Rearrangement of the Hindered Cyclobutadiene from Dimerization of 3,3,6,6-Tetramethylcyclohexyne

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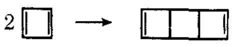
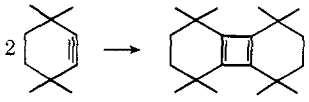
Abstract: Reaction of 1,2-dibromo-3,3,6,6-tetramethylcyclohexene with sodium or oxidation of the bishydrazone of 3,3,6,6-tetramethylcyclohexanedione-1,2 with silver oxide gave a dimeric, rearranged, bicyclic triene (**17**), believed to form from the hindered cyclobutadiene (**2**) resulting from dimerization of 3,3,6,6-tetramethylcyclohexyne. Other products from the two reactions have also been identified.

Simple cyclobutadienes, not stabilized by conjugation or fusion with neighboring π-electron systems, have thus far eluded isolation as stable substances. In the absence of other reagents with which they can react, their normal fate is dimerization to tricyclooctadienes.[1]



The aim of the present research was to thwart the dimerization by steric hindrance and thus either to obtain a stable cyclobutadiene or to force the cyclobutadiene to release its surplus energy in some new and hopefully interesting manner. The particular cyclobutadiene chosen was the dimer (**2**) of 3,3,6,6-tetramethylcyclohexyne (**1**). It was known that reaction of 1,2-dibromocyclohexene with sodium gave the product **3** of possible trimerization of cyclohexyne (probably by addition of cyclohexyne to the cyclobutadiene).[2] While the present work was in early stages, it was further shown



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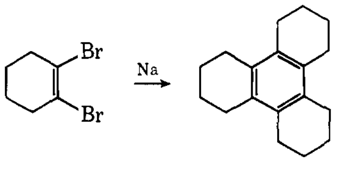
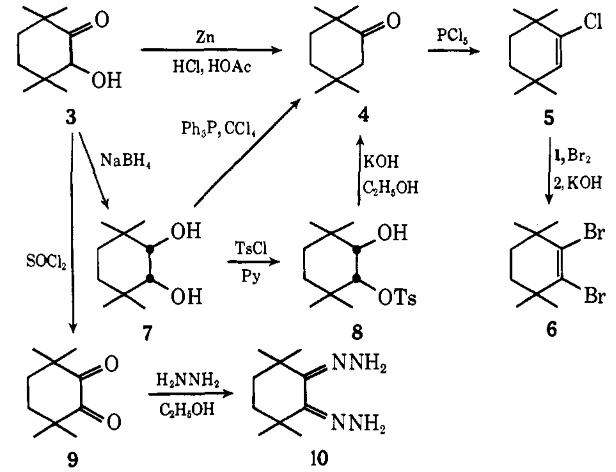


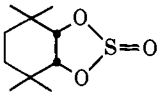
that the similar reaction of 1,2-dibromocyclohexene with magnesium gives cyclohexyne as an intermediate which may be trapped by Diels–Alder reaction with diphenylisobenzofuran,[3] that cyclohexyne can be formed also by oxidation of the bis hydrazone of 1,2-cyclohexanedione with mercuric oxide,[4] and that the reaction of 1,2-dibromocyclohexene with magnesium in the absence of the trapping agent leads to some tetramer of the cyclohexyne, presumably arising by dimerization of an intermediate cyclobutadiene in the usual manner.[5]

The tetramethylcyclohexyne precursors, **6** and **10**, needed for the present study were synthesized by the routes summarized in Chart I. The reduction of acyloin **3** to the ketone **4** by zinc was erratic and gave low yields (0–48%). The two indirect routes through *cis*-diol **7** provided satisfactory alternatives. Diol **7** was obtained in 82% yield by borohydride reduction of acyloin **3**, and was converted to ketone **4** in 61% yield by an unusual reaction with triphenylphosphine and carbon tetrachloride, or in 48% yield in a two-step sequence through the monotoluenesulfonate **8**.

Chart I



The stereochemistry of diol **7** was assigned from the nmr spectrum of its sulfite ester **11**, which showed a singlet for the hydrogens α to oxygen. The sulfite ester **12** from the *trans*-diol **13**, obtained as a minor product in the borohydride reduction of **3** and as a by-product in the acyloin condensation used to synthesize **3**, showed an AB quartet for the α hydrogens, with J = 10.5 Hz. Interestingly, the *trans*-diol **13** reacted with triphenylphosphine and carbon tetrachloride to give *trans*-chlorohydrin **14** rather than ketone **4**. The stereochemistry of **14** was again assigned from the nmr spectrum, which showed a typical trans diaxial coupling of 10 Hz be-



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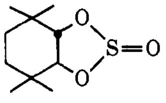

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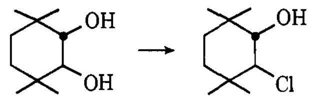
[1] (a) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957); (b) G. Wittig and U. Mayer, *ibid.*, **96**, 342 (1963); (c) E. H. White and H. C. Dunathan, *J. Amer. Chem. Soc.*, **86**, 453 (1964); (d) G. L. Closs and V. N. M. Rao, *ibid.*, **88**, 4116 (1966); (e) K. V. Scherer, Jr., and T. J. Meyers, *ibid.*, **90**, 6253 (1968); (f) R. Criegee, W. Eberius, and H.-A. Brune, *Chem. Ber.*, **101**, 94 (1968).

[2] A. Favorskii and W. Boshovskii, *Ann.*, **390**, 122 (1912).

[3] G. Wittig and R. Rohlke, *Chem. Ber.*, **94**, 3276 (1961).

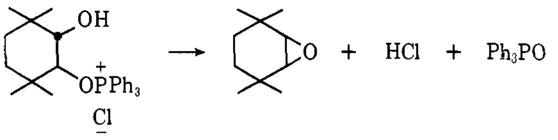
[4] G. Wittig and A. Krebs, *ibid.*, **94**, 3260 (1961).

[5] G. Wittig and U. Mayer, *ibid.*, **96**, 342 (1963).

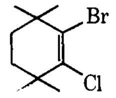


13 14

tween the protons α to oxygen and chlorine. Retention of stereochemistry in the phosphine reaction is abnormal,[6] but may result in the present case from a neighboring group participation by OH, probably with an epoxide intermediate.



The conversion of vinyl chloride **5** to the dibromoalkene **6** by a bromination–dehydrochlorination sequence depends for its success upon the trans stereospecificity of each step. Complete specificity was not realized, the final product being contaminated with up to 20% of bromo chloro olefin **15**. This substance was shown to give the same products as **6** in reactions with sodium, so separation of **6** and **15** was not generally done.



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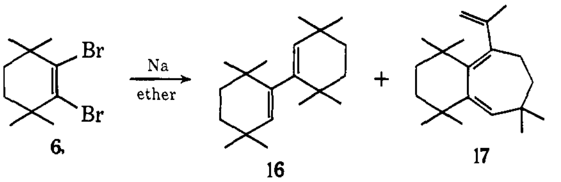
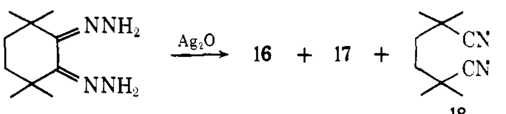
Results from Cyclohexyne Generation. The reaction of dibromide **6** with sodium in ether at room temperature gave two major hydrocarbon products, **16** and **17**, with the ratio **16**/**17** varying from 0.43 to 0.11, and the total yield of **16** and **17** being as high as 90%. Evidence for the structural assignments is outlined below. Oxidation of bis hydrazone **10** with silver oxide in benzene at 50° gave the same products in very low yield (ratio **16**/**17** *ca.* 0.09), a 25% yield of tetramethyladiponitrile **18**, and several unidentified products.



6 16 17

The formation of **16** and **17** from two such different processes is suggestive of a cyclohexyne intermediate for these two products. Further support was obtained by trapping the intermediate in a Diels–Alder reaction with diphenylisobenzofuran. In the case of the sodium reaction of **6**, the reduced adduct **19** was isolated in 7% yield, while the yield of **16** and **17** was reduced to 7% (still in the same ratio, about 0.17). In the case of the bis hydrazone oxidation, a 32% yield of the Diels–Alder adduct **20** was isolated, along with a 20% yield (essentially unchanged) of tetramethyladiponitrile.



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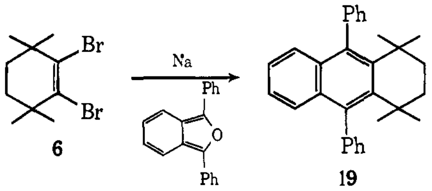

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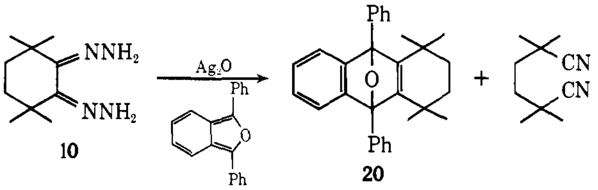
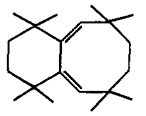


10 20

The evidence is thus strong that **17** is a dimer of the cyclohexyne **1** and presumably a rearrangement product from cyclobutadiene **2** (assuming that dimerization of **1** goes in the same manner as for cyclohexyne itself).[5]

Structures of Compounds 16 and 17. The substance assigned structure **16** was found by combustion analysis and mass spectrometry to have a molecular formula $C_{20}H_{34}$. The ultraviolet spectrum showed only end absorption, with ϵ 4800 at 220 nm and 8100 at 205 nm. The nmr spectrum consisted of just three singlets at τ 5.04 (area 2), 8.48 (area 8), and 8.99 (area 24). These facts are accommodated by structure **16** if there is steric inhibition of conjugation. A possible alternative, again requiring the assumption of steric inhibition of conjugation, is structure **21**. Structure **16** was assigned when it was found that an identical substance could be prepared by the Wurtz coupling of the vinylic chloride **5** with sodium. Since **5** was a minor contaminant in the dibromide **6** used for the cyclohexyne generations, part of the **16** formed may have come from this Wurtz coupling rather than from a cyclohexyne. However, the facts that cyclohexyne trapping by the Diels–Alder reaction did not significantly alter the **16**/**17** ratio and that **16** was formed in the bis hydrazone oxidation argue for some route other than Wurtz coupling for formation of **16**. It is of interest that some of the earlier attempts to synthesize cyclobutadiene yielded 1,3-butadiene,[7] perhaps through cyclobutadiene intermediates.



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The structure of **17** (shown to be $C_{20}H_{32}$ by analysis and mass spectrometry) is assigned from spectroscopic evidence and chemical degradation. The ultraviolet spectrum showed λ_{max} 227 nm, with ϵ_{max} 15,430, suggesting a conjugated diene. The nmr spectrum showed singlets at τ 4.46 (area 1, assigned to a vinyl hydrogen), 8.54 (area 4, nonallylic CH_2 groups), 8.77 (area 6, methyl groups), 8.95 (area 6, methyl groups), and 9.03 (area 6, methyl groups). There were narrow multiplets at 5.36 (area 2, $C{=}CH_2$) and 8.25 (area 3, vinyl methyl group), and a broad multiplet centered near 7.9 (area 4, assigned to $-C{=}CCH_2CH_2-$ system). It was shown by double resonance that the peaks at 5.36 and 8.25 were

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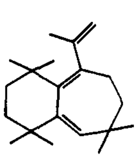
[6] (a) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635, 2639 (1965); (b) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

[7] (a) R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905); (b) M. Avram, C. D. Nenitzescu, and E. Marica, *ibid.*, **90**, 1857 (1957).

splitting each other, J = 1.0 Hz, strongly suggesting the presence of an isopropenyl group. Two structures are consistent with these data, **17** and **22**. Both are conjugated trienes rather than dienes, but both have likely steric inhibition of conjugation, at the isopropenyl group in **17** and at the interannular single bond in **22**. The spectra provide tentative support for **17** rather than **22**, there being an infrared band at 1650 cm^{-1} and the previously described nmr terminal methylene at τ 5.35, both of which are in better agreement with an unconjugated isopropenyl group than with a conjugated one.[8,9]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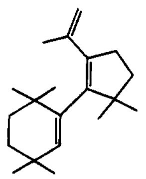
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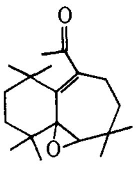
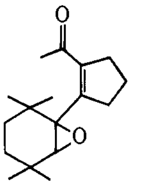
Oxidation of the hydrocarbon with periodate-permanganate gave acetic acid and $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid, as expected from either **17** or **22**. No α,α-dimethylglutaric acid was found. Ozonolysis in methanol at −70°, followed by reductive work-up with dimethyl sulfide, gave a mixture of substances, including formaldehyde (confirming the terminal methylene group) and a substance $C_{19}H_{30}O_2$, isolated in 10% yield by silica gel chromatography. The molecular formula was determined with high certainty by high-resolution mass spectrometry. Spectroscopic characterization of the substance led to the assignment of structure **23**, and hence of structure **17** to the hydrocarbon precursor. The nmr spectrum (220 MHz) showed a singlet at τ 7.23 (area 1) corresponding to hydrogen on an epoxide ring.[10] There were also triplets (splitting 8 Hz) at 7.48 and 8.38 assigned to the two methylenes in the five- or seven-membered ring, a singlet at 7.90 for the methyl ketone, and five sharp signals in the CCH_3 region, 8.8–9.0, with one of them (at 8.80) having an area corresponding to two methyl groups. The methylene groups in the six-membered ring were apparently represented by a broad unresolved multiplet at 8.4–9.0.

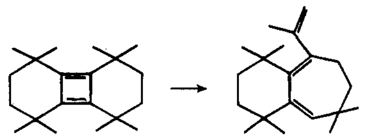

23


24

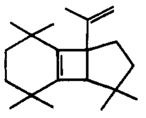
The uv spectrum of the ozonolysis product was of particular interest, showing only end absorption (ϵ 97 at 215 nm). Structure **24** would be expected to show ordinary α,β-unsaturated carbonyl absorption, while **23** would have the acetyl group forced sterically out of conjugation with the adjoining double bond. This observation is regarded as the strongest point in support of structure **23** and, therefore, of structure **17** for the cyclobutadiene isomer.

The infrared spectrum of **23** shows a carbonyl absorption at 1710 cm^{-1}, which is again in support of an effectively unconjugated carbonyl.[13,14]

The isomerization of **2** to **17**, occurring at room temperature in ether, is apparently of an unprecedented type. The reaction involves (1) a ring opening of the 4-ring, (2) a 1,2-shift to contract one of the 6-rings, and (3) a 1,4-hydrogen migration. Although the order of these steps or the possible simultaneity of them cannot be determined from the information at hand, it is clear that the hopefully inert alkane shield in which we attempted to wrap the elusive cyclobutadiene function was easily destroyed by the latter.


2 **17**

One of the most surprising features of the rearrangement is that ring contraction of the cyclohexane ring (essentially orthogonal to the π orbitals) occurred in preference to a methyl migration.[15] It is also interesting to note that if either hydrogen migration or ring contraction had occurred as an initial step, or indeed if they had occurred simultaneously, a logical intermediate would be **25**. Since **25** would surely have a cis ring juncture between the 4- and 5-rings, the final ring opening to **17** would be a forbidden disrotatory process, hardly likely to occur quickly at room temperature. One possible way out of this dilemma, which may also account for the ring contraction in preference to methyl migration, is a [$2_s + 2_s + 2_s$] cycloaddition of the three σ bonds broken (cyclobutadiene C–C, methyl C–H, and cyclohexane C–C), to give a trans isomer of **17**, which may then isomerize quickly.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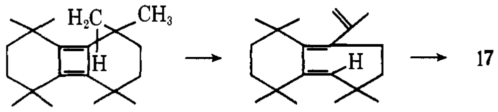

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(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1954, p 31.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 61.

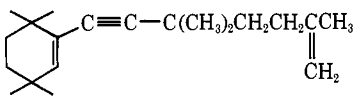
(10) The tertiary oxirane ring hydrogens in cyclohexene oxide and propylene oxide appear, respectively, at τ 7.06[11] and 7.34.[12]

(11) Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa.

(12) Reference 9, p 55.

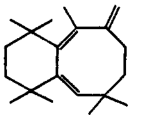
(13) Reference 8, p 117.

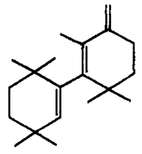
(14) A monocyclic structure which conforms to much of the data may be written


$C{\equiv}C{-}C(CH_3)_2CH_2CH_2\underset{\underset{CH_2}{\|}}{C}CH_3$

This structure is rejected here because it should show acetylenic absorption at about 2250–2270 cm^{-1} (A. A. Petrov, Yu. I. Porfiryeva, and G. I. Semenov, *J. Gen. Chem. USSR*, 27, 1250 (1957)), which is not observed, it should not give acetic acid with permanaganate–periodate, and it should probably be cleaved at all three multiple bonds with ozone.

(15) Products of methyl migration, clearly ruled out by the evidence presented, would have been the following





Experimental Section[16]

3,3,6,6-Tetramethyl-2-hydroxycyclohexanone (3) was prepared as described by Leonard and Mader.[17]

3,3,6,6-Tetramethyl-1,2-cyclohexanedione (9). To a solution of 10.2 g (0.0603 mol) of 3,3,6,6-tetramethyl-2-hydroxycyclohexanone and 9.55 g (0.12 mol, 9.72 ml) of pyridine in 60 ml of chloroform was added cautiously (highly exothermic reaction) 57.3 g (0.482 mol, 35.3 ml) of thionyl chloride while the reaction was cooled and rapidly swirled in an ice bath. The resulting yellow solution was refluxed for 10 hr and then poured onto *ca.* 200 ml of crushed ice. The mixture was extracted with ether (emulsions were usually encountered) and the combined extract was washed with a saturated sodium chloride solution, dilute sodium bicarbonate until neutral, and a saturated solution of sodium chloride. The solvent was removed after the solution was dried over magnesium sulfate and the yellow crystalline residue recrystallized from cyclohexane to give 8.50 g (84%) of light yellow prisms. mp 113.5–115.0° (lit.[16] mp 113.5–115.0°).

***cis-* and *trans*-3,3,6,6-Tetramethyl-1,2-cyclohexanediol (7 and 13, respectively).** A mixture of 37.7 g (0.222 mol) of 3,3,6,6-tetramethyl-2-hydroxycyclohexanone, 10.0 g (0.264 mol) of sodium borohydride, 0.5 g of sodium hydroxide, and 10 ml of water in 150 ml of tetrahydrofuran was heated at reflux for 5 hr. The mixture was maintained at reflux for 30 min while 25 ml of water was added.

The solution which resulted was concentrated on a Rotovap and cooled to 0°. The solid which formed was collected by filtration and extracted with hexane. The insoluble material was recrystallized from ethanol–hexane to yield 6.6 g of the trans isomer (**13**) of the diol: mp 153–153.5°; nmr ($DCCl_3$) τ 9.10 (s, 6), 8.98 (s, 6), 8.66 (m, 4), 7.92 (s, 2), 6.76 (s, 2).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.66; H, 11.77.

The hexane extracts were combined with the filtrate and concentrated on a Rotovap to yield 30.6 g of the cis isomer (**7**) of the diol: mp 80.5–82° (lit.[18] mp 78.5–80°); nmr ($DCCl_3$) τ 9.07 (s, 6), 9.02 (s, 6), 8.67 (m, 4), 7.83 (s, 2), 6.58 (s, 2).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.45; H, 11.54.

Diol **13**, mp 152.3–153.1°, was also obtained from the distillation residue in the preparation of **3** by extraction and crystallization from ligroin.

Cyclic Sulfites of Diols 7 and 13. The method of Gerrard and coworkers[19] was employed. A solution of 4.8 g (0.028 mol) of the cis diol and 4.5 ml (4.5 g, 0.057 mol) of pyridine in 100 ml of ether was cooled in an ice bath and stirred while a solution of 2.0 ml (3.34 g, 0.028 mol) of thionyl chloride in 25 ml of ether was added over a period of 15 min. The mixture was stirred at room temperature for 30 min and then poured into 50 ml of water. The ether phase was washed with 50 ml of water and 50 ml of saturated sodium chloride solution and dried over calcium sulfate. The ether solution was concentrated on a Rotovap to yield 5.6 g of material which solidified almost completely. A strong odor of pyridine indicated that the small amount of liquid was probably pyridine. A portion of the solid was placed on a column of Woelm neutral alumina (Activity I) and eluted with benzene. The eluent was concentrated on a Rotovap to yield the *cis*-sulfite ester **11**: mp 62.2–62.5°; nmr ($DCCl_3$) τ 9.00 (s, 6), 8.95 (s, 6), 8.36 (m, 4), 5.50 (s, 2).

Anal. Calcd for $C_{10}H_{18}O_3S$: C, 55.03; H, 8.31; S, 14.66. Found: C, 55.33; H, 8.35; S, 14.92.

Similar treatment of *trans*-3,3,6,6-tetramethyl-1,2-cyclohexanediol yielded the corresponding sulfite ester **12**: mp 55–56°; nmr ($DCCl_3$) τ 9.03 (s, 3), 8.97 (s, 3), 8.87 (s, 3), 8.83 (s, 3), 8.58 (s, 4), 6.38 (d, 1, J = 11 Hz), 5.90 (d, 1, J = 11 Hz).

***p*-Toluenesulfonates of Diols 7 and 13.** A solution of 5.1 g (0.030 mol) of *cis*-3,3,6,6-tetramethyl-1,2-cyclohexanediol in 50 ml of pyridine, which had been dried over potassium hydroxide, was cooled in an ice bath for 30 min. A drying tube filled with calcium sulfate was used to prevent moisture from entering the flask during the cooling period, and then 6.0 g (0.031 mol) of *p*-toluenesulfonyl chloride was added. The flask was stoppered and swirled until the solid dissolved and placed in the refrigerator for 3 days. Crystals had formed in the flask. The entire mixture was poured into approximately 300 ml of ice and water and stirred until the ice had melted. The solid which formed was collected by filtration and recrystallized from hexane to yield 5.1 g (0.015 mol, 53%) of *cis*-3,3,6,6-tetramethyl-2-hydroxycyclohexyl *p*-toluenesulfonate (**8**): mp 99.0–101.5°; nmr ($DCCl_3$) τ 9.07 (4 peaks, 12), 8.67 (m, 4), 7.80 (s, 1), 7.57 (s, 3), 6.45 (d, 1, J = 3 Hz), 5.45 (d, 1, J = 3 Hz), 2.71 (d, 2, J = 8 Hz), 2.22 (d, 2, J = 8 Hz).

Anal. Calcd for $C_{17}H_{26}O_4S$: C, 62.55; H, 8.03; S, 9.82. Found: C, 62.57; H, 8.05; S, 9.73.

Similar treatment of the trans isomer of the diol gave the *trans-p*-toluenesulfonate: mp 107.5–109.5°; nmr ($DCCl_3$) τ 9.13 (s, 3), 9.08 (s, 3), 9.05 (s, 3), 8.97 (s, 3), *ca.* 8.8 (m, 4), *ca.* [illegible] s, 1), 7.57 (s, 3), 6.20 (d, 1, J = 10 Hz), 5.52 (d, 1, J = 10 Hz).

Anal. Calcd for $C_{17}H_{26}O_4S$: C, 62.55; H, 8.03; S, 9.82. Found: C, 62.62; H, 7.94; S, 9.88.

2,2,5,5-Tetramethylcyclohexanone (4). Method A. The procedure was a modification of a literature procedure for cyclodecanone.[20] To a vigorously stirred mixture of 35.8 g (0.21 mol) of 3,3,6,6-tetramethyl-2-hydroxycyclohexanone, 52 g (0.8 g-atom) of Mallinckrodt reagent grade zinc dust, and 125 ml of glacial acetic acid, maintained at a temperature of 75 ± 5°, was added 115 ml of concentrated hydrochloric acid at as rapid a rate as foaming and temperature control would allow. It was necessary to cool the reaction slightly with a water bath during this addition to maintain the temperature within the limits. Sixty minutes after the initial addition of hydrochloric acid and again 60 min later, 115 ml portions of concentrated hydrochloric acid were added to the reactions as before. The mixture was stirred for 60 min following the final addition, cooled, and decanted from the excess zinc into *ca.* 500 ml of a saturated sodium chloride solution. The organic phase was thoroughly extracted with four portions of pentane which had first been used to rinse the residual zinc. The combined pentane extract was washed with a saturated sodium chloride solution, dilute sodium bicarbonate, and finally with a saturated sodium chloride solution. The pentane solution was dried over magnesium sulfate and evaporated, and the clear residual liquid distilled to give 3.95 g of 1,1,4,4-tetramethylcyclohexane, bp 55–57° (20 mm), and 24.1 g of crude ketone, bp 83–103° (20 mm) (mostly at 83–87°).

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.80; H, 14.21.

The impure ketone was converted to its semicarbazone,[21] which was recrystallized from ethanol to give white needles, mp 209.6–210.5° dec.

Anal. Calcd for $C_{11}H_{21}N_3O$: C, 62.52; H, 10.02. Found: C, 63.21; H, 10.00.

2,2,5,5-Tetramethylcyclohexanone semicarbazone (22.7 g, 0.175 mol) was treated with 50 ml of concentrated hydrochloric acid in a 250-ml erlenmeyer flask. The reaction mixture was warmed on a steam bath with occasional swirling to effect solution. Soon after it appeared that most of the semicarbazone had dissolved a massive white precipitate began to form. Enough water was added to dissolve this material while heating was continued. The reaction was warmed a total of 30 min at *ca.* 40–60° after which it was cooled and extracted three times with pentane. The combined pentane extract was washed with solutions of saturated sodium chloride, dilute sodium bicarbonate, and again with saturated sodium chloride. After drying over magnesium sulfate, the solvent was removed *in vacuo* and the residue distilled. There was obtained 15.67 g of colorless 2,2,5,5-tetramethylcyclohexanone, bp 84.5–85.5° (21 mm), $n^{25}D$ 1.4422; 95% yield from the semicarbazone, 48% from the starting acyloin.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.20; H, 12.07.

The nmr spectrum of the ketone (CCl_4) consisted of four singlets, at τ 7.85 (area 2), 8.4 (area 4), 8.92 (area 6), and 9.03 (area 6). The infrared spectrum showed a strong C=O band at 1702 cm^{-1}.

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[16] Melting points and boiling points are uncorrected. Microanalyses were done by Mr. J. Nemeth and associates. Nuclear magnetic resonance spectra were recorded on Varian A-60, A-60A, HA-100, and HR-220 instruments by O. W. Norton, R. Thrift, and their associates. Mass spectra were recorded on MAT Ch-4, CH-5, and SM-1B instruments by C. Cook and associates.

[17] N. J. Leonard and P. Mader, *J. Amer. Chem. Soc.*, **72**, 5388 (1950).

[18] D. Klenberg, *Ann. Acad. Sci. Fenn., Ser A2*, No. 118 (1962); *Chem. Abstr.*, **59**, 400c (1963).

[19] M. J. Frazier, W. Gerrard, G. Machell, and B. D. Shepherd, *Chem. Ind. (London)*, 931 (1954).

[20] A. C. Cope, J. W. Barthel, and R. D. Smith, *Org. Syn.*, **36**, 14 (1956).

[21] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956, p 218.

The yields of ketone by this method were erratic, and seemed to be critically dependent upon reaction temperature and upon the quality of the zinc dust.

Method B. A mixture of 4.25 g (0.0246 mol) of *cis*-diol **7** and 9.5 g (0.036 mol) of triphenylphosphine in carbon tetrachloride was stirred at room temperature for 40 min and then heated at reflux for 3 hr. The mixture was cooled and filtered and the filtrate was poured into 200 ml of petroleum ether (bp 30–60°) and allowed to stand for 3 hr. The solid which had formed was removed by filtration and the filtrate was concentrated on a Rotovap. The residue was distilled at reduced pressure to yield 2.3 g (0.015 mol, 61%) of the ketone, bp 78–80° (15 mm). The infrared spectrum of this material was identical with that of ketone prepared by method A.

Method C. A solution of 5.0 g of potassium hydroxide in 25 ml of ethanol was heated to reflux under a nitrogen atmosphere and 5.0 g (0.015 mol) of *cis*-3,3,6,6-tetramethyl-2-hydroxycyclohexyl *p*-toluenesulfonate (**8**) in 100 ml of ethanol was added dropwise over a period of 1 hr. A flocculent white solid formed after approximately 30 min. The mixture was heated at reflux for 15 min after the addition was complete and then was poured into approximately 200 ml of water. The white solid dissolved and an organic layer formed on the top of the water. The mixture was extracted with hexane and the aqueous layer was saturated with sodium chloride and extracted with hexane. The combined hexane extracts were washed twice with saturated sodium chloride solution and dried over calcium sulfate. The dry solution was concentrated on a Rotovap to yield 2.36 g (0.014 mol, 90%) of 2,2,5,5-tetramethylcyclohexanone. The infrared and nmr spectra of this material were identical with those of the ketone prepared by method A.

3,3,6,6-Tetramethyl-1-chlorocyclohexene (5). To 10.45 g (0.067 mol) of phosphorus pentachloride stirred magnetically under an atmosphere of dry nitrogen was added dropwise, without introduction of oxygen, 14.6 g (0.07 mol) of 2,2,5,5-tetramethylcyclohexanone. The resulting yellow-brown solution was stirred for 48 hr. At the end of this time an additional 8.32 g (0.04 mol) of phosphorus pentachloride was added while maintaining the dry nitrogen atmosphere. The resulting brownish yellow paste was stirred for another 48 hr. At the end of this time the reaction mixture was poured onto a crushed ice–water mixture and carefully made basic with a 20% solution of sodium carbonate. The resulting basic solution was extracted several times with low boiling petroleum ether and the combined extracts were dried over magnesium sulfate. The solvent was removed and the dark residual oil was refluxed for 4 hr with a 20% solution of ethanolic potassium hydroxide. The reaction mixture was then cooled, diluted with water, and extracted several times with low boiling petroleum ether. The organic phase was washed with a 20% solution of calcium chloride, then with a dilute solution of hydrochloric acid, finally with water, and then dried over magnesium sulfate. The solvent was removed and the dark brown oil was distilled to give one fraction, bp 83–87° (23 mm). The infrared spectrum of this oil showed medium intensity absorption bands at 1700 and 1635 cm^{-1} indicating that it was a mixture of the starting ketone and the desired chloroolefin.

The oil was treated with semicarbazide hydrochloride in the manner described by Shriner, Fuson, and Curtin[21] to remove the unreacted 2,2,5,5-tetramethylcyclohexanone and the residual oil was distilled to give 3.8 g (0.02 mol, 33%) of a faintly yellowish oil, bp 83–84° (23 mm). The infrared spectrum included the previously mentioned band at 1635 cm^{-1}. The nmr spectrum (CCl$_4$) consisted of a singlet at τ 4.54 (area 1), a multiplet at 8.45 (area 4), a singlet at 8.90 (area 6), and a singlet at 9.02 (area 6).

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.54; H, 9.92. Found: C, 69.27; H, 9.93.

Yields in this preparation were erratic.

3,3,6,6-Tetramethyl-1,2-dibromocyclohexene (6). A freshly prepared solution of 6.94 g (0.0402 mol) of **5** and 6.56 g (0.014 mol) of bromine in 50 ml of carbon tetrachloride was deoxygenated by five freeze–pump–thaw cycles. The reaction solution, maintained at a temperature of 15–20°, was then irradiated with a Sylvania sunlamp until no further color change was noted (*ca.* 3 hr). The resulting light yellow solution was shaken with a dilute sodium bisulfite solution, twice with a saturated sodium chloride solution, and dried over magnesium sulfate. Removal of solvent *in vacuo* afforded 13.38 g of an orange oily liquid, which was added dropwise over about 10 min to a stirred, refluxing solution of 13 g (0.20 mol) of potassium hydroxide in absolute ethanol. To permit efficient stirring, more ethanol was added as inorganic salts precipitated. After about 2 hr, the dark orange mixture was cooled, poured into 200 ml of saturated sodium chloride, and extracted with ether. The extract was washed with saturated sodium chloride, calcium chloride twice, and sodium chloride, then dried over magnesium sulfate and evaporated. The residue was chromatographed on 150 g of Woelm neutral alumina (Activity I). A colorless liquid (9.17 g) was eluted with 800 ml of hexane and shown by glpc to be 19.5% **5**, 7.0% 3,3,6,6-tetramethyl-1-bromo-2-chlorocyclohexene (**15**), and 73.5% **6**. A distilled mixture, bp 66–68° (0.6 mm), from a similar run was 4.8% **5**, 17.5% **15**, and 66.7% **6**.

Anal. Calcd for $C_{10}H_{16}BrCl$: C, 47.74; H, 6.41; Br, 31.76; Cl, 14.09. Found: C, 47.73; H, 6.54; Br, 31.43; Cl, 14.06. Calcd for $C_{10}H_{16}Br_2$: C, 40.56; H, 5.45. Found: C, 40.78; H, 5.71.

The nmr spectrum (CCl$_4$) of **15** consisted of singlets at τ 8.81 and 8.30, in a ratio 3:1. The nmr spectrum of **6** was very similar, the two signals being at 8.82 and 8.27, respectively.

Reaction of Dibromide 6 with Sodium. Approximately 100 ml of ether was distilled from sodium hydride into a three-necked flask which had been dried for 24 hr. The distillation and reaction were carried out under an atmosphere of dry nitrogen. To the dry ether was added 1.7 g (0.074 g-atom) of sodium which had been cut into pieces, approximately 5 × 1 × 1 mm, under Nujol and rinsed with xylene, and 2.82 g of a mixture of the cyclohexenyl halides (estimated by glpc to contain 1.98 g (0.0068 mol) of dibromide and 0.84 g (0.0033 mol) of bromochloride) was added.

The mixture was stirred for 8 hr during which time the reaction mixture turned deep blue. The mixture was filtered and the filtrate was concentrated to yield 1.43 g of a light yellow liquid. Analysis by glpc (5% Carbowax 20M on Chromosorb G at 150°) indicated three major components with retention times of 1.1, 5.0, and 7.2 min which had relative areas of 1:5.4:13.6, respectively, as well as minor components at 4.1, 9.3, and 25 min. The products with retention times of 5.0 and 7.2 min were collected by preparative glpc and shown (below) to be hydrocarbon **16** and hydrocarbon **17**, respectively.

Anal. Calcd for $C_{20}H_{34}$ (**16**): C, 87.51; H, 12.49; mol wt, 274. Found: C, 87.22; H, 12.33; mol wt (mass spectrum), 274.

Calcd for $C_{20}H_{32}$ (**17**): C, 88.16; H, 11.84; mol wt, 272. Found: C, 88.16, 88.21; H, 11.78, 11.91; mol wt (mass spectrum), 272.

In a similar run, the weight of the yellow liquid prior to chromatography corresponded to a 93% yield of hydrocarbons. In still another run, the crude product was separated by column chromatography on alumina with hexane (instead of glpc) to obtain **16** and **17** in less pure form, but still the same substances as shown by their infrared spectra.

Wurtz Synthesis of Hydrocarbon 16. An alloy was prepared from 4.3 g (0.11 g-atom) of potassium and 0.9 g (0.039 g-atom) of sodium under dry xylene in an atmosphere of dry nitrogen. The mixture was heated until the metal melted and fused. The alloy was gently stirred, allowed to cool, washed with dry ether, and left under ether.

A mixture of 0.5 ml (0.45 g, 13 mg-atoms) of alloy and 1.73 g (10 mmol) of chloroolefin **5** in 300 ml of anhydrous ether was stirred for 2 hr. The mixture was filtered and concentrated on a Rotovap to 1.45 g of a light yellow liquid which was purified by column chromatography on Woelm neutral alumina with hexane as eluent. The eluent was concentrated on a Rotovap to yield 1.09 g of liquid. The two major components of the mixture were collected by preparative glpc on a Carbowax 20M column. The component with the longer retention time was found to have nmr and infrared spectra identical with those of hydrocarbon **16** as obtained in the preceding experiment.

The component with the shorter retention time had nmr and infrared spectra consistent with the assumption that it was 3,3,6,6-tetramethylcyclohexene: nmr (CCl$_4$) τ 9.05 (s, 12), 8.55 (s, 4), 4.82 (s, 2).

Reaction of Chlorobromo Compound 15 with Sodium. To a mixture of 0.22 g (0.0099 g-atom) of sodium in 50 ml of dry ether under nitrogen was added 0.22 g (0.88 mmol) of the bromo chloro olefin. The mixture was stirred at room temperature for 8 hr and then filtered. The filtrate was concentrated on a Rotovap to yield 0.18 g of light yellow liquid. The glpc analysis of this material indicated five products with relative peaks area of 1.5:1.0:8.2:13.0:1.2 in order of increasing retention time on a Carbowax 20M column. The major component had the same retention time as a known sample of hydrocarbon **17** and the second largest component had the same retention time as a known sample of hydrocarbon **16**. The retention time of the fastest moving material was the same as that of the material presumed to be 3,3,6,6-tetramethylcyclohexene. The other products were present in about the same relative proportions as in the product mixture from the treatment of a mixture of the cyclohexenyl halides with sodium.

Reaction of 3,3,6,6-Tetramethyl-1,2-dibromocyclohexene with Sodium in the Presence of 1,3-Diphenylisobenzofuran. To a solution of 1.95 g (0.00676 mol) of 1,3-diphenylisobenzofuran in 60 ml of purified tetrahydrofuran was added 0.50 g (0.0217 g-atom) of sodium wire freshly cut into 1-cm length pieces followed by a solution of 1.00 g (0.00338 mol) of 3,3,6,6-tetramethyl-1,2-dibromocyclohexene in 20 ml of tetrahydrofuran during 5–10 min. The reaction was maintained under an atmosphere of dry nitrogen and cooled slightly (*ca.* 15°) during the addition of dibromide. After 1 hr the reaction was an orange-brown in color and after 2 hr an intense black-green. At the end of 7 hr, *ca.* 2 ml of ethanol was added and the reaction allowed to proceed for 30 min before it was poured into 200 ml of water. The aqueous phase was then saturated with sodium chloride and extracted thoroughly with ether. The combined extract was washed with a saturated solution of sodium chloride and dried over magnesium sulfate. The orange residue (2.528 g) was taken up in benzene–cyclohexane and chromatographed on a column of 75 g of neutral Woelm alumina (Activity I). The first 400 ml fraction of hydrocarbon elutant yielded 31.6 mg of a light yellow oil whose infrared spectrum showed a sharp band at 1660 (m) cm^{-1} and a strong doublet at 880 and 890 cm^{-1}, characteristic of hydrocarbon **17**, and furthermore, the spectrum of this fraction was very similar to that of the product mixture of hydrocarbons **16** and **17** obtained in the experiment without added 1,3-diphenylisobenzofuran. The vapor-phase chromatogram of this fraction showed two components in the ratio of 1.5:8.5 whose retention times were identical with those of hydrocarbons **16** and **17**, respectively. A third component amounted to *ca.* 5% of the total mixture.

A second fraction of 0.147 g of a white fluorescent solid (**19**) was obtained upon elution with 1500 ml of 10% benzene–cyclohexane. Repeated recrystallization from benzene–ethanol gave 25 mg of blue fluorescing white plates, mp 241.5–242.2°. Evaporation and sublimation of the mother liquors gave another 75 mg of nearly pure **19**, as judged by the infrared spectrum.

Anal. Calcd for $C_{30}H_{30}$: C, 92.26; H, 7.74. Found: C, 91.09; H, 7.43.

The nmr spectrum ($DCCl_3$) showed signals at τ 2.5–3.3, 8.30, and 8.80, attributed respectively, to 14 aromatic hydrogens, 4 methylene hydrogens and 12 methyl hydrogens. The uv spectrum ($CHCl_3$) showed λ_{max} 297 (log ϵ 3.94) and λ_{max} 288 nm (log ϵ 3.89).

3,3,6,6-Tetramethyl-1,2-cyclohexanedione Dihydrazone (10). Two Pyrex bombs were charged with 6.0 g (0.0357 mol) of 3,3,6,6-tetramethyl-1,2-cyclohexanedione, 60 g (1.0 mol) of 85% hydrazine hydrate, and 50 ml of ethanol. The tubes were sealed and heated at 150 ± 10° for approximately 8 hr or until the original light yellow solution had become colorless. After opening at −70° (caution, gas pressure) the contents were combined and diluted with water and saturated with sodium chloride. The organic phase was extracted three times with ether and the ethereal solution washed twice with a saturated solution of sodium chloride before it was dried over magnesium sulfate. Removal of solvent gave 6.20 g of a partially crystalline oil which was recrystallized from approximately an equal volume of ligroin by allowing the solution to cool slowly to 0°. The crystals were collected, rinsed well with cold ligroin (1.346 g, mp 122–138°), and recrystallized again from ligroin to give 1.129 g (16%), mp 130.7–140.7°. A further recrystallization from ligroin followed by sublimation gave pure, white crystalline, 3,3,6,6-tetramethyl-1,2-cyclohexanedione dihydrazone, mp 140.0–141.7°.

Anal. Calcd for $C_{10}H_{20}N_4$: C, 61.18; H, 10.27; N, 28.55. Found: C, 61.42; H, 10.53; N, 28.97.

The original mother liquor was concentrated and cooled to 0°, to yield 0.594 g of white plates; mp 101–105°, softens at 85°. More of this material (0.981 g, mp 102–106°, softens at 95°) was obtained by evaporation of the mother liquor to an oil, addition of methanol, and cooling at 0°. Further cooling of the mother liquor at −20° yielded a small third crop (mp 93–125°) which was discarded. Slow evaporation of the mother liquor in air gave rise to large crystalline plates; 1.026 g, mp 104.2–105.9°, softens at 102°. The combined crude material (2.60 g, 48%) was twice recrystallized from methanol and then sublimed to give a pure sample of 2,2,5,5-tetramethylcyclohexanone azine, mp 106.0–107.0°.

Anal. Calcd for $C_{20}H_{36}N_2$: C, 78.88; H, 11.92; N, 9.20. Found: C, 78.98; H, 12.06; H, 9.32.

A small amount of crude 2,2,5,5-tetramethylcyclohexanone azine upon treatment with concentrated hydrochloric acid yielded a slightly yellow liquid whose infrared spectrum was identical with that of an authentic sample of 2,2,5,5-tetramethylcyclohexanone.

Reaction of Dihydrazone 10 with Silver Oxide. To a stirred solution of 503 mg (2.56 mmol) of 3,3,6,6-tetramethyl-1,2-cyclohexanedione dihydrazone in 20 ml of benzene was added 1.853 g (8.0 mmol) of dry, freshly prepared[22] silver oxide, and *ca.* 8 drops of an alcoholic potassium hydroxide solution. Addition of the base gave rise to an immediate exothermic reaction with vigorous gas evolution. The mixture was stirred for 45 min at room temperature and then at 60° for 15 min at which time 0.528 g of silver oxide was added. The reaction was maintained at 60° for another 30 min and then at room temperature for 12 hr. The resulting mixture was filtered through Celite and the filter cake rinsed well with ether. The filtrate was fractionally distilled through a 6-in. Vigreux column and the ether and benzene fractions were shown by glpc to contain no extraneous peaks. The orange partially crystalline residue deposited a small amount of black tar upon standing overnight. Trituration with a little ligroin followed by filtration gave a brown crystalline mass. Sublimation at 110° and 0.1 mm gave 101 mg of white crystals, mp 136–137.8°, and left 2.3 mg of black residue. Recrystallization of the sublimate from ligroin followed by a resublimation afforded 82 mg of pure $\alpha,\alpha,\alpha',\alpha'$-tetramethyladiponitrile, mp 137.1–138.0° (lit.[23] mp 138°). A mixture melting point with an authentic sample[24] showed no depression.

In a similar run with 2.04 g (0.0104 mol) of dihydrazone, the mother liquor from recrystallization of crude dinitrile from ligroin was evaporated *in vacuo* to an orange viscous residue which was taken up in a small amount of benzene and chromatographed on a column of *ca.* 100 g of neutral Woelm alumina (Activity I). Elution with cyclohexane (600 ml) afforded 96.6 mg of a light yellow partially crystalline oil. Analysis of this product by vapor chromatography indicated a complex mixture. A Carbowax 20M column showed two peaks (ratio of 1:11) in the chromatographic fraction whose retention times were the same as hydrocarbons **16** and **17**, respectively. These two unknown components were collected as a mixture on the Carbowax 20M column and the infrared spectrum of this collected material was shown to be very nearly identical with a similar spectrum of the previously characterized **16** and **17** mixture. By peak area measurements the hydrocarbon product was obtained in 1.2% yield from the starting dihydrazone. A further product (33% of the mixture), which readily crystallized, mp 106–113°, was collected from the Carbowax 20M column, but was not identified.

Reaction of Dihydrazone 10 with Silver Oxide in the Presence of 1,3-Diphenylisobenzofuran. To a stirred solution of 500 mg (2.55 mmol) of 3,3,6,6-tetramethyl-1,2-cyclohexanedione dihydrazone and 1.35 g (5 mmol) of 1,3-diphenylisobenzofuran in 30 ml of benzene were added 1.853 g (8.0 mmol) of freshly prepared silver oxide, 1.205 g (10 mmol) of anhydrous magnesium sulfate, and *ca.* 8 drops of a saturated alcoholic potassium hydroxide solution. The ensuing reaction was stirred at room temperature for 1 hr and then at 50° for 1 hr after which another 0.492 g portion of silver oxide was added. The reaction was maintained at 50° for *ca.* 3 hr and then 0.550 g (5.6 mmol) of maleic anhydride was added. After another 3 hr at 50° the reaction mixture was filtered, the filter cake rinsed well with benzene, and the yellow filtrate evaporated under aspirator pressure to 2.608 g of an orange viscous oil. This material was dissolved in a little benzene and placed on a column of Florisil. Elution with pentane gave 0.335 g (*ca.* 32%) of crude 1,2,3,4,9,10-hexahydro-1,1,4,4-tetramethyl-9,10-diphenyl-9,10-*endo*-oxoanthracene (**20**), collected in six fractions, which was crystalline or slowly crystallized upon standing. The infrared spectra of the first and last of these fractions were almost identical. Recrystallization of the first fraction (0.1686 g) from ethanol gave 97 mg of light yellow needles, mp 166.1–167.0°; a second recrystallization from the same solvent afforded 68.6 mg of the pure adduct in the form of white needles, mp 166.3–167.2°.

Anal. Calcd for $C_{30}H_{30}O$: C, 88.63; H, 7.44. Found: C, 88.77; H, 7.53.

The nmr spectrum ($DCCl_3$) showed complex multiplets for aromatic protons at τ 1.90–3.00, a multiplet for methylene groups at 8.78, and sharp methyl singlets at 9.13 and 9.27.

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[22] Commercial silver oxide gave similar results.

[23] D. D. Coffman, E. L. Jenner, and R. D. Lipscomb, *J. Amer. Chem. Soc.*, 80, 2864 (1958).

[24] Kindly furnished by Dr. D. D. Coffman.

Further elution with benzene gave a solution shown by infrared analysis of the CN band at 2240 cm^{-1} to contain no more than about 83 mg (20% yield) of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladiponitrile.

Oxidation of 17 with Periodate–Permanganate. A stock oxidant solution was prepared from 20.86 g (97.5 mmol) of sodium periodate and 0.395 g (2.5 mmol) of potassium permanganate in 1 l. of water.[25] A small sample of hydrocarbon **17** was dissolved in 50 ml of *tert*-butyl alcohol and added to 50 ml of the stock oxidant solution (5 mmol of sodium periodate). The reaction mixture was treated with aqueous potassium hydroxide until a pH of 8 was attained and then was stirred at room temperature for 15 hr during which time the original permanganate color was partially discharged. The reaction mixture was then made acidic with a 50% hydrochloric acid solution and treated with aqueous sodium bisulfite until the solution was pale yellow. Aqueous potassium hydroxide was then added until the solution was strongly basic and, after standing for 30 min, the solution was filtered to remove the traces of flocculent brown precipitate which had appeared. The organic solvent was removed and the resulting aqueous solution made strongly acidic with concentrated hydrochloric acid and extracted several times with ether. The ethereal extracts were dried over magnesium sulfate and concentrated. Analysis of the concentrated ether solution by glpc on a Carbowax–terephthalic acid column at 95° with a flow rate of 10 ml/4 sec showed, among other peaks, a peak with retention time 12.6 min, the same as that of acetic acid.

The ether solution containing the oxidation products was then treated with an ethereal solution of diazomethane until the yellow diazomethane color was no longer discharged. The resulting solution was analyzed by glpc using a Ucon column at 71° and showed, among other peaks, a peak with retention time 4 min, the same as that of methyl acetate.

The esterified oxidation products in ether were then analyzed by glpc with a Ucon column at 200° and a flow rate of 46 ml/min. Other than the solvent peak there appeared a peak with retention time of 3.2 min and a peak with retention time 14.4 min, the same as that of dimethyl $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipate. A sample was collected from a similar run using an Apiezon L column and found to have an infrared spectrum identical with that of dimethyl $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipate.

Ozonolysis of Hydrocarbon 17. A solution of 0.226 g (0.83 mmol) of hydrocarbon **17** in 100 ml of methanol was cooled in a Dry Ice–acetone bath and treated with 0.5 mmol of ozone per minute in a stream of oxygen for 7 min. At the end of this time, the solution was clear light blue. The solution was flushed with oxygen and nitrogen and then 0.3 ml (0.25 g, 4.1 mmol) of dimethyl sulfide was added. The solution was left in the bath while it was agitated by nitrogen passing through a bubbler. It was then allowed to stand in the bath for 2 hr and at room temperature for 2 hr. At the end of this period a test for peroxides was negative (potassium iodide–starch solution).

The solvent was taken off on a Rotovap and collected in a Dry Ice trap. The addition of 2% 2,4-dinitrophenylhydrazine in 2 *N* HCl yielded a solid which had an infrared spectrum identical with that of a known sample of formaldehyde 2,4-dinitrophenylhydrazone and melted at 161–164° (lit.[26] mp 166°).

The residue was taken up in water and petroleum ether and the organic phase was washed with water and dried over sodium sulfate. The solvent was taken off on a Rotovap and the residue was purified by column chromatography on silica gel with the chloroform as elutant. The first 20 ml to contain material was concentrated to yield 22 mg of colorless oil, whose spectra are described in the discussion section.

Anal. Calcd for $C_{19}H_{30}O_2$: mol wt, 290.2246. Found: (mass spectrum) mol wt 290.2257. Other possible molecular formulae at parent mass 290 and their calculated precise masses are as follows: $C_{20}H_{34}O$, 290.2610; $C_{18}H_{26}O_3$, 290.1882; $C_{17}H_{22}O_4$, 290.1518; $C_{16}H_{18}O_5$, 290.1154; $C_{16}H_{34}O_4$, 290.2457; $C_{15}H_{30}O_5$, 290.2093.

Acknowledgments. This work was supported in part by National Science Foundation Grants G-7403, GP-166, and GP-4681, and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund.

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[25] E. von Rudloff, *Can. J. Chem.*, **34**, 1413 (1956).

[26] Reference 21, p 283.

Halogenated Ketenes. XXII. Solvolysis of Alkylhaloketene–Cyclopentadiene Adducts to 2-Alkyltropones[1]

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Abstract: The cycloadducts of alkylhaloketenes and cyclopentadiene were solvolyzed in aqueous base to produce 2-alkyltropones. A competing Favorskii-type ring contraction reaction also occurs producing 6-alkyl-6-carboxybicyclo[3.1.0]hex-2-enes. The 2-alkyltropones are produced only from the endo-alkyl isomer of the alkylhaloketene–cyclopentadiene adduct. The relative amounts of 2-alkyltropone and ring contraction product formed are strongly dependent on both the nature of the halogen and the steric size of the alkyl substituent on the alkylhaloketene. The exo-alkyl isomers of the alkylhaloketene–cyclopentadiene adducts undergo only the ring contraction reaction under the conditions used to produce 2-alkyltropone from the endo-alkyl cycloadducts. A mechanistic rationale is provided for these conversions.

There have been several reports on the conversion of the dichloroketene adduct of cyclopentadiene or a cyclopentadiene derivative to tropolone or a substituted tropolone.[2–6] This conversion has been proposed to occur either through a norcaradienone intermediate[4,5] or by substitution on the bridgehead carbon of the adduct through the enol form followed by ring

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