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FORMATION OF A CYCLIC HEMIKETAL FROM THE CHROMIC ACID OXIDATION OF A TRICYCLIC HYDROCARBON

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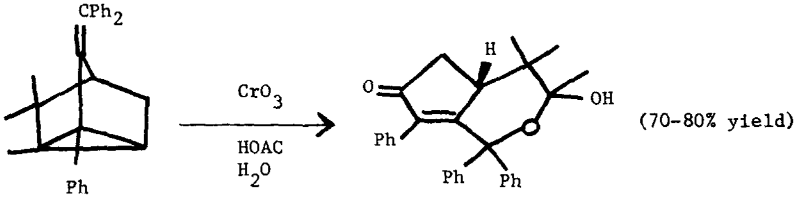
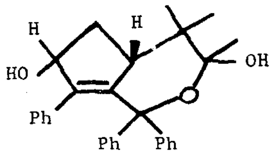
Berson(1) has noted that there is only a relatively small group of reactions involving formal cleavage of a bicyclo [2.2.1] heptane. We wish to report an unusual example of such a cleavage in the reaction of 2-phenyl-3-diphenylmethylenetricyclene(I) (2) with chromium trioxide in acetic acid. This novel oxidation involves the cleavage of both the tricyclic and bicyclic systems to give the cyclic hemiketal, II, $C_{29}H_{28}O_3$, mp 211-212°.(3)



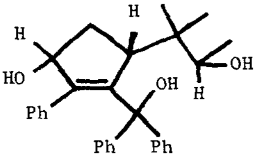
I II

Spectral data in support of II include IR (OH stretch, 3600 cm^{-1}; carbonyl stretch, 1713 cm^{-1}, UV (λmax 240 mμ, log ε 4.18), and NMR (phenyl multiplets 7.2-7.4 ppm, 5 H's, and 6.3-6.8 ppm, 10 H's; bridgehead H, 3.73 ppm; CH_2, 2.40 ppm; OH, 1.97 ppm; non-equivalent methyls, 1.40 ppm, 1.09 ppm, 1.00 ppm).

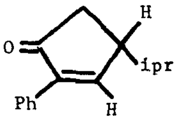
Chemical reactions in support of II include $NaBH_4$ reduction to the diol III and $LiAlH_4$ reduction to the triol IV. Distinguishing features in IV's NMR spectrum are the methyl doublet at 0.92 ppm and the coinciding quartet at 4.02 ppm (J = 6.5 cps) indicating cleavage of the cyclic hemiketal moiety. Refluxing II with KOH-EtOH gave benzophenone, potassium acetate, and 2-phenyl-4-isopropyl-2-cyclopenten-1-one(V), mp 51-52°.



III



IV

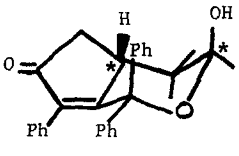


V

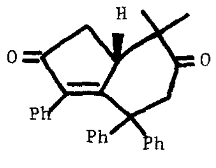
Structure V was assigned by virtue of its spectral properties and by comparison of these properties with those of 2-phenyl-2-cyclopenten-1-one VI.(4) The UV spectra of V and VI respectively showed λmax 223 mμ, log ε 4.45, λmax 263 mμ, log ε 4.11; and λmax 223 mμ, log ε 4.42, λmax 259 mμ, log ε 4.07. The 2,4-DNP's of both V and VI showed λmax 385 mμ, log ε's 4.26 and 4.32 respectively. Both carbonyl stretching vibrations in the IR were at 1711 cm^{-1} (singlets). In the NMR the olefinic protons of both absorbed at _ca._ 7.70 ppm, superimposed on the _ortho_ phenyl protons. All spectral properties markedly differ from those of 3-phenyl-2-cyclopentenone(5,6) and other 3-substituted-2-cyclopentenones(7,8) but are in accord with 2-substituted-2-cyclopentenone data.(7)

The isopropyl group was assigned to the 4-position as follows: The 1410 cm^{-1} IR absorption band of V (and VI as well) assigned to the "adjacent methylene" (-CO-CH$_2$-) absorption band(9) disappeared after dideuteration. Analysis of the dideutero derivative's NMR spectrum was quite simple relative to V. The relative intensity of the 3-proton absorption at 7.70 ppm was enhanced with a detectable $J_{3,4}$ = 2.6 cps. The 4-proton appeared at 2.57 ppm (doublet pair) with $J_{4,\text{isopropyl H}}$ = 6.2 cps. The _tert._ isopropyl H absorbed at 1.71 ppm as an octet (n + 1 rule) with $J_{CH_3,\text{isopropyl H}}$ = 6.6 cps.

The asymmetric bridgehead carbon in II suggests the possibility of two diastereomers in the formation of the new asymmetric center at the ketal ring carbon. However, the preponderance of only one diastereomer IIa is expected, due to the greater preference of the methyl group to occupy the equatorial position. In line with this assignment are the OH---π bond at 3600 cm^{-1}(IR) and the unusual downfield bridgehead H absorption (NMR) of 3.73 ppm (the corresponding H in V absorbs at 2.57 ppm), which may be due to the combined electrostatic effect of the axial hydroxyl group and the anisotropic deshielding of the axial phenyl ring.



IIa



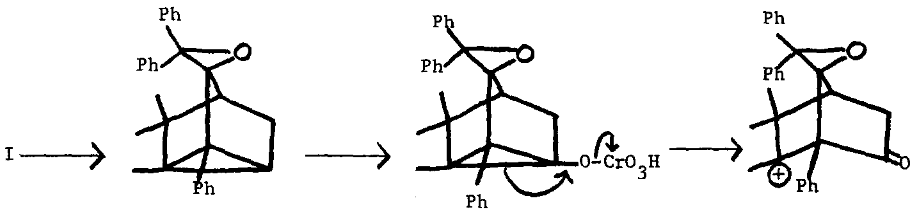
VII

Dehydration of II in acetic acid (H_2SO_4 cat.) gives the diketone VII (optically active), mp 167-168°. Refluxing VII with KOH-EtOH gives inactive diketone, mp 201-202°, apparently due to racemization of the lone asymmetric center.

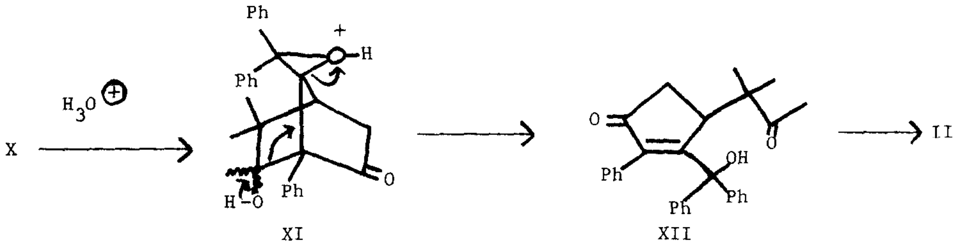
In all NMR spectra of triphenyl compounds related to II, the protons of two phenyl rings appear upfield relative to the third. In conformation IIa the cyclopentenone phenyl and the equatorial phenyl of the hemiketal ring are eclipsed, and their parallel planes mutually shield one another's protons. Consequently the plane of the cyclopentenone phenyl ring is nearly perpendicular to the plane of its ring, and the UV absorption at 240 mμ is comparable to that of an α,β-dialkyl substituted cyclopentenone.(7)

The o-anisyl analog of II is especially interesting. Its NMR spectrum shows two methoxy methyl signals (3.58 ppm and 3.79 ppm) and four methyl signals (1.48 ppm, 1.18 ppm, 1.09 ppm, 1.06 ppm) in the integral ratio of 1.5:1.5:3.0:1.5:1.5:3.0. The introduction of the o-methoxy group leads to the property of atropisomerism.(10) Restricted rotation of the o-anisyl rings leads to a 1:1 mixture of diastereomers with the methoxy "up" (syn to axial phenyl) and methoxy "down" (anti to axial phenyl). The anti methoxy orientation is sufficiently close to the axial CH_3 to cause it to absorb at a different chemical shift position relative to the axial CH_3 of II.

A proposed mechanism for the conversion of I to II presumably involves the epoxide VIII since VIII also gives II under identical reaction conditions. Epoxide formations in the reactions of hindered olefins with chromic acid are known.(11) Accompanying the formation of VIII, and in accord with the mechanisms(12) of the chromic acid oxidation of hydrocarbons, may be tertiary hydrogen abstraction to give chromate ester IX, followed by stepwise cleavage of the tricyclic and bicyclic systems resulting in the ultimate formation of II.



VIII IX X



Footnotes and References

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