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STRAINED SYSTEMS. V.[1]

FURTHER STUDIES ON PHENYL SUBSTITUTED 1-(Δ^2-CYCLOPROPENYL)-3-DIAZOPROPAN-2-ONES AND THE TRICYCLO[2.2.0.0.^{2,6}] HEXANE SYSTEM.

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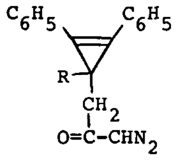
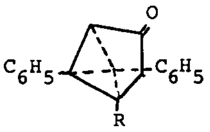
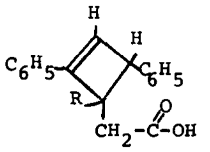
Recent communications by Small[2] and from these Laboratories[3] reported the formation of cyclobutene derivatives (Ia and Ib) from the title compounds (IIa and IIb) by treatment with silver oxide-thiosulfate in aqueous dioxane[2] and by irradiation with ultraviolet light.[3] Since the photolysis of 5,6-diphenyltricyclo[2.1.1.0^{5,6}]hexanone-2 (III) afforded 2,4-diphenylphenol but not Ib[3], we tentatively inferred that the α-ketocarbene generated photochemically



IIa R = C_6H_5
IIb R = H



III



Ia R = C_6H_5
Ib R = H

from IIb led to vibrationally excited III which then underwent the heterolytic cleavage with solvent to afford Ib. However, we felt that additional evidence was necessary to substantiate this view. We further investigated this seemingly unusual reaction and report the result herein.

According to Small's procedure (silver oxide) we prepared her compound (A), m.p. 180°, to which structure Ia was assigned previously.[2] We also found that the same compound A was obtained in comparable yield (approximately 40%) by irradiating IIa in aqueous tetrahydrofuran.

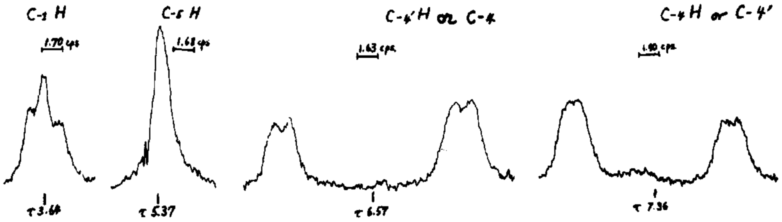
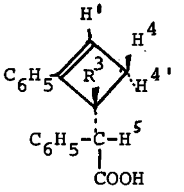


FIG. I. The 100 Mc n.m.r. spectrum of A in $CDCl_3$.

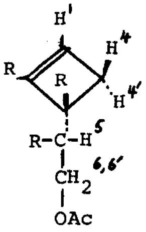
The n.m.r. spectrum (Fig. I, the aromatic region is excluded) of compound A and decoupling experiments showed that protons 4 and 4' constituted an AB type system with $J_{44'} = -12.7$ cps. and these protons coupled with proton 1 ($J_{14} = J_{14'} = 1.2$ cps.), but not with proton 5. The methyl ester of A was reduced with lithium aluminum hydride and the resulting hydroxy compound was converted to its acetate (IV). In the n.m.r. spectrum of IV, signals due to protons 1, 4 and 4' maintained their multiplicities similar to those of A (τ_1 = 3.63, τ_4 = 7.10, τ_4 = 7.54) and the coupling constants remained practically unchanged ($J_{14} \cong J_{14'}$ = 1.3, $J_{44'}$ = -14.5 cps.), whereas proton 5 (τ= 6.00) and two protons 6 and 6' (τ=5.48) introduced by lithium aluminum hydride now constituted an ABB' system ($J_{56} \cong J_{56'}$= 7.1 cps.). The validity of this assignment to these last three protons (5, 6 and 6') was confirmed by the spectrum of the corresponding deutero acetate (V) prepared by substituting lithium aluminum deuteride for lithium aluminum hydride. Compound V showed a singlet at τ = 6.00 but no signal around τ=5.5. Therefore, compound A possesses only one hydrogen attached to carbon α and no hydrogen attached to carbon β with respect to the carboxy group. The above spectral data render structure Ia untenable and suggest formula VIa as the correct



VIa, VIb

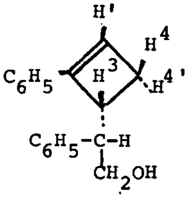
a R = C_6H_5

b R = H

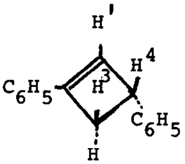


IV

R = C_6H_5



VII



IX

representation of compound A.[4]

Compound B, m.p. 146-8°, prepared from IIb in a fashion similar to that for the corresponding triphenyl derivative A exhibited a n.m.r. spectrum similar to that of A except that the proton replacing the phenyl group of A added some complications. However, decoupling experiments, aided by simple calculations provided the following data:[5] $\tau_1 = 3.72$, $\tau_3 = 6.17$, $\tau_4 = 7.15$, $\tau_{4'} = 7.68$, $\tau_5 = 6.29$, $J_{13} < 0.5$ $J_{14} \cong J_{14'} = 1.3$, $J_{34} = 4.3$, $J_{34'} = 1.5$, $J_{44'} = -14.5$, $J_{35} = 11.25$. Reduction of the methyl ester of B with lithium aluminum hydride and deuteride afforded the corresponding hydroxy compounds VII, (m.p. 91-2) and VIII, respectively. From their n.m.r. spectra, (FIG.II), we obtained $J_{13} < 0.5$, $J_{14} \cong J_{14'} = 1.55$, $J_{34} = 4.3$, $J_{34'} = 1.6$, $J_{44'} = -15.0$, $J_{35} = 6.4$, $J_{56} \cong J_{56'} = 6.6$. In view of the coupling constants and the chemical shifts reported for 2,4-diphenylcyclobutene[6] (IX) ($J_{1,3} < 1.0$, $J_{14} = 1.3$, $J_{34} = 4.9$, $J_{3'4} = 1.9$, $J_{44'} = -12.3$)[4] the spectra of A and B are in complete agreement with structure VIa and VIb, respectively. We have examined several other spectra of cyclobutenes, in particular, cis- and trans- 3,4-substituted derivatives

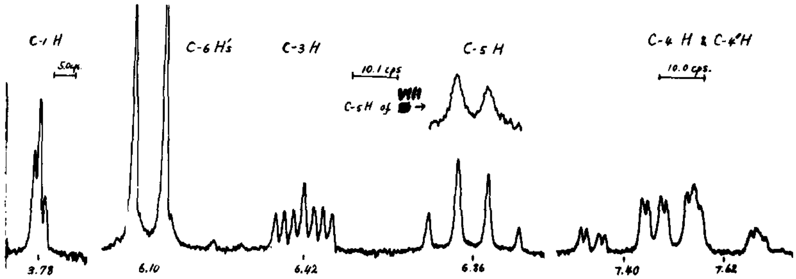
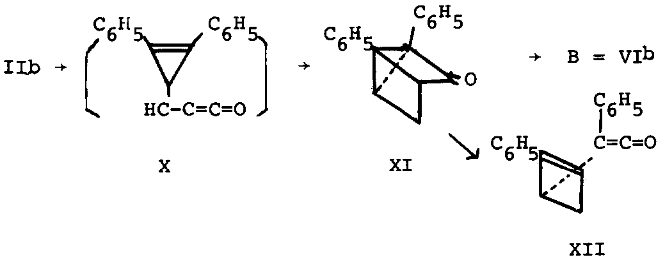


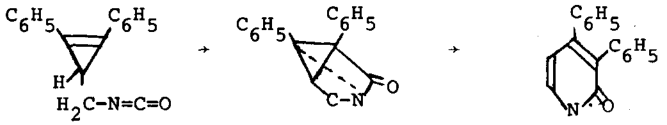
FIG. II. The 100 Mc. n.m.r. spectra of VII and observed the constancy of these coupling constants. Recently Borcic and Roberts reported the analysis of the spectrum of cyclobutene itself.[7] Their assignment of signals to each proton is arbitary and from our results it appears that the assignment to the cis- and trans- aliphatic protons should be reversed and that to the 1,3 and 1.5 protons should be corrected to 1,5 and 1,3.

Having established the structures of A and B, we propose the following mechanism for the rearrangement. Compound IIb first undergoes the normal Wolff type rearrangement with either ultraviolet light or silver oxide to provide ketene (X) which cyclizes intramolecularly. The resulting tricyclo[2.2.0.$0^{2,6}$]hexanone (XI) either reacts directly with protonic solvents or is rearranged to ketene (XII) which affords the product. In support of this mechanism we isolated XI (a major product) and XII when the photolysis of IIb was carried out in anhydrous tetrahydrofuran. Although XI and XII were not obtained in an analytically pure state due to their sensitivity to moisture, XI and XII were characterized by their spectral data. XI: $\lambda_{max.}^{CHCl_3}$ 5.64μ, n.m.r., 10 aromatic protons around τ 2.7, no olefinic protons, 4 aliphatic protons, complex multiplets at τ = 6-6.5 and 7.4-8.0. XII: $\lambda_{max.}^{Ether}$ 254 mμ (log ε 4.2), $\lambda_{max.}^{CHCl_3}$ 4.78μ, n.m.r., 10 aromatic protons around τ = 2.8, one proton, singlet, τ = 3.74, one proton, quartet, τ = 6.29 and two AB protons, broad quartet, τ = 7.22, 7.69. Compound XI and XII provided B upon treatment with water and when deuterium oxide was utilized, one deuterium was introduced into the expected position of B. Thus the photolytic or silver-



catalyzed reaction of IIa and IIb, previously considered to be unusual, is a sequence of normal reactions. The isolation of XI now provides a new means for the synthesis of the tricyclo[2.2.0.0^{2,6}]hexane system[9] with a keto function useful for studies of the system.

An intramolecular cycloaddition analogous to the above case was observed for the isocyanate corresponding to ketene (X). The acid azide (XIII), m.p. 80° (decomp.), prepared from (Δ^2-2,3-diphenylcyclopropenyl)acetyl chloride and sodium azide, underwent rearrangement slowly but quantitatively at 40° to provide isocyanate (XIV), $\lambda_{max.}^{Ether}$ 316 mμ, (log ε, 4.53) (diphenylcyclopropene chromophore). Compound XIV was converted on treatment with ammonia at 0° to the corresponding urea, m.p. 188-189°. However, when freshly prepared XIII was treated with boiling ethanol, the corresponding urethane was only a minor product (less than 15% yield) and there was obtained in 60-70% yield a new compound (XV), $C_{17}H_{13}NO$, m.p. 284-284.5°, mol. wt. 251 (thermoelectric osmometer), $\lambda_{max.}^{MeOH}$ 236 mμ (log ε 4.26), 320 (3.88), $\lambda_{max.}^{KBr}$ 6.15 μ. The ultraviolet and infrared spectra suggested that XV was a diphenyl-α-pyridone. The n.m.r. spectrum showed the presence of two protons at $\tau=3.39$ and $\tau=2.34$ ($J=6.2$ cps.) in addition to a broad signal due to N-H and a broad singlet at $\tau = 2.8$ (two phenyl's). Therefore, the two protons are located at ortho positions.[10] Since XV was proven not to be 5,6-diphenylpyridone, m.p. 272-273°, $\lambda_{\max.}^{\mathrm{MeOH}}$ 219 mμ, (log ε 4.25), 265 (4.18), 329 (3.83)[11] nor 3,6-diphenylpyridone,[12] compound XV must be 3,4-diphenylpyridone. Although it seems reasonable to postulate XVI as an intermediate in the formation of XV, the complete bond formation between the nitrogen and C-2 of XVI is not



XIV XVI XV

necessarily required.[13]

Acknowledgement: The authors are grateful to the National Research Council of Canada for financial support.

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2. A. Small, ibid., **86**, 2091 (1964).
3. S. Masamune and N. T. Castellucci, Proc. Chem. Soc., 298 (1964).

4. As to the stereochemistry of C_4-H and $C_{4'}$-H, see: S. Masamune, Tetrahedron Letters, 945 (1965).

5. Due to the misassignment of the n.m.r. signals, the coupling constants reported previously[3] for the corresponding methyl ester of V should be corrected. The incorporation of two deuterium atoms into the methyl ester[3] have now been found to be irreproducible.

6. The numbering is purposely changed to be in accord with those of VIa and VIb.

7. S. Borcic and J. D. Roberts, J. Am. Chem. Soc., **87**, 1056 (1965).

8. In the case of the photolysis of Va in tetrahydrofuran only an intermediate corresponding to XII was isolated.

9. The parent compound, tricyclo[2.2.0.$0^{2,6}$]hexane was prepared by: D. M. Lemal and K. S. Shim, ibid., **86**, 1550 (1964).

10. Y. Inubushi et al., Tetrahedron **20**, 2007 (1964).

11. A. D. Campbell, I.D.R. Stevens: J. Chem. Soc., 959 (1956).

12. The carbonyl group of XV was removed by treatment with phosphorus oxychloride, followed by dehalogenation to afford a diphenyl pyridine, m.p. 113°, molecular ion, 231, which was found not to be 2,5-diphenyl pyridine, m.p. 174-175°, (R. Wiley et al., J. Org. Chem., **23**, 280 (1958). The melting point of 2-chloro-3,4-diphenyl pyridine was 145-146°. These experiments were performed by Dr. Ch. Egli of these Laboratories.

13. E. Chandross and G. Smolinsky, Tetrahedron Letters, 19 (1960).