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STRAINED SYSTEMS. III. BOND CLEAVAGE REACTIONS OF TRICYCLO[1,1,1,$0^{4,5}$]PENTANE AND TRICYCLO[2,1,1,$0^{5,6}$]HEXANE SYSTEMS.

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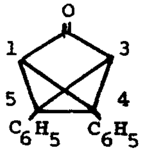
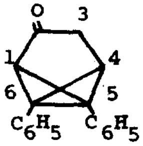
4,5-Diphenyltricyclo[1.1.1.$0^{4,5}$]pentanone-2 (I) exhibits a very high $^{13}C_1$-H coupling constant, 190 c.p.s.,* showing that great strain is involved in this system.[1] In contrast, the size of this $^{13}C_1$-H coupling constant is substantially decreased to 171 c.p.s.[2] in the next homolog, 5,6-diphenyl-



I



II

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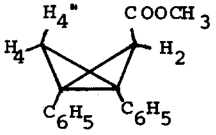
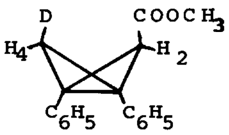
* The corresponding benzoyloxy compound, m.p. 108°, obtained from I with lithium aluminum hydride followed by benzoylation showed very similar coupling constants for both $^{13}C_1$-H and H_1-H_3 (189 c.p.s. and 13.5 c.p.s.). Therefore, the keto group of I has no influence on the magnitude of these coupling constants.

tricyclo[2.1.1.0^{5,6}]hexanone-2. (II).[3,*] We have observed remarkable differences in reactivity of the two systems and wish to report bond cleavage reactions which are undoubtedly caused by the large strain energy in the former system.

Treatment of I with 0.07 N KOH in a mixture of water, t-butanol and tetrahydrofuran (1:4:10) at room temperature for 3 hours provided an acid (III), $C_{17}H_{14}O_2$, m.p. 86-87° (decomp.), in quantitative yield. The corresponding methyl ester (IV),[**] $C_{18}H_{16}O_2$, m.p. 67-68°, showed the following spectral properties: $\lambda^{MeOH}_{max.}$ 270 mμ(log ε 3.95) n.m.r., a doublet at τ=6.01(H_2), a quartet at 7.12 (H_4), and a doublet at 7.33 (H_4') in addition to phenyl and methoxy absorption. This spectral assignment is based on the disappearance of the signal at 6.01 upon treatment of IV



IV



IVa

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[*] Physical properties of II are: m.p. 133°, $\lambda^{Chl.}_{max.}$ 1745 cm^{-1}, $\lambda^{MeOH}_{max.}$, 255 mμ(log 4.08), n.m.r., a singlet at τ = 7.96 (two H_3's), a broad singlet at 2.90 (10 aromatic H's) and two typical AB type doublets at 6.62 and 6.78 (H_1 and H_4). $|J_{1,4}|$ is 5.1 c.p.s.

[**] This methyl ester (IV) was also obtained directly from I with sodium methoxide in methanol.

with t-butoxide in t-butanol-d.* The coupling constants are $|J_{24}| = 4.4$ c.p.s. and $|J_{44'}| = 1.7$ c.p.s.

When the proton source in the reaction medium was replaced with deuterium, the sole product was methyl ester (IVa) deuterated stereospecifically at C_4 of IV. Compound IVa showed a doublet at $\tau = 7.12$ but no signal at 7.33, supporting the above assignment.

While the cleavage of non-enolizable ketones usually requires drastic treatment with strong base,[4] the facile bond cleavage of I with hydroxide ion must be caused by the internal strain. The 100% retention of asymmetry at carbon 2 of IVa as evidenced by its n.m.r. spectrum is reasonable in view of the high ratio of exchange rate over racemization observed for cyanocyclopropanes.[5]

In contrast to the behavior of I, compound II underwent only deuterium exchange at carbon 3 on treatment with sodium methoxide in a mixture of methanol-d and tetrahydrofuran (1:1). The half life of this exchange was 2 1/2 hours.

Although 1,3-diphenyl (or di-ethyl)-4-carbomethoxy-bicyclobutane-2-carboxylic acid (V)[2] is thermally stable to

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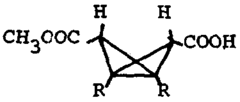
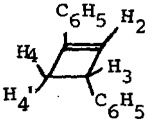
* The half life of this deuterium exchange reaction was approximately 20 hours. The rate of the deuterium exchange decreases in the order: diphenylcyclopropanecarboxylate>diphenylbicyclobutanecarboxylate>diphenylcyclopropenecarboxylate. R. Breslow and P. Dowd, J. Amer. Chem. Soc. **85**, 2729 (1963).

200°, compound III was readily decarboxylated at 85° to afford quantitatively a cyclobutene (VI), $C_{16}H_{14}$, m.p. 64-65°, $\lambda_{max.}^{MeOH}$ 254 mμ (log ε 4.26), n.m.r., a multiplet

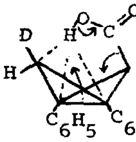


V

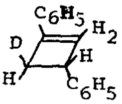


VI

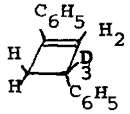
at τ =2.8 (10 aromatic H's), a doublet at 3.56 (H_2), a multiplet at 6.08 (H_3), two quartets at 6.78 (H_4) and 7.44 (H_4'). The last two signals constitute an AB type system and the signal at 7.44 is assigned to the proton <u>cis</u> to the phenyl group at carbon 3 on the basis of the diamagnetic anisotropy of the latter group.[6] Decoupling and deuterium exchange (<u>vide infra</u>) experiments provided the following coupling constants: $|J_{23}|$ = 1.3 c.p.s., $|J_{34}|$ = 4.9, $|J_{34'}|$ = 1.9, $|J_{44'}|$ = 12.3. J_{24} <1.0. Decarboxylation of compound IIIa gave a monodeuterocyclobutene, the n.m.r. spectrum of which exhibited two broad singlets at τ= 6.08 and 7.44 but no signal at 6.78. Therefore, this compound is formulated as shown in VIa. Considering the unique stereochemistry of the acidic proton of carboxylic acid IIIa with respect to the bicyclobutane ring, one can easily rationalize this extremely facile decarboxylation of IIIa as contrasted with carboxylic acid V. Furthermore, introduction of a deuterium atom at



IIIa



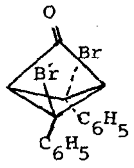
VIa



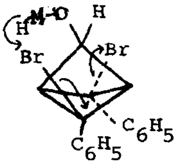
VIb

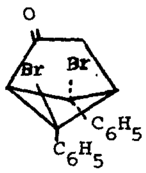
carbon 3 of VI, as shown in VIb, was effected by decarboxylating III in which the acidic proton was replaced with deuterium. The assignment of stereochemistry to the deuterium atom of VIa and VIb is thus consistent both with the above mechanistic interpretation of decarboxylation and with the spectral interpretation based on the diamagnetic anisotropy of the phenyl group at carbon 3.

Facile bond cleavage reactions were not limited to bond C_1-C_2 and bond C_1-C_5 (hydrogenation)[1] of I. Bond C_4-C_5 of I and bond C_5-C_6 of II were readily cleaved to provide a bicyclo(1,1,1)pentane (VII) and a bicyclo(2.1.1)-hexane (VIII), respectively.



VII





VIII

Treatment of II with one mole of bromine either at room temperature or at -35° afforded, in 80% yield, a dibromide (VIII), $C_{18}H_{14}OBr_2$, m.p. 147-148°, $\lambda^{\text{Nujol}}_{\text{max.}}$ 1780 cm^{-1}, * n.m.r., two doublets at 5.41 and 5.54 (H_1 and H_4)

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* The enhancement of carbonyl frequency in VIII can be explained by two effects, i) the direction of the polarized C-Br bond is almost parallel with the C=O bond and ii) the opening of bond C_5-C_6 of II would introduce more distortion of bond angles C_5-C_1-C_2 and C_3-C_4-C_5.

and a singlet at 6.4 (2 H_3) and phenyl absorption. Reduction of VIII with lithium aluminum hydride afforded in 20% yield (n.m.r. spectral analysis) a hydroxy compound, m.p. 92-93°, identical with that obtained directly from II with the same reagent.[7] In the case of I, the dibromo compound VII corresponding to VIII was very unstable and characterized only by its n.m.r. spectrum at -35°, a singlet at 5.2 (2H, the bridge head hydrogens) and a broad singlet at 2.8 (10 aromatic hydrogens). The formation of 5,6-diphenyltricyclo[1.1.$10^{4,5}$]pentanol-2 (overall yield, 70%) upon treatment of I with bromine in tetrahydrofuran at -35°.* followed by lithium aluminum hydride,[7] confirms the existence of intermediate VII. The reaction must have proceeded in a fashion similar to that for II. The stereochemistry of dibromide VII must favor this unusual bond formation with lithium aluminum hydride.

The above-mentioned reactions have provided us with many interesting strained systems. We will discuss in a separate paper the magnitude and sign of the long range coupling constants in relation to the geometry and bond character of the systems.

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* We have confirmed the disappearance of the characteristic n.m.r. absorptions of I and observed the decoloration of bromine.

Acknowledgement: The author is grateful to Dr. K. Fukumoto for his skillful assistance and to the National Research Council of Canada for financial support.

References:

(1) S. Masamune, J. Amer. Chem. Soc., 86, 735 (1964).

(2) S. Masamune, unpublished results.

(3) S. Masamune and N. T. Castellucci, Proc. Chem. Soc., 298 (1964). This reference is Part II of Strained Systems.

(4) For instance, see: D. J. Cram, K. R. Kopecky, F. Hauck, and A. Langemann, J. Am. Chem. Soc., 81, 5754 (1959).

(5) H. M. Walborsky, A. A. Youssef and J. M. Motes, ibid., 84, 2466 (1962).

(6) L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, pp. 125 -128, Pergamon Press, London, (1959), C. E. Johnson, Jr. and F. A. Bovey, J. Chem. Physics, 29, 1012 (1958). We have used Dreiding models to obtain approximate sizes of σ av.

(7) This experiment was carried out by Dr. K. Fukumoto of this Laboratory.