The ammonia–isobutane CI mass spectra of the pentasaccharide peracetates do not show a molecular AIC. The largest observable fragments correspond to a tetrasaccharide acetate for **21** and a trisaccharide acetate for **22**. The fact that pentasaccharide peracetates apparently cannot be vaporized without thermolysis will be a limitation on this method for molecular weight determination and structure analysis.

Summary. The presence of an intense molecular AIC in the ammonia–isobutane CI spectra of the peracetates of tetra-, tri-, and disaccharides will permit unequivocal molecular weight determinations. The existence of AIC's of thermolysis fragments in these spectra also allows detection of the nature of the individual monosaccharides in the chain (hexose, pentose, etc.). The mass of the glycosyl ion and the glycosydic fragment AIC's provides clear evidence concerning the nature of the reducing and nonreducing sugars in the chain. Because of the sensitivity of the spectra to source conditions it does not seem possible to use these spectra for stereochemical investigations.

The results obtained thus far suggest that alditols should be more useful in future sequencing experiments than the parent reducing sugars. If the permethyl ethers were used instead of the peracetates, the compounds should have a higher vapor pressure and be less sensitive to thermolysis. With these derivatives it might then be possible to take advantage of the relative selectivity of CI mass spectra for obtaining detailed sequence information on unknown oligosaccharides.

Experimental Section

The oligosaccharide acetates used in this study were analytical samples prepared by standard methods.[6] The spectra were obtained by use of a solid probe inlet with an AEI MS-902 mass spectrometer equipped with an SRIC chemical ionization source and a Mensor quartz monometer. All of the spectra were obtained with a 2:1 mixture of ammonia and isobutane at a total source pressure of ⅓ Torr (40 pascals). The source temperature was 250°. Small changes in source temperature generally had profound effects on the abundance of low-intensity ions in the spectra. Increasing the temperature decreased the prominence of adduct ions above the molecular AIC and increased the prominence of the thermolysis ions in the spectra.

Registry No.—**1**, 49587-30-6; **2**, 49587-31-7; **3**, 49587-31-7; **4**, 20880-60-8; **5**, 49587-33-9; **6**, 23846-69-7; **7**, 49587-35-1; **8**, 126-14-7; **9**, 49587-36-2; **10**, 49587-37-3; **11**, 49587-38-4; **12**, 49587-39-5; **13**, 25101-98-8; **14**, 32590-21-9; **15**, 6424-12-0; **16**, 49587-40-8; **17**, 49587-41-9; **18**, 49587-42-0; **19**, 6799-30-0; **20**, 25101-99-9; **21**, 49587-43-1; **22**, 49587-44-2.

References and Notes

(1) This work has been supported in part by a grant from the National Science Foundation.
(2) For a preliminary account of this work see O. S. Chizhov, V. I. Kadentsev, A. A. Solov'yov, W. W. Binkley, J. D. Roberts, and R. C. Dougherty, *Dokl. Akad. Nauk SSSR*, in press.
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Molecular Design by Cycloaddition Reactions. VIII.[1] Syntheses of σ-Tris- and σ-Tetrakis(homobenzenoid) Skeletons by Carbene Additions to Medium-Membered-Ring Unsaturated Compounds

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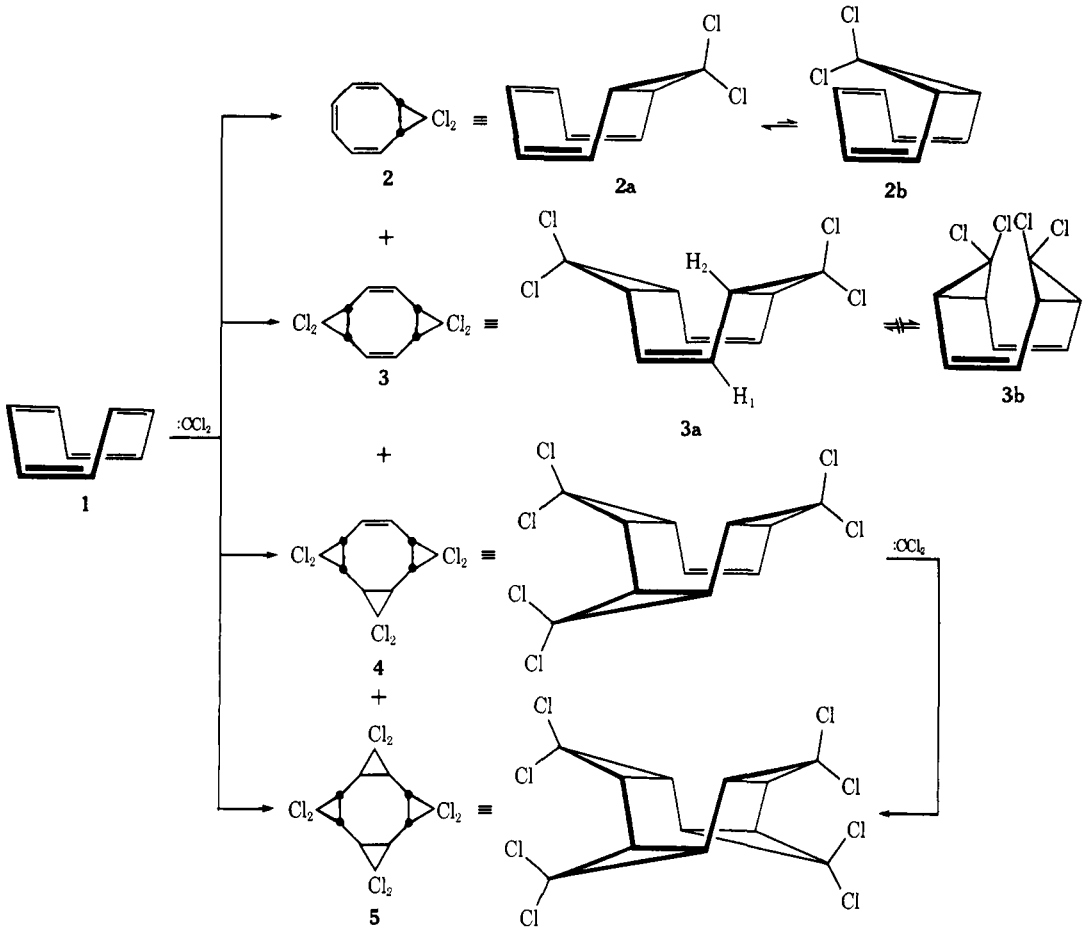
Addition of dichlorocarbene in aqueous medium to medium-membered-ring unsaturated compounds was shown to proceed in a highly stereospecific manner. Thus, cyclooctatetraene and tropone ethylene ketal gave *all-trans*-σ-tetrakis(homocyclooctatetraene) and σ-tris(homotropone) ethylene ketal derivatives together with partly dichloromethylenated products, respectively. *N*-Ethoxycarbonyl-1(1*H*)-2,3- and -4,5-homoazepine afforded the corresponding *all-trans*-σ-tris(homoazepine) derivatives. The structural elucidation of these products was accomplished by spectral evidences and chemical properties. Possible mechanisms for these reactions are also discussed.

Recently, considerable interest has been shown in the chemistry of σ-trishomobenzene derivatives. Initially Prinzbach reported the syntheses of *cis*-oxa-σ-tris(homobenzene) and *cis*- and *trans*-aza-σ-tris(homobenzene) derivatives.[2] Elegant syntheses of *cis*-[3,4] and *trans*-trioxa-σ-tris(homobenzene)[5] and *trans*-σ-tris(homobenzene) derivatives,[6] and, furthermore, the thermally allowed $3\sigma \rightarrow 3\pi$ isomerization of the cis isomer have been reported.[3,4,7] We wish to report that carbene addition reactions to medium-membered ring unsaturated compounds offer a one-step syntheses of σ-tris- and σ-tetrakis(homobenzenoid) skeletons.

Scheme I



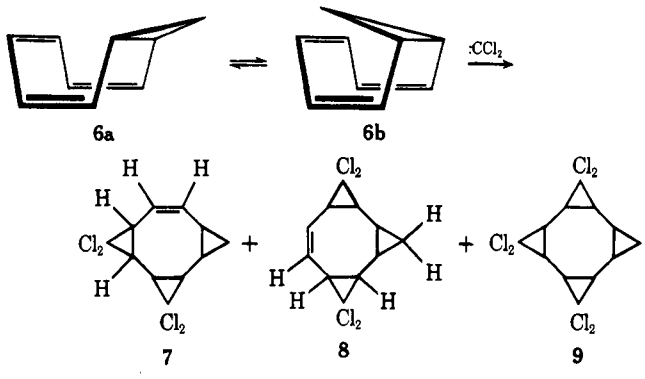
Results and Discussion

Carbene Additions to Medium-Membered-Ring Unsaturated Compounds. The reaction of cyclooctatetraene (1) with a tenfold molar excess of dichlorocarbene (DCC)[8] prepared at room temperature from chloroform in the presence of 50% aqueous sodium hydroxide–benzene with triethylbenzylammonium chloride (TEBA) as a catalyst afforded a mixture of **2**, **3**, **4**, and **5** in 22, 25, 10, and 3% yields, respectively (Scheme I).

The σ-homocyclooctatetraene skeleton in **2** (9,9-dichlorobicyclo[6.1.0]nona-2,4,6-triene) was identified by comparing its ir and nmr spectra and glpc with those of an authentic sample prepared by an independent synthesis from dipotassium cyclooctatetraenide and carbon tetrachloride.[9] Structural assignments of **3** and **5** as σ-bis(homocyclooctatetraene) and σ-tetrakis(homocyclooctatetraene) derivatives, respectively, were based on the analytical and spectral data. Compounds **3** and **5** had formulas of $C_{10}H_8Cl_4$ and $C_{12}H_8Cl_8$ from elemental and spectral analyses, respectively. Adduct **3** was indicated to be a *cis*-σ-bis(homocyclooctatetraene) derivative with C_{2v} symmetry due to a quite symmetrical pattern of the nmr spectrum; it displayed four equivalent vinyl (H_1) and methine (H_2) protons as singlets at δ 5.65 and 2.52, respectively.[10] A significant observation on the spectrum of **3** is concerned with the magnitude of the $J_{1,2}$ coupling constant (0 Hz). The relevant dihedral angles are shown from molecular models of **3** to be approximately 100° for the "extended" conformer **3a** and 10° for the "folded" counterpart **3b**, and, therefore, spin–spin coupling constants should be 0 and 7–8 Hz for the respective two conformers based on the Karplus equation. The unchanging nature of the nmr spectrum of **3** on cooling to −60° shows that **3** exists as the "extended" conformer **3a**. Compound **5** was assigned as *all-trans*-σ-tetrakis(homocyclooctatetraene) with D_{2d} symmetry from a completely symmetrical pattern of the nmr spectrum; it displayed eight equivalent methine protons as a singlet at δ 1.83. From the analysis, compound **4** was shown to be a σ-tris(homocyclooctatetraene) derivative. For its stereochemistry, the nmr spectrum of **4** in $CDCl_3$ was investigated, which showed signals at δ 5.77 (s, 2 H) and 2.0 (complete multiplets, 6 H) and a symmetrical pattern of the olefinic protons indicated that two cyclopropane groups adjacent to the double bond took the syn configuration for one another. However, it is difficult to determine the stereochemistry of three cyclopropane groups whether all-cis or all-trans isomers, because of the complex signals centered at δ 2.0. However, further treatment of **4** with DCC under the same conditions gave **5** in 60% yield. This result showed that **4** was *all-trans*-σ-tris(homocyclooctatetraene). Similar treatment of **3** with DCC afforded a mixture of **4** and **5** in 22 and 43% yields, respectively. Similarly, DCC addition to **2** gave a mixture of **3**, **4**, and **5** in 8, 46, and 18% yields, respectively. These results demonstrate that the reaction of **1** with DCC is quite stereospecific and affords only **5** in good yield when excess DCC is used.

By contrast, the reaction of bicyclo[6.1.0]nona-2,4,6-triene (**6**) with DCC under the same conditions gave a mixture of σ-tris(homocyclooctatetraene) derivatives **7** and **8** and a σ-tetrakis(homocyclooctatetraene) derivative (**9**) in 15, 6, and 41% yields, respectively (Scheme II). The symmetrical patterns of the olefinic protons in the spectra of **7** and **8** indicate that two cyclopropane groups adjacent to double bond are in a syn relationship to one another; however, the relative stereochemistry of the three cyclopropane groups is uncertain because of the complexity of the methine proton signals.

Scheme II



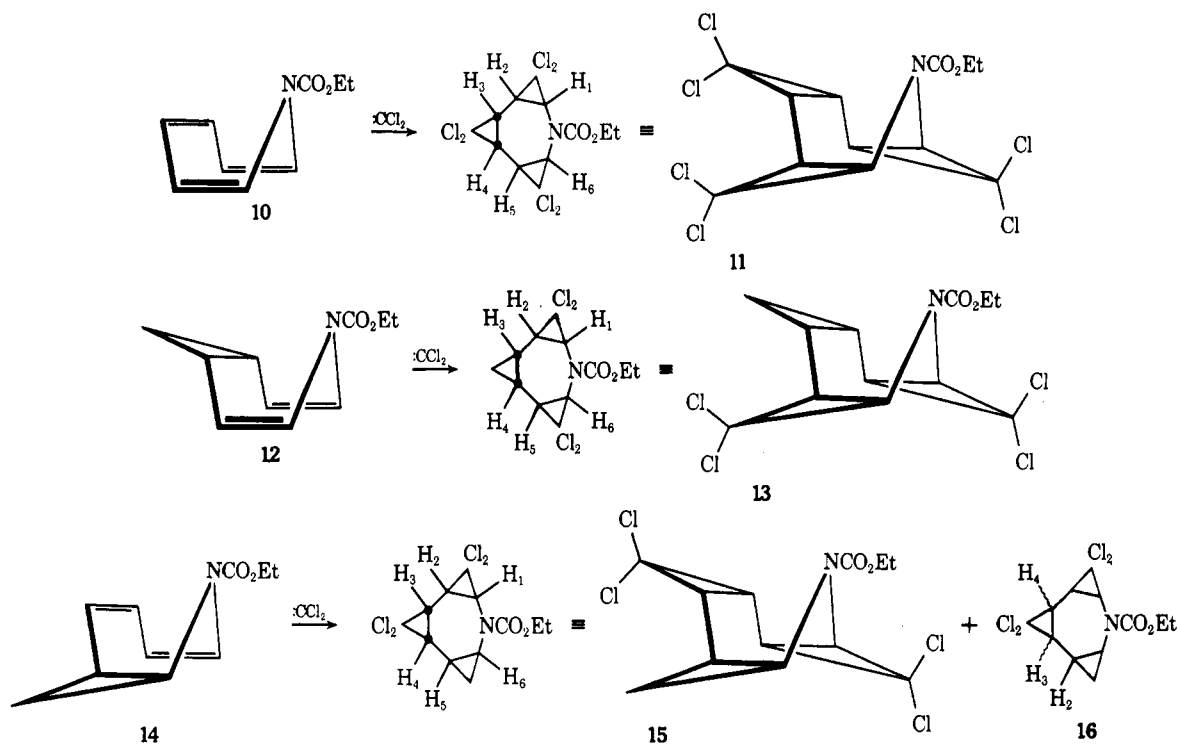
Similar reactions of *N*-ethoxycarbonyl-1(1*H*)-azepine (10) and *N*-ethoxycarbonyl-1(1*H*)-4,5-homoazepine (12) with DCC gave adducts 11 and 13 in 35 and 65% yields, respectively (Scheme III). The analyses of 11 and 13 showed both to be σ-tris(homoazepine) derivatives. The nmr spectra of 11 and 13 in $CDCl_3$ showed symmetrical patterns. The absence of appreciable coupling between H_2 and H_3 indicated that the bridgehead protons (H_2 and H_3) are trans.[11] Thus, the stereochemistry of 11 and 13 was determined to be that of the all-trans isomers.

the analytical and spectral data and some chemical conversions. The analytical data for 18 and 19 indicated them to be σ-tris- and σ-bis(homotropone) ethylene ketal derivatives, respectively. From the small magnitude of $J_{2,3}$ (<1.5 Hz) in the spectra of 18 and 19, the trans stereochemistry was indicated.

On the other hand, compound 20 showed a strong carbonyl absorption at 1650 cm^{-1} and a carbon-carbon double bond absorption at 1630 cm^{-1} in the ir spectrum and was completely identical with an acid hydrolysis product of 19. Catalytic hydrogenation of 20 gave 21 in quantitative yield. Compound 21 showed a strong absorption at 1700 cm^{-1} in the ir spectrum, which was assigned as a stretching absorption of carbonyl group in a seven-membered ring. From these results, the structures of the adducts 18, 19, and 20 were concluded to be *all-trans*-σ-tris(homo- and *trans*-(2,3)(4,5)-σ-bis(homotropone) ethylene ketal and *trans*-(2,3)(4,5)-σ-bis(homotropone) derivatives, respectively.

DCC addition to cycloheptatriene (22) under the same conditions afforded a mixture of σ-tris(homocycloheptatriene) derivative 23 and σ-bis(homocycloheptatriene) derivative 24 in 35 and 26% yields, respectively. However, it is difficult to determine their stereochemistry because of their complex signals in their nmr spectra.

Scheme III



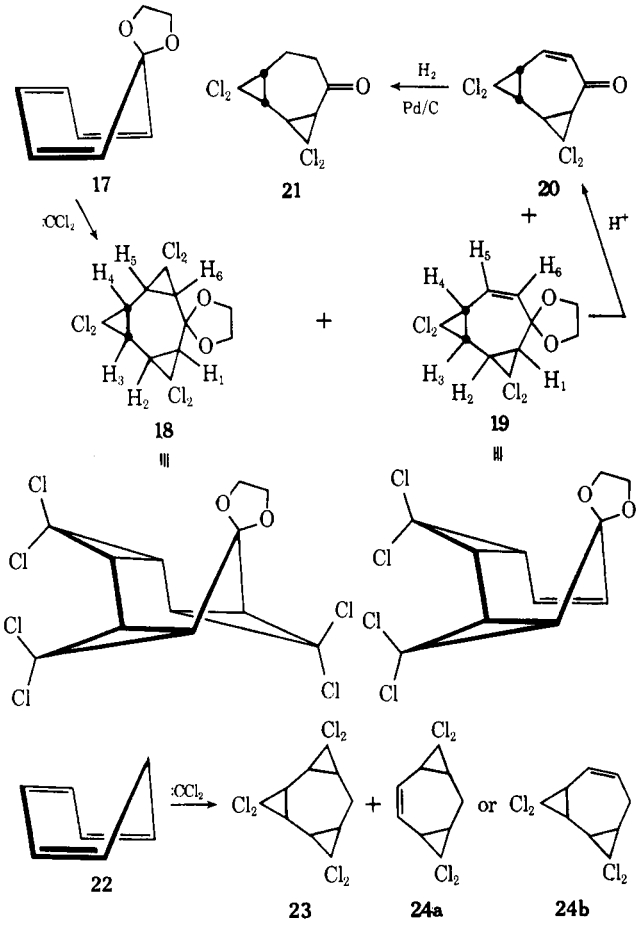
Similarly, DCC addition to 2,3-homoazepine (14) gave a mixture of 15 and 16 in 52 and 5% yields. The analyses of 15 and 16 indicated both to be σ-tris(homoazepine) derivatives. In the nmr spectrum of the major product (15) in $CDCl_3$, the appearance of a signal at δ 1.94 as a singlet ($J_{4,5}$ = 0 Hz) suggested that 15 was also an *all-trans*-σ-tris(homoazepine) derivative. From the nmr spectrum of the minor product, 16, however, it is difficult to determine the relative configurations of the cyclopropane groups, because of the complex signals centered at δ 2.00 (H_2, H_3, and H_4).

Similarly, DCC addition to tropone ethylene ketal (17) gave a mixture of 18, 19, and 20 in 13, 18, and 19% yields, respectively (Scheme IV). The structural assignments for the compounds 18, 19, and 20 were made on the basis of

Properties of *all-trans*-σ-Tris- and Tetrakis(homobenzenoid) Compounds. Vogel[3] and Prinzbach[4,7] have reported that facile 3σ → 3π thermal isomerization of *cis*-σ-tris(homobenzene) derivatives (25)[12] gave all *cis*-cyclonona-2,5,8-triene derivatives (26). By contrast, *trans*-σ-tris(homobenzene) derivatives were quite thermally stable. Compounds 5, 11, and 19 are quite stable at their melting point temperatures as expected. 19 was also stable under acidic and basic conditions. The uv spectra of 5, 11, and 18 showed only end absorptions and these results suggested that no interaction was observed among the cyclopropane rings.

Mechanism for the Formation of *all-trans*-σ-Tetrakis- and *all-trans*-σ-Tris(homobenzenoid) Skeletons. As described above, the reactions of 1, 2, 3, and 4 with DCC

Scheme IV



gave readily the *all-trans*-σ-tetrakis(homocyclooctatetraene) derivative **5**. DCC addition to **10**, **12**, **14**, and **17** afforded also *all-trans*-σ-tris(homoazepine) and *all-trans*-σ-tris(homotropone) ethylene ketal derivatives, respectively. The reaction mechanisms of those stereospecific DCC additions were explained by the conformational properties of medium-membered-ring unsaturated compounds (*i.e.*, tub conformation).

The reaction of **1** with DCC initially afforded **2**.[9] The second DCC addition gave **3** by the attack of DCC to the 5,6 double bond of "extended" conformer **2a** from the less hindered site. Thus, adduct **3** is fixed in the "extended" conformer **3a**, and successive DCC addition will also occur from the less hindered site, leading uniquely to an all-trans product. These results show that the reaction of **1** with DCC proceeds not only stetreospecifically but also in a regiospecific fashion.

In the case of **10**, whether the initial DCC addition occurs at the 2,3 or at the 4,5 double bond, the same derivative **11** should be afforded, since the reactions of **12** and **14** with DCC gave *all-trans*-σ-tris(homoazepine) derivatives **13** and **15**, respectively. On the other hand, reactions of **10** and **14** with equimolar phenyl(trichloromethyl)mercury gave a mixture of **27** and **28** and **29**, respectively (Scheme V).

Thus, the reaction pathway in the reaction of **10** with DCC might involve electrophilic attack of the reagent first at the 4,5 double bond of **10**, then at the 2,3 double bond, and finally the 2′,3′ double bond of a more favorable conformer **27** from the less hindered site affording uniquely an *all-trans*-σ-tris(homoazepine) derivative (**11**). Therefore, the addition of DCC to **10** also occurs in a stereospecific and regiospecific fashion.

Although DCC addition to **17** is stereospecific, it is not clear whether the initial DCC addition occurs at the 4,5 or the 2,3 double bond, since the reaction of **17** with phenyl(trichloromethyl)mercury gave a considerable amount of tropone together with a minor product whose structure could not be determined.

Possibility of Cope Rearrangement. Facile rearrangement of the *cis*-divinylcyclopropane system to cycloheptatriene derivatives is well known. For example, Doering has reported the Cope rearrangement of 4,5-homocyclohepta-2,6-diene.[13] DCC addition to medium-membered-ring unsaturated compounds initially gives *cis*-divinylcyclopropane derivatives; so their Cope rearrangement should be considered. Vogel[14] has reported the first observation dealing with the Cope rearrangement of bicyclo[6.1.0]nona-2,4,6-triene, a field which subsequently has been rather extensively investigated.[15]

Heating **2** at 80–90° gave 1,2-dichloro-*cis*-8,9-dihydroindene; the intermediacy of the tricyclic valence tautomer was proposed to explain this result.[16] Recently, Baldwin[17] reported that the thermal rearrangement of bicyclo[6.1.0]nona-2,4,6-triene to dihydroindene may occur through the valence isomers, bicyclo[5.2.0]nona-2,5,8-triene and *all-cis*-cyclononatriene, without intervention of any diradical intermediate from the study on deuterium-labeled analogs of **6**.

In spite of the facile tendency to the rearrangement, quite symmetrical patterns of **3** and **5** in their nmr spectra, and existence of methylene protons of the cyclopropane ring at δ 0.5–0.3 in the nmr spectra, compounds **7**, **8**, and **9** show the absence of the Cope rearrangement of the bicyclo[6.1.0]nonatriene system to dihydroindene derivatives in the reactions of cyclooctatetraene (**1**) and bicyclo[6.1.0]nonatriene with DCC. These are then the first examples where the bicyclo[6.1.0]nonatriene skeleton is retained both in the cycloaddition and in electrophilic addition reactions to bicyclo[6.1.0]nona-2,4,6-triene derivatives.[18] Prinzbach has reported the Cope rearrangement of a 4,5-dimethoxycarbonyl-4,5-homoazepine derivative,[19] but it is a special case, and 4,5-unsubstituted 4,5-homoazepine derivatives usually react without rearrangement.[20] The chemical shifts of the H_1 protons of **11**, **13**, and **15** are quite similar, and the nmr spectra of **27** and **28**, which are the precursors of **11**, show characteristic signals of enamine proteins (*cf.* Experimental Section). Therefore, these results show that the reaction of azepine derivatives with DCC afforded σ-trishomo derivatives of them without the Cope rearrangement.

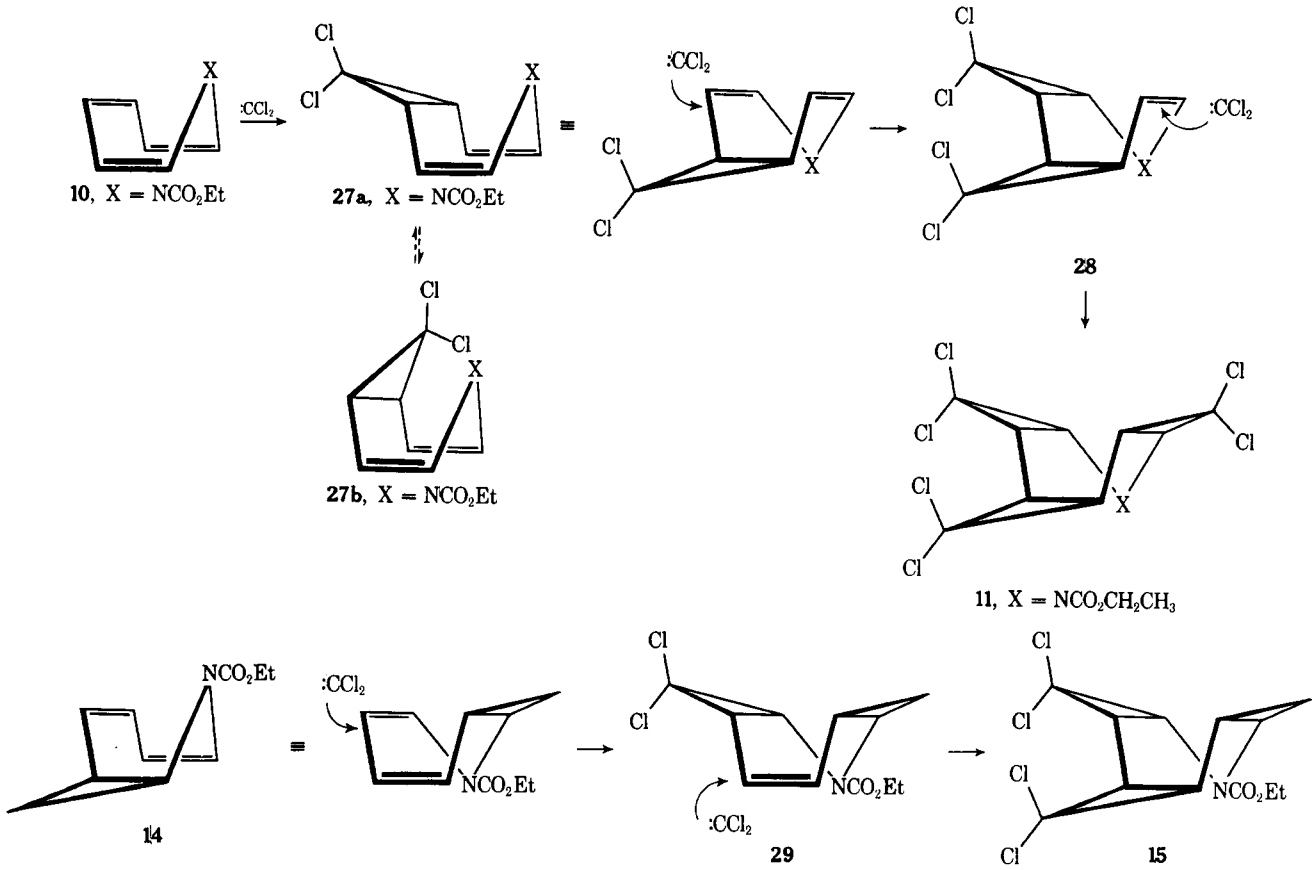
As a conclusion, the generation of DCC by this catalytic method (phase transfer)[8] compared with other procedures[21] is quite useful for syntheses of σ-tris- and σ-tetrakis(homobenzenoid) skeletons.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 Elemental Analyzer. The nmr spectra were taken with a JEOL C-60-XL recording spectrometer with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. Glpc analyses were performed on a Varian gas chromatograph Model 1400 (silicon SE-30). The ir spectra were taken with a JASCO Model IRA-1 grating infrared spectrophotometer.

General Procedure for Dichlorocarbene Addition Reactions in Aqueous Medium. In a 200-ml, three-necked flask fitted with a dropping funnel and a mechanical stirrer, a mixture of 50% (w/w) aqueous sodium hydroxide (40 ml), benzene (4 ml), triethylbenzylammonium chloride (0.08 g), and unsaturated compound (0.02 mol) was vigorously stirred at room temperature. Then the stirring was continued, and chloroform (16 ml, 0.2 mol) was added slowly to the mixture for 2 hr. The brown slurry was poured into water, and the mixture was extracted with methylene chloride. The extract was dried and evaporated to give a dark

Scheme V



brownish oil. It was purified by silica gel chromatography and recrystallization.

Reaction of Cyclooctatetraene (1) with DCC. Reaction products **2**, **3**, **4**, and **5** were obtained as a mixture in 60% yield. The mixture was purified by silica gel chromatography with *n*-hexane as an eluent.

2 had identical spectroscopic properties and glpc retention time with those of an authentic sample.[9,10]

3 had mp 138–141° (recrystallization of MeOH); δ ($CDCl_3$) 5.65 (4 H, s), 2.52 (s, 4 H) (lit.[10] mp 130–135°).

4 had mp 180–183° (from MeOH); δ ($CDCl_3$) 5.77 (s, 2 H), 2.0 (complex multiplets, 6 H).

Anal. Calcd for $C_{11}H_8Cl_6$: C, 37.44; H, 2.29. Found: C, 37.74; H, 2.35.

5 had mp 303–305° (from $CHCl_3$); λ_{max} (EtOH) end absorption; δ ($CDCl_3$) 1.83 (s, 8 H).

Anal. Calcd for $C_{12}H_8Cl_8$: C, 33.07; H, 1.85. Found: C, 32.83; H, 1.91.

Reaction of 4 with DCC. Compound **5** was obtained as colorless needles in 60% yield. The nmr spectrum was completely identical with that of the product prepared from the reaction of **1** with DCC.

Reaction of 3 with DCC. Compounds **4** and **5** were obtained as a mixture in 65% yield (by the nmr inspection).

Reaction of 2 with DCC. Reaction products **3**, **4**, and **5** were identified as a mixture in 72% yield by the nmr analyses.

Reaction of Bicyclo[6.1.0]nona-2,4,6-triene (6) with DCC. Reaction products **7**, **8**, and **9** were obtained as a mixture in 62% yield. The mixture was purified by silica gel chromatography with *n*-hexane as an eluent.

7 had mp 95–98° (from MeOH); δ ($CDCl_3$) 5.75 (s, 2 H), 2.40 (dd, J = 10.5, 1.5 Hz, 1 H), 2.03 (dd, J = 10.5, 5.5 Hz, 1 H), 1.9–1.0 (complex multiplets, 6 H).

Anal. Calcd for $C_{11}H_{10}Cl_4$: C, 46.52; H, 3.55. Found: C, 46.71; H, 3.58.

8 had mp 157–163° (from MeOH); δ ($CDCl_3$) 5.82 (s, 2 H), 2.30 (d, J = 10.5 Hz, 2 H), 1.70 (br d, J = 10.5 Hz, 2 H), 1.4–0.3 (complex multiplets, 4 H).

Anal. Calcd for $C_{11}H_{10}Cl_4$: C, 46.52; H, 3.55. Found: C, 46.76; H, 3.55.

9 had mp 187–195° (from MeOH); δ ($CDCl_3$) 1.85 (br s, 2 H), 2.0–0.7 (complex multiplets, 7 H), 0.53 (m, 1 H).

Anal. Calcd for $C_{12}H_{10}Cl_6$: C, 39.82; H, 2.75. Found: C, 39.97; H, 2.76.

Reaction of *N*-Ethoxycarbonyl-1(1*H*)-azepine (10) with DCC. Compound **11** was obtained as colorless needles in 35% yield: mp 178–180° (from MeOH); ν_{max} (KBr) 1720 and 1710 cm^{-1}; ν_{max} ($CHCl_3$) 1730 cm^{-1} (C=O); λ_{max} (EtOH) and absorption; δ ($CDCl_3$) 4.25 (q, J = 7.2 Hz, 2 H), 3.10 (d, J = 9.0 Hz, H_1 and H_6), 2.08 (s, H_3 and H_4), 2.05 (d, J = 9.0 Hz, H_2 and H_5), 1.38 (t, J = 7.2 Hz, 3 H).

Anal. Calcd for $C_{12}H_{11}O_2NCl_6$: C, 34.82; H, 2.68; N, 3.38. Found: C, 34.92; H, 2.66; N, 3.53.

Reaction of *N*-Ethoxycarbonyl-1(1*H*)-4,5-homoazepine (12) with DCC. Compound **13** was obtained as colorless needles in 65% yield: mp 112–114° (from EtOH); ν_{max} (KBr) 1720 and 1710 cm^{-1}; ν_{max} ($CHCl_3$) 1725 cm^{-1} (C=O); δ ($CDCl_3$) 4.28 (q, J = 7.2 Hz, 2 H), 3.10 (d, J = 9.0 Hz, H_1 and H_6), 1.95 (d, J = 9.0 Hz, H_2 and H_5), 1.40 (t, J = 7.2 Hz, 3 H), 1.5–0.85 (complex multiplets, H_3, H_4, and one of methylene protons), 0.4 (m, 1 H).

Anal. Calcd for $C_{12}H_{13}O_2NCl_4$: C, 41.77; H, 3.80; N, 4.06. Found: C, 41.80; H, 4.03; N, 3.73.

Reaction of *N*-Ethoxycarbonyl-1(1*H*)-2,3-homoazepine (14) with DCC. Reaction products **15** and **16** were obtained as a mixture in 57% yield. The mixture was purified by silica gel chromatography with benzene as an eluent.

15 had mp 92–93° (from EtOH); ν_{max} (KBr) 1710 cm^{-1}; ν_{max} ($CHCl_3$) 1715 cm^{-1} (C=O); δ ($CDCl_3$) 4.30 (q, J = 7.2 Hz, 2 H), 3.12 (d, $J_{1/2}$ = 9.0 Hz, H_1), 2.55 (sextet, J = 6.8 and 4.5 Hz, H_6), 2.07 (d, J = 9.0 Hz, $J_{1/2}$ = 9.0 Hz, H_2), 1.94 (s, H_3 and H_4), 1.33 (t, J = 7.2 Hz, 3 H), 1.5–0.7 (m, H_5 and methylene protons).

Anal. Calcd for $C_{12}H_{13}O_2NCl_4$: C, 41.77; H, 3.80; N, 4.06. Found: C, 41.58; H, 3.91; N, 4.14.

16 had mp 128–129° (from EtOH); ν_{max} (KBr) 1700 cm^{-1}; δ ($CDCl_3$) 4.25 (q, J = 7.0 Hz, 2 H), 3.70 (sextet, J = 7.5, 6.0 Hz, 1 H), 2.85 (d, J = 8.3 Hz, 1 H), 2.00 (m, 3 H), 1.37 (t, J = 7.0 Hz, 3 H), 1.6–0.6 (m, 3 H).

Anal. Calcd for $C_{12}H_{13}O_2NCl_4$: C, 41.77; H, 3.80; N, 4.06. Found: C, 41.80; H, 3.86; N, 4.32.

Reaction of Tropone Ethylene Ketal (17) with DCC. Reaction products **18**, **19**, and **20** were obtained as a mixture in 50% yield. The mixture was purified by silica gel chromatography with benzene–*n*-hexane (1:1) as an eluent.

18 had mp 176–181° (from MeOH); λ_{max} (EtOH) end absorp-

tion; δ ($CDCl_3$) 3.94 (octet, J = 4.5 Hz, 4 H), 2.24 (d, J = 11.5 Hz, H_1 and H_6), 2.00 (br s, H_3 and H_4), 1.83 (br d, J = 11.5 Hz, H_2 and H_5).

Anal. Calcd for $C_{12}H_{10}O_2Cl_6$: C, 36.13; H, 2.53. Found: C, 36.35; H, 2.55.

19 had mp 105–108° (from MeOH); δ ($CDCl_3$) 6.01 (br d, J = 10.5 Hz, H_5), 5.56 (br d, J = 10.5 Hz, H_6), 3.92 (m, 4 H), 2.23 (br s, H_1 and H_2), 2.15 (br d, J = 12.0 Hz, H_3), 1.85 (br d, J = 12.0 Hz, H_4).

Anal. Calcd for $C_{11}H_{10}O_2Cl_4$: C, 41.81; H, 3.19. Found: C, 41.83; H, 3.17.

20 had ν_{max} (neat) 1650 (C=O), 1630 cm^{-1} (C=C); δ (CCl_4) 6.35 (dd, J = 12.0, 6.0 Hz, 1 H), 6.00 (d, J = 12.0 Hz, 1 H), 2.9–D.3 (complex multiplets, 4 H).

Reaction of Cycloheptatriene (22) with DCC. Reaction products **23** and **24** were obtained as a mixture in 61% yield. The mixture was purified by silica gel chromatography with *n*-hexane as an eluent to give **23** and **24**.

23 had mp 139–142° (from MeOH); δ ($CDCl_3$) 2.6–1.4 (complex multiplets).

Anal. Calcd for $C_{10}H_8Cl_6$: C, 35.23; H, 2.37. Found: C, 35.47; H, 2.43.

24 had mp 48–51° (from MeOH); δ ($CDCl_3$) 5.70 (m, 2 H), 2.58 (m, 2 H), 2.48–1.82 (m, 4 H).

Anal. Calcd for $C_9H_8Cl_4$: C, 41.90; H, 3.13. Found: C, 41.96; H, 3.10.

Hydrolysis of 19. A mixture of **19** (500 mg) and concentrated HCl (30 ml) was kept at 65–70° for 5 hr. The solvent was removed under reduced pressure and water was added to the residue. The mixture was extracted with methylene chloride. The extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel chromatography with benzene as an eluent to give **20** as a colorless liquid in quantitative yield. This compound was used in subsequent reaction without further purification.

Hydrogenation of Compound 20. A solution of **20** (300 mg, 1.1 mol) in 20 ml of methanol was hydrogenated over 10% Pd/C (100 mg) at room temperature. Uptake of hydrogen was complete after 3 hr and amounted to a total of 26 ml (1.1 mol). The catalyst was then separated by filtration and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography with benzene as an eluent to give **21** as a colorless liquid in quantitative yield: ν_{max} (neat) 1700 cm^{-1} (C=O); δ ($CDCl_3$) 2.8–1.0 (complex multiplets). The 2,4-dinitrophenylhydrazone of **21** was obtained as yellow crystals from EtOH, mp 196–198°.

Anal. Calcd for $C_{15}H_{12}N_4O_4Cl_4$ (2,4-dinitrophenylhydrazone): C, 38.04; H, 2.74; N, 12.67. Found: C, 38.12; H, 2.71; N, 12.50.

Reaction of *N*-Ethoxycarbonyl-1(1*H*)-azepine with Phenyl(trichloromethyl)mercury. The mixture of **27** and **28** was obtained by refluxing a benzene solution (20 ml) of *N*-ethoxycarbonyl-1(1*H*)-azepine (1.65 g, 0.01 mol) and $PhHgCCl_3$ (4.0 g) for 1.5 hr. The cooled mixture was filtered and the precipitate was washed with petroleum ether (bp 30–60°). The filtrate was evaporated under reduced pressure to give a yellow oil. It was purified by silica gel chromatography with *n*-hexane–benzene (70:30) as an eluent.

27 had mp 64–67° (20%, from EtOH); ν_{max} (KBr) 1735 cm^{-1} (C=O); δ ($CDCl_3$) 6.90 (d, J = 9.8 Hz, H_1 and H_6), 5.03 (dt, J = 9.8, 2.5 Hz, H_2 and H_5), 4.25 (q, J = 7.2 Hz, 2 H), 2.35 (t, J = 2.5 Hz, H_3 and H_4), 1.22 (t, J = 7.2 Hz, 3 H).

Anal. Calcd for $C_{10}H_{11}NO_2Cl_2$: C, 48.41; H, 4.47; N, 5.65. Found: C, 48.30; H, 4.55; N, 5.62.

28 had mp 84–87° (5%, from EtOH); λ_{max} (EtOH) 223 nm (log ε 3.98); ν_{max} (KBr) 1710 cm^{-1} (C=O); δ ($CDCl_3$) 6.44 (br d, J = 8.5 Hz, H_6), 4.98 (br d, J = 8.5 Hz, H_5), 4.27 (q, J = 6.8 Hz, 2 H), 3.42 (d, J = 9.0 Hz, H_1), 2.39 (d, J = 9.0 Hz, H_2), 2.32 (br s, H_3 and H_4), 1.35 (t, J = 6.8 Hz, 3 H).

Anal. Calcd for $C_{11}H_{11}NO_2Cl_4$: C, 39.91; H, 3.35; N, 4.23. Found: C, 39.83; H, 3.30; N, 4.15.

Reaction of *N*-Ethoxycarbonyl-1(1*H*)-2,3-homoazepine with Phenyl(trichloromethyl)mercury. Compound **29** was obtained by the reaction of $PhHgCCl_3$ (4.0 g) and **14** (1.8 g): $n^{17.5}D$ 1.5268 (20% yield); λ_{max} (EtOH) 215 nm (log ε 3.37); ν_{max} (neat) 1720 cm^{-1}; δ ($CDCl_3$) 5.80 (br d, J = 11.0 Hz, H_3 or H_4), 5.43 (br d, J = 11.0 Hz, H_3 or H_4), 4.20 (q, J = 6.8 Hz, 2 H), 3.39 (d, J = 9.0 Hz, H_1), 2.90 (dt, J = 6.8, 3.8 Hz, H_6), 2.25 (br d, J = 9.0 Hz, H_2), 1.24 (t, J = 6.8 Hz, 3 H), 1.5–0.5 (complex multiplets, H_5 and methylene protons).

Anal. Calcd for $C_{11}H_{13}NO_2Cl_2$: C, 50.40; H, 5.00; N, 5.34. Found: C, 50.32; H, 5.08; N, 5.46.

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(11) The dihedral angle between H_2 and H_3 is estimated to be approximately 100° from molecular models of **11** and **13**, while the dihedral angle of the related all-cis isomers is 30°; $J_{2,3}$ coupling constants are calculated to be 1 and 6 Hz, respectively, for the trans and cis isomers.
(12) **25a**, $t_{1/2}$ (100.5°) 5.3 min, E_a = 26.5 kcal/mol, A = 8.3 × 10^{12} sec^{-1}; **25b**, $t_{1/2}$ (120°) 6.9 min, E_a = 27.4 kcal/mol, A = 3.2 × 10^{12} sec^{-1}; and **25c**, 80% conversion at 200° for 40 hr. See ref 3, 4, and 7.
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