of intensity 1, 2 and 16, respectively) the last of which corresponds to the parent mass peak of diimide.[10] Since the m/e 30 peak is not produced from anthracene, hydrazine or nitrogen under our conditions and since this peak is shifted to m/e 32 in the mass spectrum from N^1N^1-dideuteriated I, it appears most probable that we are dealing with diimide as a thermal decomposition product of I.

The experiments described above provide additional evidence for the effective role of diimide in the reduction of multiple bonds and also for the interpretation advanced by Cohen and co-workers[11] to explain the anomalous products from saponification of the cyclopentadiene–diethyl azodiformate adduct.

[10] An m/e 30 peak has been observed previously in the mass spectrum of diimide produced by decomposition of hydrazine or hydrazoic acid in the gas phase: S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).

[11] S. G. Cohen, R. Zand and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961).

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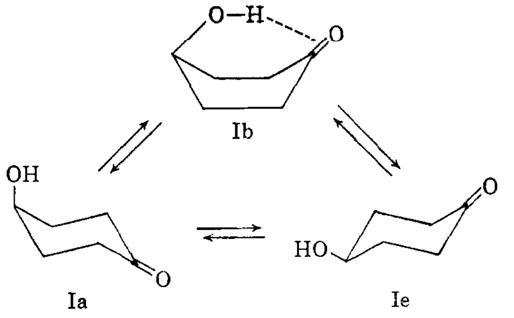
RECEIVED JANUARY 8, 1962

CONFORMATIONS OF 4-HYDROXYCYCLOHEXANONES

Sir:

The conformations of 4-hydroxycyclohexanone (I) include boat conformation Ib, in which intramolecular hydrogen bonding might be possible, as well as chair conformations Ia and Ie. This communication reports that *no* evidence of intramolecular hydrogen bonding in I was detected by infrared spectroscopy. It is concluded that the population of Ib is small.



Examination of a Stuart–Briegleb model of 4-hydroxycyclohexanone suggests that intramolecular hydrogen bonding might occur in conformation Ib between the hydroxyl group and the π electrons of the carbonyl group. The internuclear oxygen-oxygen distance of 2.95 Å., estimated for a Dreiding model of Ib, does not exceed the limits reported[1] for hydrogen bonds of the type O—H····O.[2]

Recently, it has been reported that 4-hydroxycyclohexanone is, perhaps, intramolecularly hydrogen bonded.[3] It is stated that observed infrared absorption at 3425 cm.$^{-1}$ is not inconsistent with an intramolecularly hydrogen bonded OH.[3] Such absorption might also be attributable to the first overtone of the carbonyl stretching vibration.[4] One of these two possibilities can be eliminated by observing the fate of the 3425 cm.$^{-1}$ absorption band when the OH group is transformed into an OD group by deuterium exchange.[4]

The infrared spectrum of a 0.0024 *M* solution of 4-hydroxycyclohexanone (I) in tetrachloroethylene[5] exhibits two absorption bands in the region 3000–4000 cm.$^{-1}$. The concentration dependence of the two bands is consistent with their assignment to monomeric I.[1,3] The first, a strong, sharp band at 3626 ± 2 cm.$^{-1}$, is replaced by a similar band at 2678 ± 4 cm.$^{-1}$ when the hydroxyl hydrogen of I is replaced by deuterium. The second, a weak, broad band at 3427 ± 5 cm.$^{-1}$, is not affected by deuterium exchange; no new band[7] appears near 2530 cm.$^{-1}$. Therefore, the band at 3427 cm.$^{-1}$ is not attributable to the hydroxyl group, but is most probably the first overtone of the carbonyl stretching vibration[8] (fundamental[5] at 1725.5 ± 1 cm.$^{-1}$). The band at 3626 cm.$^{-1}$ is attributable to the OH stretching vibrations of the hydroxyl groups *not* involved in hydrogen bonding.[1]

In the light of the results above for I, a reexamination of the evidence cited[3] for intramolecular hydrogen bonding in 4-hydroxy-4-phenylcyclohexanone (II) was undertaken. A 0.0060 *M* solution of II in tetrachloroethylene[5] exhibits two absorption bands in the region 3200–4000 cm.$^{-1}$. Upon replacing OH by OD in II, a strong band at

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[1] (a) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, California, 1960; (b) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952), and subsequent publications.

[2] As Ib is rotated slightly in either direction toward a twist conformation, eclipsed interactions are reduced, but the hydrogen bond is lengthened. Let Ib represent the small range of non-chair conformations, formed by twisting Ib, in which the oxygen-oxygen distance is less than 3.2 Å.

[3] W. von E. Doering and A. A.-R. Sayigh, *J. Org. Chem.*, **26**, 1365 (1961).

[4] See R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Vol. IX of A. Weissberger's "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 424.

[5] Mr. John Larsen prepared I and II by the reported procedures.[3] The tetrachloroethylene was Matheson, Coleman and Bell, spectroquality reagent, stored over Drierite. Spectra were recorded as previously described.[6] In addition, 1 mm. sodium chloride cells were used with 0.01 *M* solutions in the region 4000–680 cm.$^{-1}$ Calibration of the hydroxyl and carbonyl stretching bands was done by recording with these bands, the atmospheric water vapor absorption in the regions 3760–3560 and 1750–1690 cm.$^{-1}$ at scan speed 7 cm.$^{-1}$/min., plotting 5 or 10 cm.$^{-1}$/cm. with good resolution. Calibration required special attention because of the discrepancies between the frequencies reported here, and some of the values given in ref. 3.

[6] R. D. Stolow, *J. Am. Chem. Soc.*, **83**, 2592 (1961).

[7] The 3626 cm.$^{-1}$ band is shifted by deuteration by the factor $\nu_{OH}/\nu_{OD} = 1.354$. If the 3427 cm.$^{-1}$ band were an O–H band, it would be expected to shift by a similar factor upon deuteration. See ref. 1a, p. 112, and ref. 6.

[8] Further evidence in support of this assignment is provided by the infrared spectrum of cyclohexanone in tetrachloroethylene.[5] Found: carbonyl overtone, 3420 ± 4 cm.$^{-1}$; fundamental, 1720 ± 2 cm.$^{-1}$. Reported:[9] fundamental 1720 ± 1 cm.$^{-1}$. Reported for carbon tetrachloride solution:[10] overtone, 3418 cm.$^{-1}$; fundamental, 1718 cm.$^{-1}$.

[9] L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

[10] H. W. Thompson and D. A. Jameson, *Spectrochim. Acta*, **13**, 236 (1958).