and sodium bicarbonate (12 g). The heterogeneous mixture was heated at 150° with a nitrogen purge for 10 min and cooled.[36] Water was added and the material then was extracted with ether. Most of the ether was removed from the dried extracts by aspiration, and the residual oil was vigorously shaken with saturated aqueous sodium bisulfite to afford the bisulfite adduct (4.5 g). The sulfurous by-products in this adduct were removed by ether extraction in a Soxhlet apparatus for 40 hr. The purified bisulfite adduct was then mixed with aqueous sodium hydroxide (5%) and the liberated oil taken up in ether. Distillation of the neutral, dried extracts produced aldehyde **22** as a colorless oil with a slight floral odor: 0.87 g, 40%, bp 105–108° at 0.2 mm; δ^{CCl_4} 10.0 t (–CHO, J = 2 cps), 7.10 sharp m (Ar–H), 3.33 m (bridgehead H), 2.92 eight-line m ($-CH_2CHO$, AB portion of ABX, J_{AB} = 15 cps, J_{AX} = 2 cps, lines 1,2 and 7,8 very weak), 1.00–2.23 m (other ring H's); λ^{neat} 3.55, 3.72, 5.83 (–CHO), 13.3. The analytical sample was collected by glpc (SE-30, 190°).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.57. Found: C, 83.60; H, 7.67.

The **2,4-dinitrophenylhydrazone** derivative was routinely prepared (yellow needles from aqueous methanol, mp 129–131°).

Anal. Calcd for $C_{19}H_{18}O_4N_4$: N, 15.29. Found: N, 15.45.

Decarbonylation of Aldehyde 22.—A 1 *M* solution of **22** (2 mmol) in chlorobenzene (2 ml) was sparged with helium for 15 min and then treated at 140° with three successive 0.2-mmol portions of freshly distilled di-*t*-butyl peroxide equally spaced over 14 hr. Carbon monoxide (92% of theory, analyzed by glpc at 25° on a molecular sieve 5A column) was evolved steadily and the reaction half-time was *ca.* 260 min. The entire reaction contents were analyzed by glpc (SE-30) and showed only one product from **22**, 1-methylbenzonorbornene (**17**), identical in retention time and spectra with authentic material. Some 5% of the unchanged **22** was also detected. The other possible hydrocarbon products (**18–20**) were absent. On the scale employed, yield data were difficult to obtain but calibration studies indicated at least a 70% yield of **17**.

Acidity Constants.—*Ca.* 0.3-mmol portions of the acids in Table II were dissolved in 50 ml of either 50% (v/v) aqueous ethanol or 75% (v/v) acetone–25% water. The acidic solutions were then titrated at 25° with sodium hydroxide (0.05 *N*) from a microburet using a Leeds and Northrup pH meter with a Beckman glass electrode and a Coleman saturated calomel electrode. The pK_a was obtained from the pH at the half-neutralization point.

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Registry No.—**1**, 15642-38-3; **2**, 13733-46-5; S-benzylisothiuronium salt of **2**, 24452-99-1; 1,4-methanodecahydronaphthalene-1-carboxylic acid, 24453-00-7; 1,4-methanodecahydronaphthalene-1-carboxamide, 24453-01-8; **4**, 16166-88-4; methyl ester of **4**, 15642-40-7; **5**, 15642-39-4; **6**, 13733-44-3; **7**, 13733-45-4; methyl ester of **7**, 24453-07-4; **8**, 13733-48-7; **8**-OAc, 24453-09-6; *ar*-tetrachlorobenzonorbornenyl-1-carbinol, 24453-10-9; **11**, 24453-11-0; **13**, 24453-12-1; **13**-OAc, 24453-13-2; **12**-OTs, 24453-14-3; **17**, 24453-15-4; **18**, 15391-62-5; methyl ester of **23**, 24453-17-6; **22**, 24453-18-7; 2,4-dinitrophenylhydrazone of **22**, 24453-19-8; **23**, 24453-20-1; aceto-*p*-toluidide derivative of **23**, 24453-21-2; **24**, 24453-22-3; tosylate of **24**, 24453-23-4.

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Notes

Studies of Benzonorbornene and Derivatives. V. Adduction of Benzyne with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. A Convenient Synthesis of 1,2,3,4-Tetrachloronaphthalene[1]

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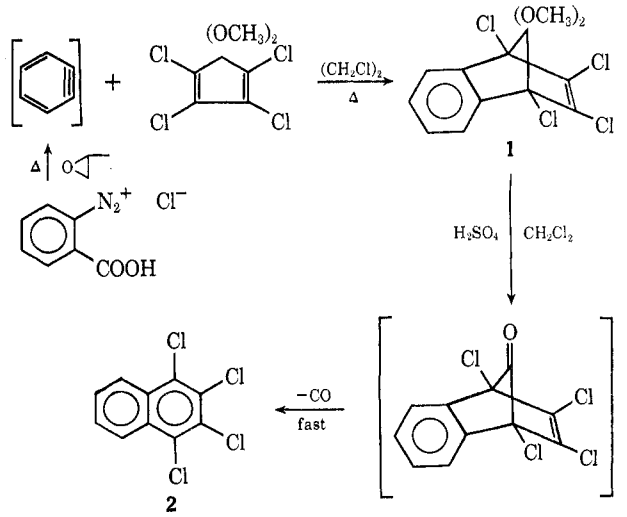
The adduction of benzyne with cyclopentadiene[3] is the method of choice for the synthesis of benzonorbornadiene. As part of a general research program in benzonorbornene chemistry, the addition of benzyne to 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene was achieved (76% based on diene). Of the numerous interesting reactions of the adduct **1**,[4] its conversion



into the rare 1,2,3,4-tetrachloronaphthalene (**2**) is particularly efficient (quantitative yield).

Syntheses of **2** are recorded.[5] None of them has,

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(2) National Defense Education Act Fellow, 1966–1968.

(3) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958). For a convenient recent modification, *cf.* L. Friedman and F. M. Logullo, *J. Org. Chem.*, **34**, 3089 (1969).

(4) J. W. Wilt and E. Vasiliauskas, to be published.

(5) (a) From *ar*-tetrachlorotetralin, J. von Braun, *et al.*, *Ber.*, **56B**, 2332 (1923), and modified by W. P. Wynne, *J. Chem. Soc.*, **61**, (1946); (b) from naphthalene, A. A. Danish, M. Silverman, and Y. A. Tajima, *J. Amer. Chem. Soc.*, **76**, 6144 (1954); (c) from trichloroethylene, W. L. Howard and R. E. Gilbert, *J. Org. Chem.*, **27**, 2685 (1962).

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 → 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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