hydroxyl absorption at 3250–3325 cm^{-1} and no carbonyl absorption: $\lambda_{max}^{CH_3CN}$ 242 mμ (ε 20,5000), 312 (14,400), 358 (5110).

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.26; H, 6.28; N, 3.79. Found: C, 81.09; H, 6.36; N, 3.85.

B. From 3,3-Diphenyl-2-morpholinoacrylophenone (9).—To a solution of 0.70 g (0.0019 mol) of **9**[4] in 30 ml of anhydrous benzene was added 0.25 ml (0.002 mol) of boron trifluoride etherate. The solution was stirred for 2 hr at room temperature and then the solvents were distilled off under reduced pressure. The off-white solid residue was collected, washed once with 1% sodium hydroxide solution, twice with water, and twice with cold ethanol. Recrystallization (charcoal) from ethanol provided white crystals, 0.25 g (36%), of **10**, mp 198–199°. A mixture melting point with a sample of **10** prepared from **11** and phenyllithium was undepressed, and the infrared spectrum of the product was superimposable on that of **10** prepared by procedure A above.

2-Bromo-1,3-diphenyl-3-methoxyindene.—A solution of 1.00 g (0.0024 mol) of **4** in 20 ml of methanol was refluxed for 10 min. On cooling, 2-bromo-1,3-diphenyl-3-methoxyindene precipitated as large, colorless crystals, 0.80 g (95%), mp 96–96.5°. The nmr spectrum ($CDCl_3$) showed a complex multiplet at τ 2.35–2.95 (14 aromatic H) and a singlet at 6.88 (3 methyl H); uv $\lambda_{max}^{CH_3OH}$ 234 mμ (ε 31,300), 293 (5600), and 309 sh (4000).

Anal. Calcd for $C_{22}H_{17}BrO$: C, 69.87; H, 4.51; Br, 21.19; OCH_3, 7.69. Found: C, 69.72; H, 4.53; Br, 21.17; OCH_3, 8.12.

3-Acetoxy-2-bromo-1,3-diphenylindene.—A mixture of 2.0 g (0.0047 mol) of **4**, 0.772 g of anhydrous sodium acetate and 10 ml of acetic anhydride was heated under reflux for 1.5 hr. After cooling, the solution was poured into 150 ml of water and extracted with ether. The ether extract was washed with water and dried ($CaSO_4$). Evaporation of the solvent left a brown oil that was crystallized by triturating with petroleum ether (bp 60–70°). Recrystallization from petroleum ether provided 1.37 g (72%) of 3-acetoxy-2-bromo-1,3-diphenylindene, mp 117–118° (lit.[8] mp 115–117°). This compound was identical (mixture melting point, infrared spectra) with a sample prepared according to the procedure of Weiss and Luft[8] by the action of phenylmagnesium bromide on 2-bromo-1-phenyl-indenone and treatment of the crude 2-bromo-1,3-diphenyl-3-hydroxyindene with sodium acetate and acetic anhydride.

Registry No.—**9,** 13118-12-2; **10,** 18742-06-8; 2-bromo-1,3-diphenyl-3-methoxyindene, 18742-07-9.

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Nuclear Magnetic Resonance Spectra of Exocyclic Methylene Epoxides

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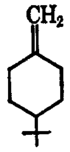
Carlson and Behn have reported[2] nmr data for epimeric epoxides derived from olefins I–IV. While no correlation was found between the chemical shift of the epoxide methylene protons and the pseudoaxial or pseudoequatorial character of the methylene group, the half band width of the methylene signal (singlet) was shown to be larger (1.23–1.61 *vs.* 0.14–0.16 cps) for the pseudoaxial methylene epoxides. This difference in half band width was ascribed to the long-range coupling of the epoxide methylene groups with the immediately adjacent methylene protons of the cyclohexane ring, the theoretical coupling constants[3] for pairs of epoxides being in accord with the observed half band widths.



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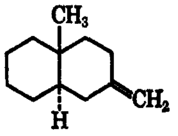

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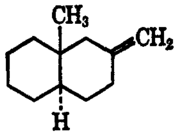

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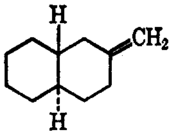

IV

We wish to report the nmr data for a series of exocyclic methylene epoxides in the steroid series (see Table I). For the epoxides[4] derived from 3-methylenecholestane, in which the environment of the epoxide function is similar to the limited range of structures examined by Carlson and Behn, the same correlation of large half band width and pseudoaxial epoxide methylene group was observed. However, for epoxides where the cyclohexane ring environment was less symmetrical, namely for the epoxides[4] derived from 3β-acetoxy-6,-6′-methylenecholestane, 3β-acetoxy-7,7′-methylenecholestane and 3β-acetoxy-12,12′-methylenetigogenin, the pattern of data was significantly more complicated. For these epoxides the epoxide methylene protons gave rise to an AB quartet, although for the 12α,12′ epoxide the central components of the quartet were not completely separated. Again there was no correlation between the chemical shift of the epoxide methylene proton signals and the pseudoaxial or pseudoequatorial character of the methylene group. A marked pattern was discernible in the half band widths of the components of the AB quartet and the orientation of the epoxide methylene group. While the half band widths of the upfield pair of signals of the AB quartet were within the range 0.81–1.41 cps (tending to the upper limit for pseudoaxial cases, and to the lower limit for pseudoequatorial epoxide–methylene groups), the half bands widths of the downfield pair of signals were markedly dependent upon the orientation of the methylene epoxide protons. For compounds with a pseudoequatorial methylene group the downfield pair of signals had half band widths within the range 0.94–1.46 cps, in contrast to the pseudoaxial methylene groups which gave downfield signals with half band widths over the wide range 2.14–3.50 cps.

It seems probable that this marked increase in half band widths for the downfield proton *only* of a pseudoaxial epoxide methylene group must reflect long-range coupling of the downfield proton additional to that considered by Carlson and Behn, in accounting for the difference between pseudoaxial and pseudoequatorial methylene groups in the systems which they examined. It should be noted for the upfield proton no simple pattern of half band widths is discernible in terms of the pseudoaxial or pseudoequatorial nature of the group.

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(1) To whom correspondence should be addressed.

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(3) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

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TABLE I

Compound	Position of CH_2	Signal	Chemical shift, ppm	$W_{h/2}$,[a] cps
3α,3′ epoxide[b]	Equatorial	Singlet	2.40	0.40 ± 0.05
3β,3′ epoxide[b]	Axial	Singlet	2.34	1.37 ± 0.09
6α,6′ epoxide[b]	Axial	Quartet	2.28	1.35 ± 0.02
			2.36	1.41 ± 0.05
			2.50	2.16 ± 0.05
			2.58	2.14 ± 0.07
6β,6′ epoxide[b]	Equatorial	Quartet	2.03	0.81 ± 0.07
			2.11	0.90 ± 0.06
			2.56	1.00 ± 0.05
			2.63	0.94 ± 0.05
7α,7′ epoxide[b]	Equatorial	Quartet	2.11	1.06 ± 0.06
			2.18	1.07 ± 0.08
			2.97	1.46 ± 0.05
			3.04	1.36 ± 0.03
7β,7′ epoxide[b]	Axial	Quartet	2.13	1.16 ± 0.04
			2.21	1.27 ± 0.04
			2.58	3.20 ± 0.06
			2.66	3.20 ± 0.03
12α,12′ epoxide[c]	Equatorial	Quartet	2.43	1.05 ± 0.08
			2.51 2.54	Peaks merged
			2.61	1.20 ± 0.09
12β,12′ epoxide[c]	Axial	Quartet (?)	2.40	0.96 ± 0.04
			2.47	0.99 ± 0.06
			2.93 2.96	3.48 ± 0.05
			3.00 3.03	3.50 ± 0.05

[a] $W_{h/2} = (CH_2O)_{h/2} - (TMS)W_{h/2}$. The average deviation is that for the experimentally measured $W_{h/2}$. All spectra were measured on a Varian A-60 spectrometer at a 0.2-cps sweep time, 50-cycle sweep width, a filter band width of 4, and radiofrequency field setting of 0.04. [b] The samples were 20% w/v in carbon tetrachloride containing 1% TMS. [c] The samples were 20% w/v in chlorofor containing 1% TMS.

The additional coupling of the downfield proton for the pseudoaxial epoxide methylene group in the 12β,12′ epoxide is reflected in the appearance of the downfield proton as a poorly resolved quartet.

Registry No.—3α,3′ epoxide, 18744-05-3; 3β,3′ epoxide, 18744-06-4; 6α,6′ epoxide, 18744-07-5; 6β,6′ epoxide, 18744-08-6; 7α,7′ epoxide, 18744-09-7; 7β,7′ epoxide, 18744-10-0; 12α,12′ epoxide, 4965-90-6; 12β,12′ epoxide, 4965-91-7.

The Cycloaddition of Diphenylketene to 2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane

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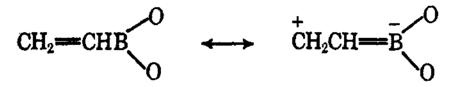
The interest in cycloaddition reactions of ketenes has recently received attention in regard to mechanism.[2-6] Since there have been no reports of electrophilic olefins[7] undergoing a cycloaddition reaction to diphenylketene, we thought it of interest to study the cycloaddition of diphenylketene to a vinylborono compound.



$$CH_2{=}CHB\begin{matrix}O\\O\end{matrix} \longleftrightarrow \overset{+}{C}H_2CH{=}\overset{-}{B}\begin{matrix}O\\O\end{matrix}$$

Vinylborono compounds are unusual in that a partial delocalization of the π electrons to a vacant 2p orbital is opposed by an electron-donating inductive effect.[8] Thus diphenylketene and 2-vinyl-4,4,6-trimethyl-1,3,-2-dioxaborinane (VTDB)[9] were heated at 110° for 360 hr to give a 26% yield of 2-(2′,2′-diphenylcyclobut-3′-on-1′-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (1) (eq 1).

Compound 1 had the characteristic infrared absorption of a cyclobutanone carbonyl at 5.63 μ (Nujol). The nmr spectrum of 1 (CCl_4, TMS) gave the typical AB portion of an ABX spectrum which consisted of two overlapping quartets[10] centered at τ 7.05 (a, b) ($J_{ab} = -17.0$ cps, $J_{ac} + J_{bc} = 24$ cps) whose coupling constants and chemical shifts were consistent with those pre-

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[8] For an excellent review of vinylboron chemistry, see D. S. Matteson, *Organometal. Chem. Rev.*, **1**, 1 (1966).

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