would seem to indicate that a cathodic shift of $E_{1/2}$ is the result, not the anodic shifts observed by Rieke, *et al.*[28] The reason for a cathodic shift is not apparent at this time.

That 1,8-DMeF falls very close to the correlation line is perhaps surprising. However, this good correlation is actually indicative of the breakdown of the hyperconjugative correction procedure for this nonalternant hydrocarbon. In all other cases discussed so far, alkyl substitution has been seen to produce a shift of the ultraviolet conjugation band to lower energies, while substitution in the 1 and 8 positions of fluorene has the opposite effect. Sandorfy has stated that, for nonalternant hydrocarbons, methyl substitution can cause either bathochromic or hypsochromic shifts, depending on the position of substitution.[30] Despite the fact that, in this case, methyl substitution would be expected to yield a cathodic shift in addition to that resulting from the inductive effect, the actual measured $E_{1/2}$ is more anodic than that of fluorene itself. It appears then that the usual relationships between ultraviolet spectral and polarographic data do not hold for the nonalternant hydrocarbon fluorene.

The polarographic reduction potential for 2-methylbiphenyl has also been determined. However, the usual hyperconjugative correction is not possible because the shift of the conjugation band is composed of two components acting in opposite directions.[13] Conjugation of the methyl group with the biphenyl π system causes the typical bathochromic shift, while steric overlap of the ortho methyl with the ortho proton, resulting in increased twist about the bridging bond (58°),[13] causes a hypsochromic shift because of reduced $\pi-\pi$ interaction. (The decrease in resonance interaction across the bridging bond has been estimated by Braude and Forbes[5] to be 7 kcal/mol, but their interpretation has been strongly disputed by Suzuki.[13]) Therefore the hyperconjugative shift for 4-methylbiphenyl, multiplied by the ratio of the HMO coefficients for the 2 and 4 positions, has been applied as a correction to 2-methylbiphenyl. When this is done, $E_{1/2}$ falls about 145 mV above the correlation line, equivalent to a strain effect of about 3.3 kcal/mol. This energy results from methyl–proton interaction at the ortho position, as well as decreased $\pi-\pi$ interaction across the bridging bond with respect to biphenyl.

It is seen then that using the inductive model of alkyl substitution in alternant aromatic hydrocarbons, and applying an appropriate correction for hyperconjugative effects, a rough estimate of steric interaction can be obtained polarographically. It appears, however, as if this procedure is not valid for substituted nonalternant aromatic hydrocarbons such as fluorene.

Registry No.—Phenanthrene, 85-01-8; 2,7-DMeP 1576-69-8; 4,5-DMeP, 3674-69-9; 4,5-MeP, 203-64-5; 2,4,5,7-TMeP, 7396-38-5; 3,4,5,6-TMeP, 7343-06-8; biphenyl, 92-52-4; fluorene, 86-73-7; 9,10-DHP, 776-35-2; 4,5-Me-9,10-DHP, 27410-55-5; 1,8-DMeF, 1207-11-0; 2-methylbiphenyl, 643-58-3; 4-methylbiphenyl, 644-08-6.

Acknowledgments.—The authors wish to sincerely thank Professor M. S. Newman for the methyl-substituted phenanthrenes which he so kindly supplied, and Professor R. C. Lawton for helpful discussions.

---

(30) C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 344.

The Acetylation of Cyclooctene, 1,3-Cyclooctadiene, and 1,5-Cyclooctadiene

THOMAS S. CANTRELL[1a] AND BURT L. STRASSER[1b]

Department of Chemistry, Rice University, Houston, Texas 77001

Received April 14, 1970

The acetylation of the three title olefins in the presence of aluminum chloride and of stannic chloride, employing a variety of conditions, has been surveyed. Acetylation of cyclooctene using pure acetyl chloride and aluminum chloride gives mainly ring-contraction products reported earlier, whereas use of stannic chloride leads mainly to 1-acetyl-4-chlorocyclooctane and 4-acetylcyclooctene. Acetylation with acetic anhydride in several solvents gives mixtures of acetylchlorocyclooctane, acetoxycyclooctyl acetate, and acetylcyclooctenes. From the acetylation of 1,3-cyclooctadiene in the presence of stannic chloride, there was isolated 1-acetyl-4-chlorocyclooctene and a mixture of 1- and 2-acetyl-1,3-cyclooctadiene; aluminum chloride gives only tars. Acetylation of 1,5-cyclooctadiene using either catalyst produces 50–60% of 2-acetyl-6-chlorobicyclo[3.3.0]octane, which was degraded to bicyclo[3.3.0]octane-2,6-dione.

The Friedel–Crafts acylation of eight-membered cyclic olefins is of interest both as part of the chemistry of medium-ring compounds, a class noted for multitudinous rearrangements and transannular reactions,[2] and as a synthetic entry into substituted eight-carbon mono- and bicyclic systems. In an early investigation the reaction of acetyl chloride–stannic chloride with cyclooctene, followed by distillation of the product from base, was employed in the preparation of 1-acetylcyclooctene.[3] More recently, Jones, Taylor, and Rudd stated that aluminum chloride catalyzed acetylation of cyclooctene, followed by treatment with base, gave the same product.[4] This result was subsequently shown to be incorrect by two groups. We reported in preliminary fashion the finding that aluminum chloride catalyzed acetylation of cyclooctene gave 4-chloro-4-ethyl-1-acetylcyclohexane (40%) and 4-methyl-1-ace-

---

(1) (a) Author to whom correspondence should be addressed; (b) National Defense Education Act Fellow, 1965–1968.

(2) See, for example, V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. I., P. DeMayo, Ed., Wiley, New York, N. Y., 1963, Chapter 9.

(3) L. Ruzicka and H. A. Boekenhoogen, *Helv. Chim. Acta*, **14**, 1319 (1931).

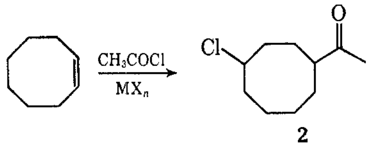
(4) N. Jones, H. T. Taylor, and E. J. Rudd, *J. Chem. Soc.*, 1342 (1961).

TABLE I

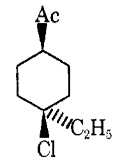
Substrate	Catalyst	Acylating agent	Solvent	Temp, °C	Products (yields, %)
	$SnCl_4$	AcCl	CH_2Cl_2	−10	2 (67), 5 + 6 (20)
	$AlCl_3$	AcCl	CH_2Cl_2	−10	3 (45), 4 (12), 2 (9)
cis-Cyclooctene	$SnCl_4$	AcCl	CS_2	−10	2 (54), 5 + 6 (28)
	$SnCl_4$	Ac_2O		−27	2 (~4), 5 + 6 (19, 1:1), 9 (~9)
	$SnCl_4$	Ac_2O	CH_2Cl_2	−5	2 (60), 6 (11), 9 (6)
	CF_3COOH	$(CF_3CO)_2O$		−27	6 (73)
	$SnCl_4$	AcCl	CS_2	25	2 (32) + 5 and 6 (40)
1,3-Cyclooctadiene	$AlCl_3$	AcCl	CH_2Cl_2	−55	Polymer
	$SnCl_4$	AcCl	CH_2Cl_2	−55	10 (40), 11 (~8), 12 (12)

tylcycloheptane (10%), in addition to minor amounts of an acetylchlorocyclooctane.[5] Very recently Jones and Groves have published their results of a reinvestigation of the acetylation reaction, in which they find the nature of the products to be dependent on the state of the aluminum chloride used.[6] Freshly sublimed aluminum chloride gave the ring-contracted products mentioned above, whereas commercial material from a bottle opened several days before gave almost exclusively 1-acetyl-4-chlorocyclooctane. We now report the results of an exhaustive investigation conducted in our laboratories of the acetylation of the three eight-membered ring olefins, cyclooctene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene, employing a variety of Lewis acid catalysts, solvents, and reaction temperatures.

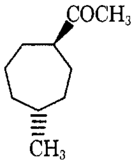
Cyclooctene.—The results of our study of the acylation of cyclooctene are summarized in Table I. As was reported earlier by one of us, the use of highly pure aluminum chloride leads to the ring contraction products 4-chloro-4-ethyl-1-acetylcyclohexane (**3**, 40–45%) and 1-acetyl-4-methylcycloheptane (**4**, 10–12%); under the best conditions, less than 5% of 1-acetyl-4-chlorocyclooctane (2) is produced. However, when aged aluminum chloride is employed, high yields of 2 are obtained, in agreement with the findings of Jones and Groves.[6]



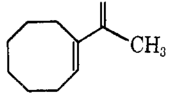
2



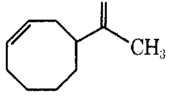
3



4

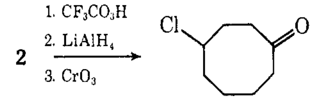


6



5

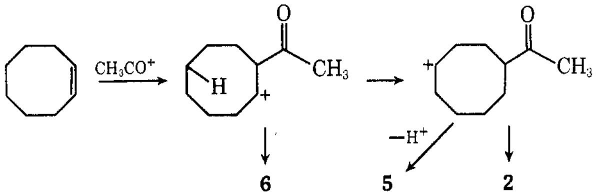
When stannic chloride is employed as catalyst, again in methylene chloride at −10°, 1-acetyl-4-chlorocylooctane (2) is obtained in 60–70% yield, accompanied by 18% of a mixture of 4-acetyl- and 1-acetylcyclooctene (**5** and **6**). Compound 2 was initially identified by means of analytical and spectral data (see Experimental Section); its structure was confirmed by chemical degradation as shown below. Thus, Baeyer–Villiger oxidation of 2 gave the corresponding chloro acetate which was reduced with lithium aluminum hydride to the carbinol. Subsequent oxidation with Jones reagent 4-chlorocyclooctanone (**7**), identical in every respect with an authentic sample.[7]



7

The structure of compound **5** was inferred from spectral data; particularly helpful was the infrared carbonyl stretching band at 1710 cm^{-1}, whose location is indicative of a saturated ketone. Catalytic hydrogenation of **5** gave 1-acetylcyclooctane, whose semicarbazone showed no melting point depression on admixture with that of an authentic sample.[6]

The formation of 2 and of **5** can be accounted for by the occurrence of 1,5- or 1,3-hydride transfers in the initially formed 2-acetylcyclooctyl cation. Such hydride shifts are a common phenomenon in medium-ring compounds.[2]



Olefin acylations performed in carbon disulfide have been reported to give improved yields of unsaturated ketones.[8] Jones and Groves reported that acetylation of cyclooctene with stannic chloride in carbon disulfide at room temperature gave 1-acetylcyclooctene (**6**, 38%) and 2 (25%). Groves[6,8c] ascribes the increased yields of the conjugated ketone **6** in carbon disulfide to a medium effect, whereby in the solvent of lower polarity hydride transfer is less efficient and more of the β-chloro ketone which gives rise to **6** is produced. However, we believe that the critical factor is the temperature employed, rather than the medium. Conducting the acetylation of cyclooctene with stannic chloride in carbon disulfide at −10° gave a reaction mixture whose composition was essentially identical with that obtained using methylene chloride as solvent. Several years ago Cantrell and Shechter had obtained 1-acetylcyclooctene as a major product of the stannic chloride

---

[5] T. S. Cantrell, *J. Org. Chem.*, **32**, 1667 (1967).

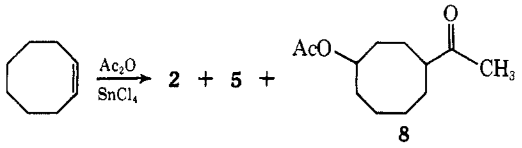
[6] J. K. Groves and N. Jones, *J. Chem. Soc. C*, 1718 (1969).

[7] J. G. Traynham and T. Couvillon, *J. Amer. Chem. Soc.*, **89**, 3205 (1967); we are grateful to Professor Traynham for furnishing us with a sample of this material.

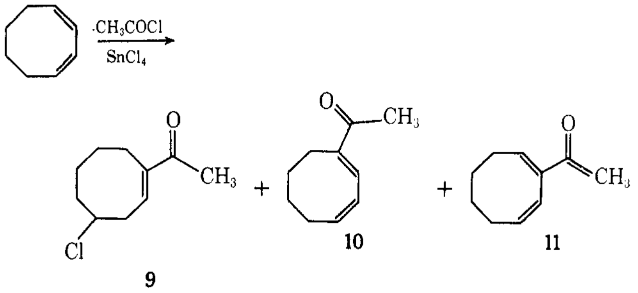
[8] R. E. Christ and R. C. Fuson, *ibid.*, **59**, 893 (1937); (b) W. Taub and J. Szmuszkovicz, *ibid.*, **74**, 2117 (1952); (c) J. K. Groves, private communication.

catalyzed acetylation of cyclooctene in carbon disulfide, in contrast to our present experiences.[9] The earlier result may have been the consequence of impurities in the solvent or catalyst employed, or of longer reaction times. Certainly Jones and Groves[6] and we have found cases of profound changes in product distribution caused by seemingly minor changes in reaction conditions, *e.g.*, reagent purity, in the acylation of olefins. Finally, we have observed that, when **2** is stirred with stannic chloride in carbon disulfide at 25°, there is formed 1-acetylcyclooctene (**6**, 25%) and 4-acetylcyclooctene (**5**, 15%). Treatment of **2** with stannic chloride at −15° for a similar period produced far less rearrangement. Thus, the temperature at which the olefin acylations are conducted seems to be of considerable importance in determining product ratios. The work of Lansbury[10] has given indication that transannular hydride transfers may sometimes have a large activation energy and the rates of various such processes should therefore by strongly temperature dependent.

Acetylation of olefins using acetic anhydride has been reported to give cleaner reaction mixtures with less residual chlorine in the dehydrohalogenated products.[11] Acetylation of cyclooctene using stannic chloride–acetic anhydride without solvent gave a mixture of products in low yield, with the unsaturated ketones **5** and **6** predominating. When the reaction was conducted in methylene chloride, greatly improved yields were obtained, the chloro ketone **2** now predominating. Appreciable quantities of an acetoxyacetylcyclooctane (**8**) are obtained when acetic anhydride is employed. The location of the acetoxy group has been established by conversion of **2** to **8** on treatment with silver acetate. Even in the presence of excess acetic anhydride the chloro ketone is the major product, rather than the acetoxy ketone, **8**.



1,3-Cyclooctadiene.—Acylation of 1,3-cyclooctadiene with acetyl chloride–aluminum chloride in methylene chloride at −60° afforded a mixture of products which decomposed before they could be purified or characterized. However, acetylation of 1,3-cyclooctadiene using stannic chloride as catalyst did afford tractable products. Under the above conditions there was produced a mixture from which could be isolated 1-acetyl-4-chlorocyclooctene (**9**) and 1-acetyl-1,3-cyclooctadiene (**10**) (in yields of 12 and 40%, respectively), together with 2-acetyl-1,3-cyclooctadiene (**11**, *ca.* 8%) which appears to be an artifact produced by isomerization of **10**. When the reaction was quenched at low temperatures, the crude product showed infrared absorption for only a nonconjugated carbonyl group; it seems likely that the actual primary product of the acylation is 3-acetyl-8-chlorocyclooctene, which undergoes facile isomerization to **9** and elimination to give **10**.



The structure of compound **9** was suggested by analytical and spectral data. The infrared and ultraviolet spectra were as expected for an unsaturated ketone. The nmr spectrum, which displays a one-hydrogen triplet at τ 3.35 (J = 8 H_z), a complex multiplet at τ 5.8 (hydrogen on C-4), a one-hydrogen doublet at τ 7.19 (J = 8 Hz, H_A on C-3), a one-hydrogen pair of doublets at τ 7.28 (J = 8, J' = 2 Hz, H_B on C-3), a two-hydrogen multiplet at τ 7.5 (H on C-8), a methyl singlet at τ 7.72, and a six-hydrogen complex pattern at τ 8.1–8.6, is in fair accord with structure **9**. Irradiation of the signals at τ 7.2–7.3 caused partial collapse of the multiplet at 5.8, showing that the two hydrogens responsible for the 7.2 signals are coupled to the hydrogen on the chlorine-bearing carbon. Structure **9**, in which the C-3 methylenes would be expected to couple to the hydrogen α to chlorine, is in best accord with this result.

Attempted dehydrohalogenation of chloro ketone **9** by distillation from sodium carbonate gave no reaction. However, distillation from 1,5-diazabicyclo[4.3.0]nonene-5 (DBN) was successful, an 85:15 mixture of dienones **10** and **11** being produced. Analysis of a sample of pure **10** which had been stored for several weeks at 5° showed that it had undergone isomerization to an identical mixture of **10** and **11**. Thus **11** seems likely to be a secondary product derived from **10**.

Compound **10**, purified by regeneration from the semicarbazone, was initially identified by its spectral properties, including infrared bands at 1662 and 1610 cm^{-1}, indicative of an α,β-unsaturated ketone, its ultraviolet spectrum [λ_{max} 276 nm (ϵ 10,000)], which corresponds closely to that calculated for **10** using Woodward's rules[12] (λ_{max} 273 nm), and the nmr spectrum, which exhibits, *inter alia*, a one-hydrogen apparent triplet at τ 3.06 (J = 2.0 Hz) whose chemical shift is indicative of a vinyl hydrogen β to a carbonyl group. The signal of the vinyl hydrogen β to carbonyl in structure **11** (H-8) might also appear as a triplet. However, in the nmr spectra of known 1,3-cyclooctadienes,[13] the coupling constant between vinyl and adjacent allylic hydrogens (H-1 and H-8 of **11**) is observed to be 7–8 Hz, in contrast to our observed coupling of 2 Hz. This small splitting is consistent with that reported for $J_{2,3}$ of 1,3-cyclooctadienes and other twisted dienes. In compound **10**, $J_{2,4}$ should be of the same magnitude, thus producing the observed apparent triplet for the hydrogen at C-2. This assign-

---

[9] T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5867 (1967).

[10] P. T. Lansbury and F. D. Saeva, *ibid.*, **89**, 1890 (1967).

[11] For pertinent references, see C. D. Nenitzescu and A. T. Balaban in "Friedel-Crafts and Related Reactions," G. Olah, Ed., Interscience, New York, N. Y., 1964, Chapter 37.

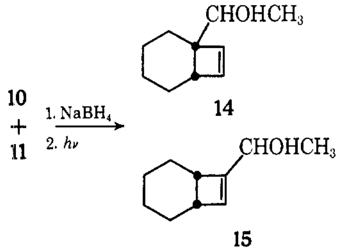
[12] See L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 15 ff.

[13] (a) J. G. Atkinson, D. W. Ayer, G. Büchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963); (b) L. A. Paquette and R. W. Begland, *J. Org. Chem.*, **34**, 2896 (1969).

ment was confirmed by a double resonance experiment. Irradiation of the vinyl signal at τ 4.2 while simultaneously sweeping the low field signal at 3.06 caused the low field signal to collapse to a singlet, as expected for structure **10**. In the cross-conjugated dienone **11** this would not occur, since the coupling of H-1 would be to the allylic hydrogens at C-8.

On standing in the refrigerator for several weeks, compound **10** underwent partial isomerization to **11**. This dienone was never obtained completely pure due to the great similarity of the retention times of **10** and **11**; a sample had been enriched in **11** by gc exhibited a one-hydrogen vinyl signal as an apparent triplet at τ 3.26 (J = 7 Hz) and an acetyl methyl singlet at τ 7.78. Gas chromatographic analysis indicates that *ca.* 8% of **11** was present in the original reaction mixture.

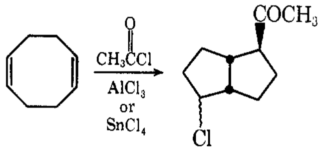
In an attempt to secure additional proof of structure for **10**, this dienone (as an 85:15 mixture with **11**) was reduced with sodium borohydride to the corresponding carbinol **12** (contaminated with **13**). The carbinol mixture was irradiated in ether solution in order to effect electrocyclic closure to bicyclo[4.2.0]oct-7-enes.[14] The linear dienone **10** would afford compound **14** which possesses two vinyl hydrogens, whereas the bicyclic carbinol **15** derived from the cross-conjugated dienone 11 would possess only one vinyl hydrogen. Irradiation through Vycor of an ether solution of the dienol mixture gave, even after extended periods of time, only a 70% conversion to two new compounds, with ~30% of **12** and **13** still being present. The nmr spectrum of this mixture exhibited quartets at τ 5.85 and 6.35. The lower field position of the first quartet suggests a methine hydrogen which is both allylic and α to hydroxyl; we assign this signal to compound **15**. The proton at τ 6.35 is evidently a methine which is no longer allylic but is α to hydroxyl and is still split by an adjacent methyl. The nmr spectrum exhibits overlapping quartets near τ 5.8 due to the unreacted dienols **12** and **13**. Unfortunately, the precise ratio of vinyl hydrogens could not be determined from the complexity of the mixture and overlapping signals; however, it is evident that the predominant product is that exhibiting the quartet at τ 6.35, *viz.*, **14**, and that the major dienone has structure **10**.



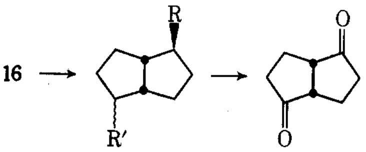
15

Thus, the intermediate allylic cation formed in the acylation of 1,3-cyclooctadiene does not undergo transannular hydride transfer, but rather the simple chloride capture or proton loss characteristic of cations produced from simpler enes and dienes. This would be expected, since hydride transfers to produce less stable cations from more stable ones are not favored.

1,5-Cyclooctadiene.—We previously reported the isolation of 2-acetyl-6-chlorobicyclo[3.3.0]octane (**16**) from the aluminum chloride catalyzed acetylation of 1,5-cyclooctadiene.[5] Ketone **16** appears to be a mixture of the *endo*- and *exo*-chloro compounds, as shown by capillary gc. Use of stannic chloride as catalyst also gave **16**, albeit contaminated with a small amount of an isomer which exhibited vinyl hydrogen nmr signals, probably 5-acetyl-6-chlorocyclooctene. The location of the chlorine atom in ketone **16** had not been securely established in our earlier work but only inferred from spectral data. Its presence at C-6 has now been confirmed by the chemical degradation outlined below. The accessibility of **16** and the reasonable yields in the degradative scheme offer a practical synthetic route to 2,6-disubstituted bicyclo[3.3.0]octane derivatives. The identity of the dione **20** was established by comparison with an authentic sample.[15] The first step in the sequence could also be accomplished with potassium acetate in refluxing acetic acid; however, this method also led to considerable amounts of the elimination products **21**, **22**, and **23**. The structure of the major component of the mixture (**21**) followed from the presence of an infrared absorption band characteristic of an unsaturated ketone function (1681 cm^{-1}) and the absence of any vinyl hydrogen signal in its nmr spectrum. Hydrogenation gave *endo*-2-acetylbicyclo[3.3.0]octane, identical with an authentic sample. The two minor components of the elimination product mixture were not separated; the structures are inferred from the nmr data (see Experimental Section). The formation of **21** seems to require a 1,4- or 1,3-hydride shift. This seems quite reasonable for the *exo*-chloro isomer of **16**. Here abstraction of a

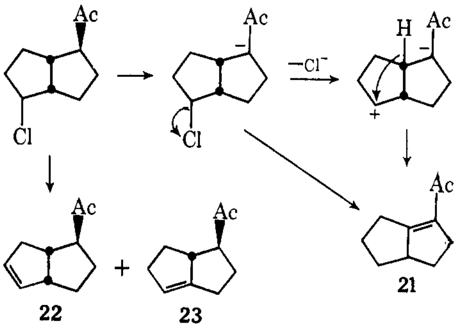


16



17, R = Ac; R′ = OAc
18, R = R′ = OAc
19, R = R′ = OH

20



---

[14] For pertinent examples, see R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, pp 32 ff.

[15] V. R. Ben, Ph.D. Thesis, University of Washington, Seattle, Wash., 1953; see *Chem. Abstr.*, **52**, 16309 (1958).

proton at C-2 could be followed by (or concerted with) ionization of the chlorine and 1,3-hydride transfer from C-1 to C-6, the ionization being assisted by the enolate ion moiety.

Experimental Section

General.—The aluminum chloride used was from a freshly opened bottle of Baker and Adamson sublimed reagent grade material, unless stated otherwise. Stannic chloride was Baker and Adamson reagent grade. The methylene chloride and carbon disulfide were reagent grade materials, used without further purification. Magnesium sulfate was used for all drying operations. The infrared spectra were obtained on a Beckman IR-8 instrument and the nmr spectra on a Varian A-56/60-A instrument operating at 46°. Gas chromatographic work was performed on a Varian Aerograph Model 202-1 instrument (thermal conductivity detector) utilizing the following columns: column A, 5 ft × 0.25 in., 20% SE-30 on Chromosorb P; column B, 6 ft × 0.25 in., 10% QF-1 fluorosilicone on Chromosorb W; column C, 5 ft × 0.25 in., 15% Carbowax 20 M on Chromosorb P; and column D, 5 ft × 0.25 in., 20% diethylene glycol succinate on Chromosorb W. Elemental analyses were performed by Elek Laboratories, Torrance, Calif.

Acetylation of *cis*-Cyclooctene in the Presence of Aluminum Chloride.—This reaction has been described earlier;[5] repetition of the reaction using identical conditions gave, in addition to the acetylcyclohexane and cycloheptane derivatives **3** and **4**, 9% of the saturated chloro ketone previously mentioned; this material proved to be identical with 1-acetyl-4-chlorocyclooctane (**2**), obtained as described below.

Acetylation of *cis*-Cyclooctene Using Stannic Chloride as Catalyst.—To a solution of stannic chloride (26 g, 0.10 mol) in 50 ml of methylene chloride at −10° was added dropwise a solution of acetyl chloride (7.8 g, 0.10 mol) and cyclooctene (11.0 g, 0.10 mol) in 50 ml of methylene chloride over 40 min. The reaction mixture was stirred at −10° for 1 hr, allowed to warm to 0°, and then poured onto a slurry of ice and dilute hydrochloric acid. The aqueous layer was washed once with methylene chloride and the washings were combined with the original organic layer. The organic extracts were washed with water until neutral, dried, and concentrated under reduced pressure to give a yellow oil (15.6 g). Analysis on column B at 160° indicated the presence of 77% (68% yield) of **2** and 23% (22% yield) of three products of shorter retention times. The oil was fractionally distilled to afford two fractions: A, bp 35–60° (0.5 mm), was a mixture of **5** and **6**; B, bp 95–100° (0.5 mm), was $\sim$90% 1-acetyl-4-chlorocycloctane (**2**). Further fractional distillation led to considerable losses through decomposition; a more efficient method of purification was by cleavage of the semicarbazone of **2**. This derivative, obtained from the distilled material by a standard procedure, crystallized from aqueous ethanol as white flakes, mp 152–153° (lit.[6] mp 157–158°). *Anal.* Calcd for $C_{11}H_{20}N_3OCl$: C, 53.76; H, 8.14. Found: C, 54.01; H, 8.49. Pure **2**, from cleavage of the semicarbazone, exhibited the following spectral parameters: ir (film) 1710 cm^{-1}; nmr (CCl_4) τ 5.85 (1 H, pentet, $J \sim 5$ Hz, -CHCl-), 7.55 (1 H, m, -CHCO), 7.93 (3 H, s, CH_3CO), and 8.3–8.6 (12 H, m, methylenes).

Fraction A showed the presence of two major and one minor products on column B; the infrared spectrum of the mixture displayed both conjugated and nonconjugated carbonyl stretching bands (1660 and 1710 cm^{-1}). Conversion of the mixture to the semicarbazones was performed in the usual manner; fractional crystallization gave the semicarbazone of 4-acetylcyclooctene as white prisms, mp 176–177° (lit.[6] mp 177–178°). The less soluble semicarbazone, mp 202–203°, was identical with that of an authentic sample of 1-acetylcyclooctene semicarbazone. The ratio of **5** to **6** was $\sim$30:70.

Cleavage of the semicarbazone of **5** by steam distillation from phtahalic anhydride afforded pure **5**: bp 52–56° (0.4 mm); nmr (CCl_4) τ 4.3 (2 H, m, C=CH), 7.7 (5 H, m, CHCO and CH_2-C=C), 7.91 (3 H, S, $COCH_3$), and 8.2–8.5 (6 H, m).

Degradation of 1-Acetyl-4-chlorocyclooctane to 4-Chlorocyclooctanone (7).—A solution of trifluoroperacetic acid was prepared by dropwise addition of trifluoroacetic anhydride (3.8 ml) to 90% hydrogen peroxide (0.74 ml) in 20 ml of cold (0°) methylene chloride. The solution thus obtained was added dropwise to a vigorously stirred solution of ketone **2** (5.0 g) whose infrared spectrum indicated it to be the desired ester contaminated with *ca.* 20% of unchanged ketone **2**. The ketone was removed by treatment with Girard's reagent. A solution of the crude ester (5.2 g) and 4.7 g of Girard's reagent T and 5 ml of acetic acid was refluxed in ethanol (50 ml) for 1 hr. The reaction mixture was cooled, poured into water, and extracted with ether. The ether extracts were washed with 10% sodium carbonate, with saturated brine, and with water, and then dried and concentrated under reduced pressure. Distillation gave the chloro ester as a colorless liquid (2.9 g): bp 92–98° (0.5 mm); ir (film) 1733 and 1240 cm^{-1}.

A solution of the chloro ester as obtained above (2.9 g) in ether (25 ml) was added dropwise to lithium aluminum hydride (0.5 g) in ether (25 ml) over 0.5 hr. The reaction mixture was refluxed for an additional hour, after which the excess hydride was destroyed by addition of water (0.5 ml). The solution was poured into ice and aqueous ammonium chloride. The ether layer was separated, washed with water, dried, and concentrated to give 4-chlorocyclooctanol as a colorless cloudy oil: ir (film) 3460 and 1045 cm^{-1}; no carbonyl absorption was present.

A solution of the crude 4-chlorocyclooctanol obtained above (0.47 g) in reagent grade acetone (15 ml) was treated dropwise at 20–30° with Jones reagent until the color persisted for at least 0.5 hr (*ca.* 0.4 ml). The acetone was evaporated and the residue was stirred with ice water (10 ml) and extracted four times with ether (20 ml each); the combined extracts were dried and evaporated. The residue was $\sim$85% 4-chlorocyclooctanone, as shown by comparison on columns B and C with an authentic sample.[7] The 2,4-dinitrophenylhydrazone was prepared in the usual manner and recrystallized from ethyl acetate–ethanol to give orange needles, mp 151–152°, undepressed on admixture with the 2,4-dinitrophenylhydrazone of authentic **7**.

Acetylation of *cis*-Cyclooctene Using Stannic Chloride in Carbon Disulfide.—To a solution of stannic chloride (26 g, 0.10 mol) in carbon disulfide (50 ml) at −10° was added over 0.5 hr a solution of acetyl chloride (7.8 g, 0.10 mol) and cyclooctene (11 g, 0.10 mol) in carbon disulfide (40 ml). The solution was stirred for 15 min at −10°, let warm to 0°, and worked up as before. Evaporation of the solvents gave a yellow oil (18 g) whose composition, as shown by gas chromatography on columns B and D was essentially identical with that of the mixture obtained when the acetylation was run in methylene chloride. The infrared spectra of the two mixtures were identical.

When the acetylation in carbon disulfide was performed at 25–30°, the crude mixture obtained exhibited a gc pattern different from that of the reaction run at −10° in that the shorter retention time peaks composed considerably more of the mixture. Collection of the material of retention time 2–3 min at 160° gave material which was shown to be **5** and **6** by preparation of the semicarbazones and fractional crystallization. The **5**:**6** ratio was $\sim$1:2 by analysis on column D, on which partial resolution was obtained.

Treatment of 1-Acetyl-4-chlorocyclooctane (2) with Stannic Chloride.—A solution of ketone **2** (0.2 g) and excess stannic chloride (2 g) in carbon disulfide (50 ml) was stirred at room temperature for 6 hr. The black solution was poured onto ice and worked up in the usual manner to give an orange oil (0.12 g). Analysis of this material on columns B and D showed it to be composed of *ca.* 45% **6**, 20% conjugated ketone **5**, and 35% unchanged **2**.

Acetylation of Cyclooctene Using Stannic Chloride–Acetic Anhydride in Methylene Chloride.—The reaction was performed exactly as in the previously described cases with the exception that acetic anhydride (10 g, 0.10 mol) was employed as the acylating agent. There was obtained 16 g of an orange oil, which analysis on column A at 180° indicated to be composed of 15% **6**, 75% **2**, and 8% of 4-acetoxy-1-acetylcyclooctane (**8**). Fractional distillation of this material on a 24-in. spinning-band column gave a fairly pure sample of **6**, bp 60–63° (0.5 mm), identified by comparison of its semicarbazone with that of material previously obtained and by comparison of spectral properties; a second fraction, bp 110–112° (1.2 mm), was almost pure chloro ketone **2**. The third fraction, bp 135–137° (1.2 mm) (1.4 g total) appeared on the basis of spectral data [ir (film) 1720 (ester C=O), 1706 (ketonic C=O), and 1250 cm^{-1}; (CO) nmr (CCl_4) τ 5.1 (1 H, m, -CHOAc-), 7.3 (1 H, br, -CHAc) 7.91 and 8.04 (3 H each, singlets, CH_3CO), and 8.1–8.7 (12 H)] to be the acetoxyacetylcyclooctane **8**. The positions of the acetate and acetyl groups were established by treatment of **2** (1.0 g) in acetic acid (20 ml) with silver acetate (0.8 g) overnight at room temperature. Distillation of the reaction mixture gave a sample of 8 (~95% pure), identical with that obtained as described above.

When the acetylation using acetic anhydride was performed without additional solvent at 25°, there was obtained as crude product a red oil (7.1 g) which was shown by gc to be mainly (60%) the acetylcyclooctenes 5 and 6, with *ca.* 10% of 2 and 20% of 9.

Acetylation of 1,3-Cyclooctadiene with Acetyl Chloride–Stannic Chloride.—A solution of 1,3-cyclooctadiene (21.6 g, 0.20 mol) in methylene chloride (80 ml) was added dropwise to a solution of stannic chloride (52 g, 0.20 mol) and acetyl chloride (15.6 g, 0.20 mol) in methylene chloride (200 ml) over 0.5 hr at −50 to −60°. The reaction mixture was stirred at this temperature for an additional 0.5 hr, warmed to 0°, and then poured onto ice–dilute hydrochloric acid slurry. The layers were separated; the water layer was washed once with methylene chloride. The combined organic phases were washed with water until neutral (four times) and with brine, and then dried and concentrated under reduced pressure to afford a yellow oil (16.9 g). This material showed five peaks on column B at 155°, of retention times 2.2 (1% of area), 2.8 (28%), 3.5 (7%), 6 (2%), and 8 min (62%). Rapid distillation, without fractionation, gave 14.5 g of pale yellow liquid, bp 32–80° (0.2 mm). Redistillation on a 24-in. spinning-band column gave the following fractions.

A, bp 46–49° (0.4 mm), was essentially pure 1-acetyl-1,3-cyclooctadiene (10, 9.9 g, 41%), containing a small amount of 11 as shown by analysis on column B: ir (film) 3015, 1661, 1613, and 695 cm^{-1}; nmr (CCl_4) τ 3.06 (1 H, t, J = 2 Hz, H-2), 4.17 (2 H, m, H-3 and H-4), 7.5–7.7 (4 H, m, allylic CH_2), 7.72 (3 H, s, CH_3CO), and 8.4–8.6 (4 H, m); uv (EtOH) max 276 nm (ϵ 10,000). A semicarbazone was prepared by the usual procedure and recrystallized from aqueous ethanol to give white leaflets, mp 204–205°. *Anal.* Calcd for $C_{11}H_{17}ON_3$: C, 63.77; H, 8.21. Found: C, 63.79; H, 8.24.

On standing at room temperature for several days, 10 was converted to a mixture of 80–85% 10 and 15–20% 11, as shown by the appearance of a second peak on column B at 155° (retention time 2.1 min, as compared to 1.9 min for 10) and the new triplet at τ 3.3 in the nmr spectrum of the sample.

B, bp 50–73° (0.4 mm), 1.4 g, was a mixture of four components; the two major ones were 10 and 11; one of the minor components was a nonconjugated ketone, as shown by infrared absorption at 1714 cm^{-1}.

Fraction C, bp 75–77° (0.4 mm) (1.9 g), a pale yellow oil which darkened rapidly on standing, was fairly pure 1-acetyl-4-chlorocyclooctene, 9. This material exhibited the following spectral properties: ir (film) 3010, 1668, and 1639 cm^{-1}; nmr (CCl_4) τ 3.35 (1 H, t, J = 8 Hz, H-2), 5.82 (1 H, m, CHCl-), 7.19 (1 H, d, J = 8 Hz, H_A on C-3), 7.28 (1 H, 2 d, J = 8, J' = 2 Hz, H_B on C-3), 7.50 (2 H, m, H on C-8), 7.72 (3 H, s, CH_3CO), and 8.1–8.6 (6 H, m); uv (EtOH) max 240 nm (ϵ 11,100). The semicarbazone, prepared in the usual manner, was recrystallized from ethanol to give white prisms, mp 210–211° dec. *Anal.* Calcd for $C_{11}H_{18}N_3OCl$: C, 54.33; H, 7.39. Found: C, 54.58; H, 7.74.

Distillation of compound 12 from sodium carbonate gave only starting material. However, distillation of a mixture of 1.0 g of 9 and 1.0 g of 1,5-diazabicyclo[4.3.0]nonene at 1 mm gave a distillate (0.4 g) which was a mixture of 10 and 11 in a ratio of 85:15; this material had an infrared spectrum identical with that of a sample obtained by redistillation of dienone 10 which had stood at room temperature for 2 weeks.

When the reaction mixture from acylation of 1,3-cyclooctadiene as described above was not allowed to warm to 0° but was poured while still cold into an ice–dilute hydrochloric acid slurry, there was obtained as crude product a yellow oil whose infrared spectrum showed only one carbonyl band, at 1712 cm^{-1}, indicative of a nonconjugated ketone. The nmr spectrum of this material exhibited, *inter alia*, a multiplet at τ 4.3 (vinyls) and two acetyl singlets at 7.82 and 7.87. Distillation of the material so obtained was accompanied by evolution of hydrogen chloride and the only products in the distillate were 9, 10, and 11.

Conversion of Dienones 10 and 11 to Bicyclic Alcohols 14 and 15.—A solution of an 80:20 mixture of 10 and 11 (1.9 g) in methanol (40 ml) was added at 0° to a solution of sodium borohydride (1.0 g) in methanol (20 ml). The mixture was stirred for 1 hr in the ice bath after addition was complete and was then concentrated under reduced pressure. The residue was treated with ice water and then extracted with three portions (30 ml) of ether. The combined extracts were washed with saturated sodium chloride, dried, and evaporated to give a colorless oil (1.8 g, 95%) which on column A at 165° showed one major peak (retention time 7.8 min) and an incompletely resolved minor peak (retention time 7.5) in a ratio of 88:12, assigned to compounds 12 and 13. This material exhibited infrared absorption at 3600, 3410, 1650, and 695 cm^{-1}; no carbonyl absorption was present. The nmr spectrum (CCl_4) displayed signals at τ 4.15 (1 H, m, vinyl), 4.32 (2 H, m, vinyls), 5.84 (1 H, quartet, J = 7 Hz, $CHOHCH_3$), 7.09 (1 H, br, OH), 7.8 (4 H, *m*, $CH_2{=}C{=}C$), and 8.75 (3 H, d, J = 7 Hz, CH_3).

The 80:20 mixture of dienols obtained above (0.7 g) was dissolved in dry ether (100 ml) and irradiated through a Vycor filter, using a Hanovia 450-W medium-pressure mercury arc, for 13 hr. Evaporation of the ether and distillation of the residue in a short-path apparatus gave 0.26 g of a pale yellow oil, bp 98–115° (bath) (0.3 mm). Analysis on column A at 145° showed the presence of four components, the two minor ones of retention times identical with those of the starting dienols. The two major components could be isolated by preparative gc on column A at 150°. Silica gel tlc of the collected material showed two spots; preparative scale tlc gave no separation. The nmr spectrum (CCl_4) of the product mixture displayed signals at (*inter alia*) τ 4.1–4.5 (complex vinyl absorption), 5.85 (q, J = 7 Hz, $C{=}C{-}CHOHCH_3$), 6.4 (q, J = 8 Hz, $-CHOHCH_3$), 6.8 (broad singlet, OH), and 8.85 and 8.80 two doublets, J = 7 and J = 8 Hz, respectively, $CHOHCH_3$). The number of vinyl hydrogens could not be accurately determined; however, the quartet at τ 6.4 was of much greater intensity than that at 5.85, allowing the assignment of structure 14 to the major component. *Anal.* Calcd for $C_{10}H_{16}O$: C, 80.03; H, 9.30. Found: C, 79.75; H, 9.51.

Acetylation of 1,5-Cyclooctadiene with Acetyl Chloride and Aluminum Chloride.—The acetylation was carried out as described previously,[5] on a 0.2-mol scale; a temperature of −15 ± 3° was maintained. The crude product was distilled rapidly at 0.5 mm to give 27 g of faintly yellow oil. Fractional distillation of this material at 0.3 mm gave, first, a fraction, bp 32–50° (0.3 mm), which consisted of chlorocyclooctenes and chlorocyclootadienes, and then the product, *exo*-2-acetyl-6-chlorobicyclo[3.3.0]octane (16), bp 88–90° (0.3 mm) (identified by comparison of its spectra with those of a sample prepared earlier.[5]) Analysis on a 20-ft column of silicone rubber showed two partially resolved peaks in a ratio of ~70:30, the *exo-* and *endo*-chloro compounds, respectively.

When stannic chloride was added slowly to a equimolar mixture of acetyl chloride and 1,5-cylooctadiene at −50°, there was obtained on work-up a fraction which was mainly ketone 16, corresponding to a yield of *ca.* 45%. However, the sample obtained in this manner appeared to be less pure than that obtained using aluminum chloride, as shown by the presence of vinyl hydrogen signals at τ 4.2 in its nmr spectrum. The intensity suggests a content of ~5% of an unsaturated chloro ketone.

Conversion of Chloro Ketone 16 to Dione 20.—To a solution of chloro ketone 16 (92 g, 0.50 mol) in acetic acid (400 ml) was added silver acetate (100 g, 0.60 mol) and the resulting suspension was heated at 100 ± 5° for 12 hr. The bulk of the acetic acid was removed by evaporation under reduced pressure; ether (300 ml) was added; and the suspension was filtered through Celite. The solvents were evaporated from the filtrate and the residue was distilled. After a small forerun of unsaturated ketones, bp 45–50° (0.2 mm) (4 g), the mixture of 2-acetyl-6-acetoxybicyclo[3.3.0]octane epimers, 17, bp 90–96° (0.2 mm), ir (film) 1705 and 1727 cm^{-1}, was collected (59 g, 56%). Analysis on columns A and B showed three components; however, the resolution was poor. When potassium acetate in refluxing acetic acid was employed instead of silver acetate as described above, there was obtained on distillation two fractions. The higher boiling fraction, bp ~95° (0.2 mm) (45 g, 43%), was a mixture of stereoisomers of structure 17, contaminated with ~2% of unchanged 16. The lower boiling fraction, bp 40–46° (0.3 mm) (17 g, 22%), consisted of three components in the ratio 16:26:58 (10 ft × 0.25 in. QF-1). The major component 21 was obtained pure by collection from column A, or in larger amounts, by purification and cleavage of the semicarbazone. A sample thus obtained exhibited the following spectral properties: ir (film) 1681 cm^{-1}; nmr (CCl_4) complex absorption at τ 6.9–8.6; uv (CH_3OH) max 244 nm. Hydrogenation at 10 psi, over palladium/charcoal in ethyl acetate solution, gave a quantitative yield of *endo*-2-acetylbicyclo[3.3.0]octane, identical with an authentic sample. The semicarbazone of 21 crystallized from ethanol as shiny white leaflets, mp 208.5–209.5°. *Anal.* Calcd for $C_{11}H_{17}N_3O$: C, 63.77; H, 8.21. Found: C, 63.40; H, 8.33.

The isomeric olefins **22** and **23** were identified by the spectral properties of the mixture [ir (film) 1712 and 3070 cm^{-1}; nmr (CCl_4) τ 4.5 (1.3 H, m)].

A solution of the 2-acetyl-6-acetoxybicyclo[3.3.0]octane isomers (**17**, 36 g) in chloroform (200 ml) was treated with *m*-chloroperbenzoic acid (85%, 45 g) and was refluxed gently for 16 hr. Hexane was added to the warm solution and the mixture was chilled in the refrigerator. The crystalline mass of *m*-chlorobenzoic acid was filtered and washed twice with 9:1 hexane–chloroform. The combined filtrates were evaporated to give a colorless, faintly cloudy oil whose infrared spectrum [ν_{max} (film) 1729 cm^{-1}] indicated it to be the desired diacetate, **18**. Distillation gave a colorless oil, bp 84–88° (0.2 mm). The diacetate thus obtained (32 g) was hydrolyzed by stirring overnight at 5–15° with 100 ml of 10% aqueous sodium hydroxide. The reaction mixture was extracted continuously with ether for 30 hr; the ether extracts were washed with saturated sodium chloride solution and concentrated under reduced pressure. The residue was distilled to give a mixture of stereoisomers of bicyclo[3.3.0]octane-2,6-diol (**19**) as a colorless, extremely viscous syrup: bp 90–96° (0.3 mm) (11.4 g, 81% from **17**); ir (film) 3500 (broad) and 1050–1100 cm^{-1}. Analysis on a 20 ft × $^1/_8$ in. SE-30 column showed two components in a ratio 63:37, of respective retention times 10.8 and 11.6 min at 215°. Treatment of a sample with phenyl isocyanate at 80–100° without solvent for 0.5 hr and fractional crystallization of the reaction mixture from ethyl acetate–benzene gave two bis(phenylurethanes). The major, less soluble, isomer had mp 190–192°, whereas the minor isomer melted at 136–137°.

The diol mixture was oxidized by treatment of a solution in reagent grade acetone (10 g in 100 ml) with Jones reagent[16] (20 ml, 8 *N* in oxygen) and stirring at 20–30° for 6 hr. Most of the acetone was removed by evaporation under reduced pressure and the residue was treated with water (100 ml). The resulting mixture was extracted continuously with ether overnight; the ether extract was washed with saturated sodium chloride solution, dried, and concentrated under reduced pressure. The oil thus obtained (6.4 g) showed two peaks on column B at 200°, in a ratio of 80:20. The major component, collected from a 5 ft × $^3/_8$ in. Carbowax column, was identical (infrared spectrum and mixture melting point) with an authentic sample of bicyclo[3.3.0]octane-2,6-dione. The minor component appeared to be a mixture of the epimers of 6-hydroxybicyclo[3.3.0]octan-2-one.

Registry No.—*cis*-Cyclooctene, 931-87-3; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; **9**, 26908-76-9; **9** semicarbazone, 26908-77-0; **10**, 26908-78-1; **10** semicarbazone, 26963-84-8; **14**, 26908-79-2; **21**, 26908-80-5; **21** semicarbazone, 26908-81-6.

Acknowledgments.—The authors are grateful to the Robert A. Welch Foundation for partial support of this work. We also thank Mr. Richard Gandour for performing the nmr double resonance experiment.

---

[16] See L. F. Fieser and M. Fieser, "Reagents in Organic Synthesis," Wiley, New York, N. Y., 1967, pp 142–144.

The Isomerization and Chlorination of Decachlorobi-2,4-cyclopentadien-1-yl

VICTOR MARK* AND EDWARD D. WEIL

Research Department, Hooker Chemical Corporation, Niagara Falls, New York 14302

Received November 3, 1969

Decachlorobi-2,4-cyclopentadien-1-yl, $C_{10}Cl_{10}$, mp 125° (1), yielded on heating above its melting point or on contacting with aluminum chloride a mixture of isomeric chlorocarbons with extended conjugation (linear and cross). Structural assignments are given to the three major constituents of the equilibrium mixture, which is obtainable also from each of the pure isomers. A new structure is offered for the major photochlorination product of 1, $C_{10}Cl_{12}$, mp 221–223° (7), replacing the methanoindene structure ("Diels–Alder dimer" of C_5Cl_6) previously assigned to this derivative. Two novel $C_{10}Cl_{12}$ compounds, obtained from the chlorination of 1, were shown to be the endo and exo isomers of the true methanoindene chlorocarbons. A new structure is assigned to the known $C_{10}Cl_{14}$ chlorocarbon, mp 169°. ^{13}C nmr, ^{35}Cl nqr, ultraviolet, infrared, and mass spectral data as well as mechanistic rationalizations are given in support of the new structures and of the chemistry involved.

In the course of a study of the thermal stability of decachlorobi-2,4-cyclopentadien-1-yl, $C_{10}Cl_{10}$, mp 125° (**1**), a commercial acaricide, it was observed that the heating of **1** above its melting point, but below 240°, brought about complete isomerization.[1] When the isomerization was carried out to the point where the infrared spectrum of the mixture remained constant, none of the characteristic bands of **1** was detectable.

By elution chromatography over alumina or by suitable crystallization from acetic acid, the reaction mixture was separated into two pale-yellow (nearly colorless) $C_{10}Cl_{10}$ isomers of melting point 111° (**3**) and 82° (**4**) and one bright yellow isomer of melting point 114° (**5**). By heating each of these isomers under the original isomerization conditions, a mixture of all three was produced.

The ease of equilibration suggested that the three isomers differed from **1** only in regard to the position of the double bonds. That **3**, **4**, and **5** have the same carbon skeleton as the starting material **1** was confirmed by their catalytic hydrogenation to bicyclopentyl, $C_{10}H_{18}$, and by their photochemical chlorination to the known chlorocarbon $C_{10}Cl_{14}$, mp 169° (**6**), which also has been shown to yield bicyclopentyl on catalytic hydrogenation.[2]

Eight double bond position isomers of the $C_{10}Cl_{10}$ chlorocarbons with the bicyclopentyl skeleton are possible (excluding strained cumulene structures). Of these structures A was assigned[2] to the isomer with mp 125° (**1**) and confirmed by its ready dechlorination to perchlorofulvalene under mild reaction conditions.[3-5]

In the selection of structures for **3**, **4**, and **5** from the remaining seven alternatives (B to H), two with the

---

[1] E. D. Weil, U. S. Patent 3,219,710 (1965); *Chem. Abstr.*, **64**, 3377c (1965).

[2] E. T. McBee, J. D. Idol, and C. W. Roberts, *J. Amer. Chem. Soc.*, **77**, 4375 (1955).

[3] V. Mark, *Tetrahedron Lett.*, 333 (1961); *Org. Syn.*, **46**, 93 (1966).

[4] (a) None of the new $C_{10}Cl_{10}$ isomers, **3–5**, yield perchlorofulvalene under the conditions reported. Instead they undergo an alkylation reaction, similar to that described for polyhalocyclopentadienes[4b] which will be the subject of a separate publication. (b) V. Mark, *Tetrahedron Lett.*, 296 (1961).

[5] D. C. F. Law, Ph.D. Thesis, The University of Wisconsin, 1966.