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THE OXIDATIVE PHOTODIMERIZATION OF 2-METHOXYNAPHTHALENE

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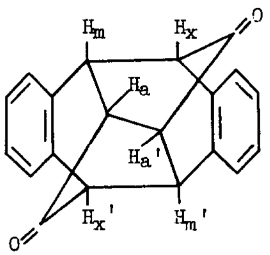
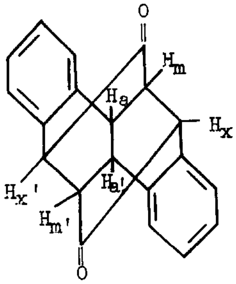
Irradiation of a dilute (ca. 0.01 M) 1:1 aqueous methanolic solution of 2-methoxynaphthalene with ultraviolet light[1] in a pyrex vessel gives more than a 50% yield, based on unrecovered starting material, of 5,6,11,12-tetrahydro-5,12,6,11-[1,2,3,4]butanetetrayldibenzo[a,e]cycloöctene-13,16-dione (I). The infrared spectrum of this unusual dibenzopentacyclic diketone (mp 350° dec, disemicarbazone mp 289°)



I



II

displayed a single strong absorption at 1747 cm^{-1} expected of an unconjugated ketone in a strained ring and aromatic absorption in a pattern indicative of a 1,2-disubstituted benzene. No absorption attributable to a naphthalenic moiety or to a methylene function adjacent to a carbonyl group can be seen. The ultraviolet spectrum [$\lambda_{max}^{CH_3OH}$ 266 mμ (ϵ = 440) 274 (427), 292 (345), sh 310 (207)] further indicates a benzenoid system containing an unconjugated ketone. In addition to the molecular ion ($^m/e$ 286) the major fragmentation observed in the mass spectrum of this diketone corresponds to a loss of one ($^m/e$ 258) and two molecules ($^m/e$ 229) of carbon monoxide. The nmr spectrum (hexafluoroacetone deuterate) consists of three distinct multiplets in the aliphatic and a multiplet in the aromatic regions which integrate in a ratio of 1:1:1:4 demonstrating the symmetric nature of the compound. The splitting of the aliphatic protons (Figure 1) is in good agreement with that of a calculated[2] XMAA'M'X' system in which $J_{MX}=J_{M'X'}=8.0$, $J_{AX}=J_{A'X'}=-1.5$, $J_{AM}=J_{A'M'}=J_{AA'}=10.6$, $J_{A'X}=J_{AX'}=J_{M'X}=J_{MX'}=J_{A'M}=J_{AM'}=J_{MM'}=0$ Hz. The multiplets centered at 3.10, 3.58 and 4.40δ are assigned to the Ha, Hx, and Hm protons respectively; the aromatic multiplet is found centered at 6.90δ. Consideration of its composition and spectral properties reduced the question of the structure of this diketone to a choice between structures I and II, both incorporating previously unknown multicyclic ring systems.

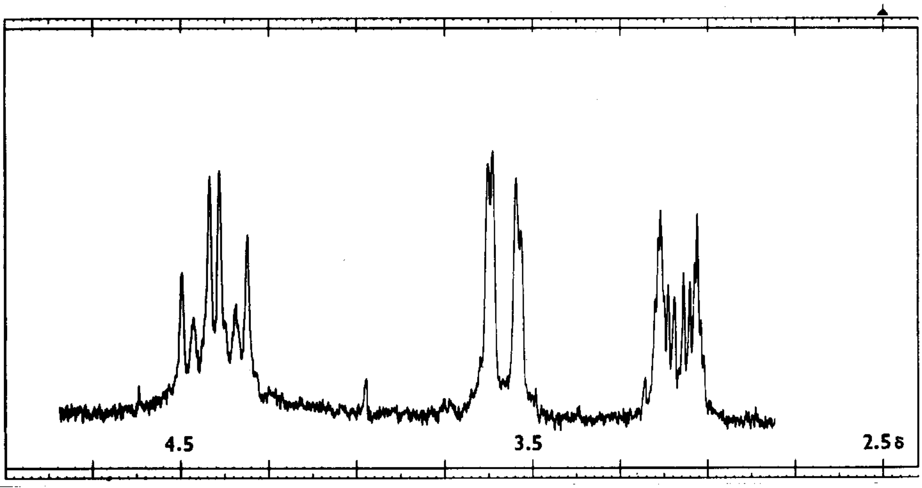
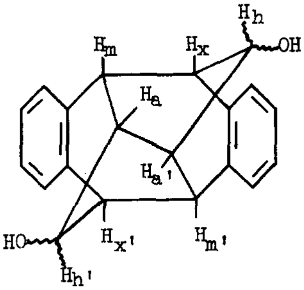
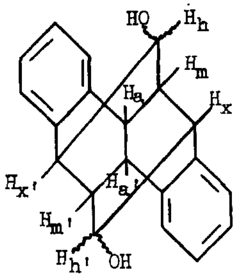


FIGURE 1. ALIPHATIC PROTON REGION OF NMR SPECTRUM (100 MHz) OF DIKETONE DERIVED FROM 2-METHOXYNAPHTHALENE.

Detailed nmr investigation of the single symmetrical dialcohol obtained from lithium aluminum hydride reduction of the diketone permits differentiation between these structures. In the dialcohol III, which would be obtained from reduction of I, the proton H_h attached to the hydroxyl bearing carbon is strongly coupled to both proton H_x and $H_{a'}$, but not to proton H_m. On the other hand, proton H_h in the isomeric dialcohol IV derived from diketone II, is strongly coupled only to proton H_m and $H_{x'}$ and not to H_a. In the nmr spectrum (CD_2Cl_2) of this dialcohol (Figure 2) the octet centered at 4.42δ alone changes (to a quartet) in deuterated methanol allowing assignment of this absorption to H_h. When this 4.42δ region is irradiated, the multiplet at 3.80δ, assigned to proton H_m, is unaffected as predicted for structure III, but not structure IV. In addition the multiplets attributed to protons H_x at 2.48δ and to H_a at 3.36δ collapse to yield a spectrum identical in pattern to that of the diketone precursor verifying the proton assignments.



III



IV

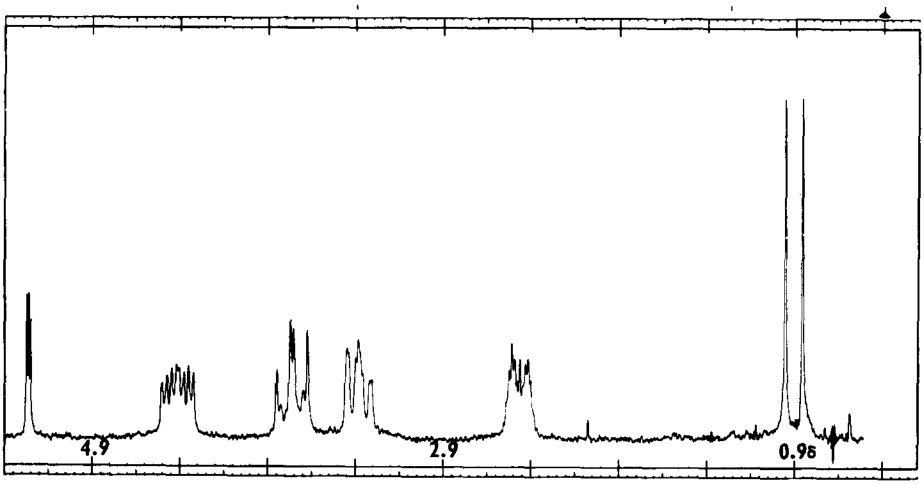


FIGURE 2. ALIPHATIC PROTON REGION OF NMR SPECTRUM (100 MHz) OF DIALCOHOL DERIVED FROM DIKETONE.

Further evidence for structure I was obtained by chemical degradation. The diketone, upon treatment with 45% peracetic acid in acetic acid, was converted in 80% yield to a single, symmetric dilactone (mp 384°, ir carbonyl absorption 1755 cm^{-1} in CH_2Cl_2),[3,4] which was hydrolysed without rearrangement in 2% methanolic potassium hydroxide to a dihydroxydiacid (mp 370° dec).[4] Cis β-hydroxy acids such as that which would be derived from II characteristically undergo dehydrative decarboxylation when refluxed in quinoline in the presence of copper powder.[5] This dihydroxydiacid, however, was recovered unchanged after four hours of such treatment as would be anticipated for a compound derived from I. The diketone I might be conceived as arising from a 4-1', 1-4' dimerization of 2-methoxynaphthalene, coupled with an oxidative 3-3' bond formation. The possibly related photoreaction of 2-alkoxynaphthalenes which occurs in the absence of oxygen is under further investigation. The relationship of these photochemical processes to the photochemical dimerization[6] of some 2-alkoxynaphthalenes at higher concentrations in other solvents is also being examined.

Acknowledgement

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References

1. A Rayonet Reactor (The Southern New England Ultraviolet Company, Middletown, Connecticut) fitted with RPR-3500A° lamps was employed.
2. The calculations were carried out with the LAOCOON III program on an SDS 930 computer.
3. The possible dilactone structures involving migration of a benzylic carbon to oxygen would certainly be preferred to the alternatives resulting from aliphatic carbon migration. c.f., P. A. S. Smith, in "Molecular Rearrangement", Vol. I, P. De Mayo, Ed., Interscience Publishers, New York, New York (1963), p. 585.
4. Elemental analyses and spectroscopic (ir, uv, nmr and mass) data of the degradation products are consistent with either of the proposed series of structures. Significantly, the nmr spectra of these degradation products show an XMAA'M'A' pattern in the aliphatic region similar to that of the original diketone.
5. M. Wilkas and N. A. Abraham, Bull. Soc. Chim. France, 1960, 1196; N. A. Abraham and M. Wilkas, Compt. rend., 248, 2880 (1959).
6. J. S. Bradshaw and G. S. Hammond, J. Am. Chem. Soc., 85, 3953 (1963); J. S. Bradshaw, N. B. Nielson and D. P. Rees, J. Org. Chem., 33, 259 (1968).