however, the convenience, ease, and yield of the present synthesis, particularly for small scale work (3–5 g).

Experimental Section

1,2,3,4-Tetrachloro-7,7-dimethoxybenzonorbornadiene (1).—Under reflux, a stirred mixture of *o*-carboxybenzenediazonium chloride[6] (25.16 g, 0.137 mol), 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene[7] (59.57 g, 0.226 mol), propylene oxide (commercial material used as is, 20.6 g, 0.355 mol), and ethylene chloride (300 ml) was heated for 3 hr. The solvent was removed by rotary evaporation and the residual dark oil was then chromatographed on alumina (400 g). Benzene (20%) in petroleum ether (bp 30–60°) eluted a milky oil (64.77 g) which upon refrigeration for 1 day deposited white crystals of 1 (16.43 g). A second crop of 1 (3.00 g) was obtained upon further standing. The filtrate was distilled to recover excess starting diene (bp 70–81° at 0.3 mm, 37.64 g, 63% recovery). The residual oil was taken up in boiling hexane and filtered. Further crystals of 1 (2.4 g) were obtained upon refrigeration of this hexane solution. The total yield of 1 was 21.83 g (47% based on diazonium salt, 76.5% based on consumed diene). Recrystallization of 1 from hexane afforded white rhombs: mp 121.5–122°; δ^{CDCl_3} (60 MHz) 7.55 (symmetrical m, A_2B_2, Ar-H), 3.77 (s), 3.47 (s, OCH_3's); λ^{KBr} 3.4 (w), 6.22 (w), 8.3 (s), 8.65 (s), 8.86 (s), 9.02 (sh), 9.8 (sh), 9.9 (m), 10.3 (m), 11.05 (m), 11.45 (w), 11.9 (w), 12.4 (w), 13.6 (s), 14.8–15.7 (broad m).

Anal.[8] Calcd for $C_{13}H_{10}O_2Cl_4$: C, 45.92; H, 2.96. Found: C, 46.16; H, 2.91.

1,2,3,4-Tetrachloronaphthalene (2).—A mixture of 1 (5.00 g, 14.7 mmol), concentrated sulfuric acid (125 ml), and methylene chloride (200 ml) was stirred at 25° as carbon monoxide evolved. A solid deposited during the course of the reaction. After 20 min the reaction appeared completed, but further stirring for a few hours was arbitrarily allowed. Evaporated solvent was replenished by addition of methylene chloride (100 ml), the phases separated, and the acid layer extracted with more solvent. The organic phase and the extracts were combined, washed well with water, dried, and evaporated. The residual solid (3.92 g, 100%) was quite pure 2 by spectra. Recrystallization once from ligroin (bp 60–90°) produced long, colorless needles: mp 200–201° (lit.[5b] mp 199–200°); δ^{CDCl_3} A_2B_2 m centered at 8.53 and 7.87; λ^{Nujol} 7.6 (s), 8.02 (m), 11.2 (m), 13.3 (s), 14.3–14.4 (m).

Registry No.—1, 24472-15-9; 2, 20020-02-4.

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Self-Association in Axial β-Hydroxycyclohexanones

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Infrared spectra of aliphatic hydroxy ketones in the hydroxyl region (3000–3700 cm^{-1}) are sometimes difficult to interpret even at the millimolar concentration level, where intermolecular hydrogen bonding usually does not interfere. Recently, Joris and Schleyer[1] examined a number of such spectra; they note that in some cases the overtone of carbonyl vibration occurring around 3400 cm^{-1} has been mistaken for the absorption of an intramolecular hydrogen bond. The present note shows that some hydroxy ketones associate unusually strongly by intermolecular hydrogen bonding, also giving bands around 3400 cm^{-1} which have on occasion been incorrectly assigned. Such associations are sterically specific, and therefore useful for stereochemical elucidation.

Type I compounds (R = H, CH_3, C_2H_5, *n*-propyl, phenyl, and 1-furyl) show strong absorption around 3400 cm^{-1} (5×10^{-3} *M* solutions in CCl_4), which was attributed to an intramolecular hydrogen bond[2,3] and used in the elucidation of the stereochemistry of the system. Later, the discovery of the strong intermolecular association of some diols by Eglinton, *et al.*,[4,5] and our own experience with that phenomenon[6] led to reexamination of the assignment, and bands at 3400 cm^{-1} were tentatively attributed to the intermolecularly bonded species.[7,8] Nevertheless, Joris and Schleyer[1] assign these strong bands to the carbonyl overtones, contradicting their own contention that such bands should be relatively weak; they also note that the stereochemistry of I has not yet been determined.

The following experiments substantiate our previous view that the absorption at 3400 cm^{-1} is due to intermolecular hydrogen bonding. Compound I, with R = CH_3, was recrystallized from CH_3OD; the deuteration thus achieved ($OH \rightarrow OD$) shifted the bands originally at 3604 and 3395 cm^{-1} to 2662 and 2514 cm^{-1} (5×10^{-3} *M* solutions in CCl_4). Consequently, these bands must be attributed to the stretching vibration of the hydroxyl group. The dependence of the apparent molar absorption coefficients ϵ on the concentration of I, R = CH_3, was measured (CCl_4 solutions in thermostated 30° cells, 0.2 and 1 cm; Beckman IR-12); the results are in Figure 1. The data can be explained by a monomer–dimer equilibrium; the presence of other oligomers at higher concentration cannot be excluded, however. A trial and error procedure (final mean square of the residuals is 3) gave a dimerization constant of 58 l. mol^{-1}; $\epsilon_{monomer}$ at 3604 cm^{-1} is 112; the broad band of dimer (slightly asymmetric, half-width 125 cm^{-1}) has ϵ_{dimer} 316 at 3395 cm^{-1} and ϵ_{dimer} 25 at 3604 cm^{-1}, the last value approximately corresponding to the simple overlap contribution (Cauchy curve[9] shape assumption). Following the argument of Liddel and Becker[10] the dimer must have the cyclic structure II, as proposed previously.[7,8] This dimer structure implies[8] that compound I has the stereochemistry as proposed;[2] furthermore, comparison of the band posi-

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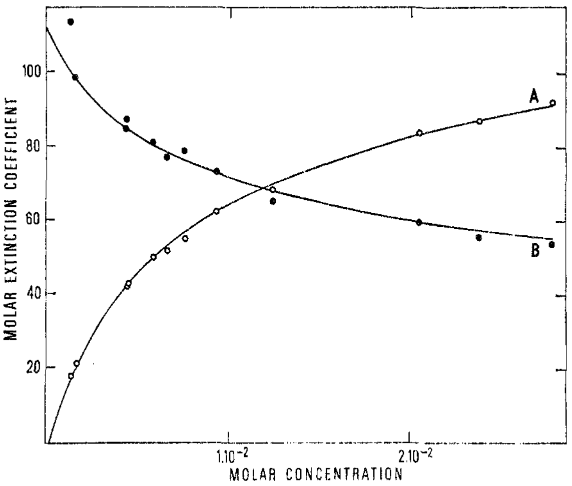
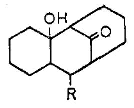


Figure 1.—Concentration dependence of the apparent molar extinction coefficients of compound I, R = CH_3. Carbon tetrachloride solutions at 30°: values observed at 3604 cm^{-1}, ●; at 3395 cm^{-1}, ○. Lines A and B represent the corresponding calculated values for monomer–dimer equilibrium [K_{dimer} = 58 l. mol^{-1} ($\epsilon_{\text{monomer}}$ 112 at 3604 cm^{-1}; ϵ_{dimer} 316 at 3395 cm^{-1} and 25 at 3604 cm^{-1})].

tion for the monomer species with data of Joris and Schleyer[1] gives additional support for the axial position of the hydroxy group. Last, but not least, the stereochemistry of the system I was studied independently by different methods with the same results (*cf.* ref 11 and references therein; also ref 7, p 189).

The dimerization constant of I (58 l. mol^{-1}) is an order of magnitude higher than that of *t*-butyl alcohol[10] (0.8 l. mol^{-1}) or the association constant of *t*-butyl alcohol-acetone[12] (1.0 l. mol^{-1}); nevertheless, it is lower than the dimerization constant of *n*-nonanoic acid[13] (1500 l. mol^{-1}, all data at 30° and in CCl_4 solutions). In the case of I no special forces can be invoked to assist dimerization, such as resonance effects in carboxylic acids or diols[14] or π–π interaction in hydroxyacetophenones.[5] The only possible factor is the steric arrangement which allows the simultaneous formation of two hydrogen bonds in the dimer II. In line with that interpretation all six known derivatives of type I give the same pattern.[2,3] It may be pointed out that in all these compounds the cyclohexane rings probably have a slightly distorted chair conformation.[15,16] Further, relatively strong and broad bands around 3400 cm^{-1} were observed for dilute solutions (around 5 × 10^{-3} *M*; *cf.* ref 15) of the following compounds: 4-hydroxy-2-butanone[17] (also alleged to be[1] a carbonyl overtone), and decalone and cholestane derivatives containing a cyclohexanone moiety with an axial β-hydroxy group.[18] These substances may constitute a new class of strongly self-associating compounds.[5]



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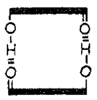

II

Registry No.—I (R = Me), 1614-94-4.

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Synthesis of Allenic Acetals from Unsaturated Carbenes[1]

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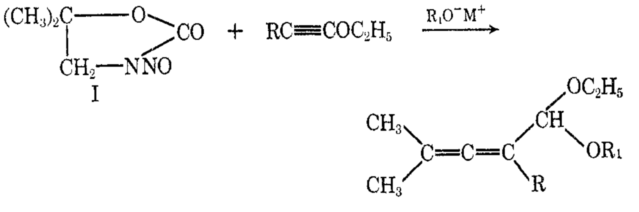
Dihalocarbenes[2] and carbethoxycarbene[3] react less easily with acetylenes than with olefins. We undertook this study to see if unsaturated carbenes[4,5] could add to acetylenes, since substituted methylenecyclopropenes might thus be synthesized.

On treatment of a solution of ethoxyacetylene and 5,5-dimethyl-N-nitrosooxazolidone (1)[5] in 1,2-dimethoxyethane (glyme) with solid lithium ethoxideethanolate,[6] the theoretical amount of nitrogen was rapidly evolved. By suitable procedures 4-methyl-2,3-pentadienal diethyl acetal (II) was isolated in 35% yield.



II, R = H; $R_1 = C_2H_5$
III, R = H; $R_1 = CH_3$
IV, R = CH_3; $R_1 = C_2H_5$

When sodium methoxide was used instead of lithium ethoxide, the mixed ethyl methyl acetal III was formed in 33% yield. In addition to the allenic acetals II and III, there was formed a mixture of higher boiling products which on alkaline hydrolysis yielded quantities of

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