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Oxidation of a Bicyclobutane-Bridged Diene with $^1O_2$ and O_3. Wittig Reactions of the Corresponding Enone and Dione

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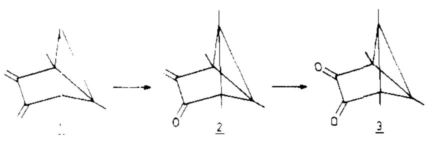
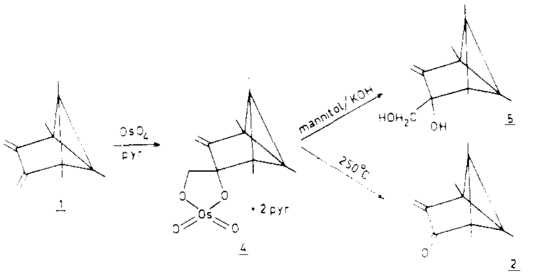
Oxidation of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane upon treatment with OsO_4, $^1O_2$, and O_3 is reported. The corresponding bicyclobutane-bridged α,β-unsaturated ketone and α-diketone are used as starting materials in Wittig reactions, which in one case result in cyclopropane formation.

Oxidation of organic compounds constitutes a subject with numerous ramifications.[1-5] Hydrocarbon oxidation using transition-metal compounds, peracids, and peroxides together with photosensitized oxygenations and ozonization rank among the frequently employed methods in this area in which phase-transfer catalysis[6] and crown ether chemistry[7] are of increasing importance.

In view of the intriguing reactivity of tricyclic diene 1,[8,9] e.g., in Diels–Alder reactions, we aimed at synthesizing the corresponding enone 2 and diketone 3 from 1. Two types of ketone preparation involving carbon–carbon bond breaking, one-step and two-step cleavage reactions, are opportune. Apart from realization of the diene → enone → dione transformations, attention has to be paid to keep the bicyclobutane moiety intact. Generally speaking this leaves out the modes of oxidation which involve the use of acids and those in which the presence of certain transition metals is required. In the present paper the results of some oxidation reactions (e.g., O_3, $^1O_2$) of compound 1 are described, together with those of the Wittig reactions of enone 2 and dione 3.



Oxidation of 1. A. Osmium Tetroxide. The highly poisonous osmium tetroxide can be employed to convert olefins to glycols or ketones, depending upon reaction conditions; the initially formed adducts in many cases are of sufficient stability to permit their isolation.[10,11] Upon addition of osmium tetroxide at room temperature to diene 1 in ether containing pyridine (10:1), a brown precipitate was formed immediately. To this compound structure 4 is tentatively assigned. Supporting data for the proposed structure were obtained by performing a reductive cleavage of 4 by mannitol in an alkaline solution, leading to glycol 5, and a pyrolysis at 250 °C, affording α,β-unsaturated ketone 2, which was trapped at −196 °C. However, this expensive route did not allow a large scale preparation of 2 and was abandoned for this reason.



B. Singlet Oxygen. Rearrangements of [2 + 4] adducts from singlet oxygen ($^1O_2$) and conjugated dienes[12] to α,β-unsaturated [2 + 2] adducts are known in the literature.[13-15]

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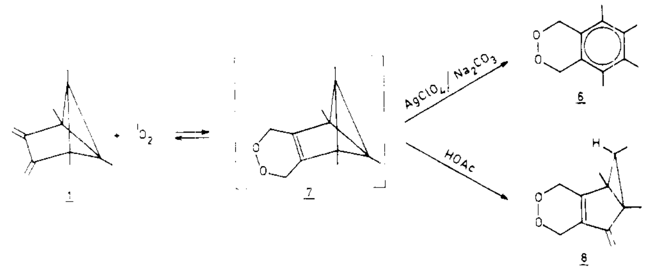
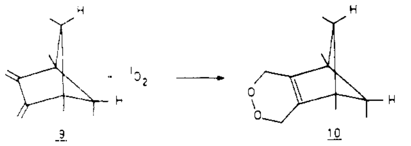
Furthermore, fragmentation of dioxetanes is a common process.[16,17] In view of these data, singlet oxygen addition to diene 1 was investigated. However, no reaction between $^1O_2$ and 1 was observed at room temperature ($^1O_2$ was generated in a methylene blue sensitized reaction). When this experiment was repeated after addition of a catalytic amount of silver perchlorate together with sodium carbonate to the methylene chloride solution, diene 1 was rapidly converted to peroxide 6.[18,19] Because of the fact that $AgClO_4/Na_2CO_3$ was not found to accelerate the addition of $^1O_2$ to other conjugated dienes (cyclohexadiene and 9), the smooth formation of aromatic compound 6 may indicate that a benzvalene (7) participates in an equilibrium which exists under the prevailing experimental conditions. Since it has been reported[20] that, apart from their behavior towards $AgClO_4/Na_2CO_3$, benzvalenes are extremely sensitive to acids, $AgClO_4/Na_2CO_3$ was replaced by acetic acid (20 mol %) in another $^1O_2$ experiment. As expected,[20] a homofulvene (8) could be isolated in this case, which reinforces the idea of a preequilibrium in the singlet oxygen reaction. The hope of being able to prove this experimentally by performing the reaction of 1 with $^1O_2$ at −70 °C and running the ^1H NMR spectra of the sample at the same temperature was not fulfilled, however.

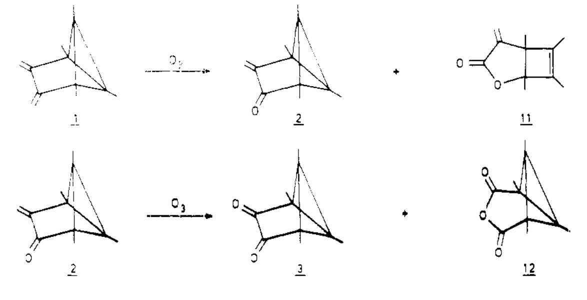
It is of interest to note that bicyclic diene 9 does react with $^1O_2$ at room temperature, leading to 10.[21] Although the observed difference[22] between 1 and 9 is intriguing, no progress was made in this approach as far as the synthesis of 2 and 3 is concerned.





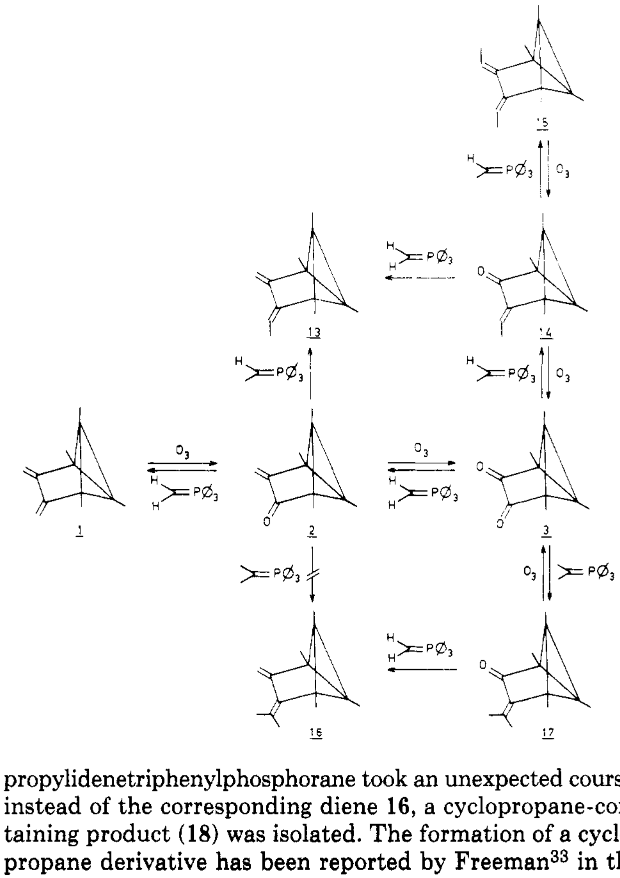
C. Ozonolysis. In a third attempt to convert 1 to 2 and subsequently to 3, we made use of O_3. There are reasons to assume that the initial interaction between a carbon π system and ozone leads to the reversible formation of a π complex,[23] the fate of which depends on the character of the organic substrate. The possibilities are in principle the entrance into a 1,3-dipolar cycloaddition, leading ultimately to ozonolysis products via a 1,2,3-trioxolane, and the conversion to a σ complex followed by loss of an oxygen molecule, resulting in epoxide formation. The ratio of epoxide to cleavage products increases with increasing steric hindrance around the double bond in question.

Initially, ozonolysis of diene 1[24] was performed in chloroform at room temperature. Ozone was added until no ^1H NMR signals due to olefinic protons of the diene could be observed anymore. Two products were formed in a 1:4 ratio and identified as the α,β-unsaturated ketone 2 and the rearranged ester 11, respectively, When the ozonolysis was carried out in the presence of Na_2CO_3 or pyridine, the product ratio changed to 1:1 in the former and 4:1 in the latter case. Ozonolysis of ketone 2 under similar conditions in chloroform containing pyridine was performed: again two products were isolated from the reaction mixture, the α-diketone 3[25] and the anhydride 12, which were formed in a 9:2 ratio. Bicyclic diene 9 reacts with ozone in a different manner: epoxides are formed exclusively.[21] Data provided by Story and Burgess[28] support the idea that most abnormal ozonolysis products are in fact normal Baeyer–Villiger products generated by the action of the peracid formed in the reaction. Actually, in our case the *m*-chloroperbenzoic acid oxidation of 2 leads to 11 and that of 3 to 12. Thereupon, more detailed investigations led to the conclusion that both 2 and 3 can be made the sole identifiable products in their respective reaction steps: the former by performing the reaction at low temperatures in methylene chloride and pyridine, and the latter by performing the ozonolysis of 2 in methanol at room temperature followed by addition of dimethyl sulfide.[29] Of course, the Baeyer–Villiger reactions mentioned earlier make it possible to synthesize exclusively both 11[30] and 12.

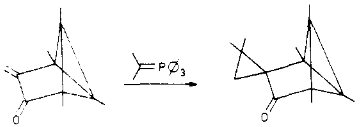


Wittig Reactions of 2 and 3. Investigations concerning the chemical aspects of diene 1[18,19,32] made it desirable to have a route to substituted dienes at one's disposal. Of course, both enone 2 and dione 3 can in principle take part in Wittig reactions. Experiments performed in this area are jointly represented in Scheme I. The reaction between enone 2 and isopropylidenetriphenylphosphorane took an unexpected course: instead of the corresponding diene 16, a cyclopropane-containing product (18) was isolated. The formation of a cyclopropane derivative has been reported by Freeman[33] in the reaction between methylidenetriphenylphosphorane and mesitoylphenylethylene, in which attack at the carbonyl carbon is sterically hindered. However, steric effects alone are not enough as a motive for cyclopropane formation in our case

Scheme I

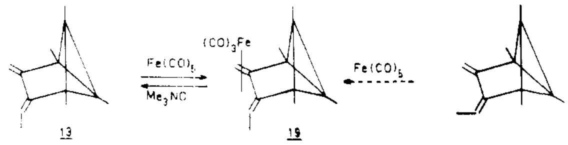


since **17** could be prepared in high yield from **3**, in which case the ylide was given no alternative. Hence, as to be expected,



2 18

steric and electronic aspects of both reactants affect the outcome of the reaction. On the basis of the observed mode of attack of **2** by isopropylidenetriphenylphosphorane, one may wonder whether in **13** and **14** the methyl substituent is in a syn or anti position. Addition of successive portions of Eu(fod)$_3$ gave rise to ^1H NMR shift enhancements which indicate the substituent to be in a syn position in **14**. A second method to solve syn–anti problems in conjugated dienes rests on the principle of complexation[34] followed by decomplexation:[35] the fact that **13** as a starting material proved to be identical with the diene obtained by oxidation of **19** is in agreement with the



13 19

presence of a syn-methyl group in **13** (the synthesis and chemical aspects of the iron tricarbonyl complex of **1** have been reported[36]).

Experimental Section

General Remarks. Melting points are uncorrected. Mass spectra were run on a AEI MS-902. Infrared spectra (Nujol mull) were recorded on a Perkin-Elmer Infracord 257 spectrophotometer. ^1H NMR spectra were taken with a Jeol C-60 HL spectrometer with deuteriochloroform as the solvent and Me$_4$Si as an internal reference. ^{13}C NMR spectra were run on a Varian XL-100 with deuteriochloroform as the solvent and Me$_4$Si as an internal reference. Preparative TLC was performed with aluminium oxide (Merck; 10–40 μm, not activated).

OsO$_4$ Addition to 1. To a solution of diene **1** (0.160 g, 1.00 mmol) in ether (10 mL) and pyridine (1.0 mL) was added OsO$_4$ (0.254 g, 1.00 mmol) while stirring at room temperature. A brown precipitate was formed immediately, which in part was filtered. This solid material (0.217 g) was heated at 250 °C under reduced pressure (1.0 mm) for 10 min, and both enone **2** (22 mg) and pyridine (49 mg) were trapped at −196 °C. Spectroscopic data of **2** were identical with those of material obtained from ozonolysis of **1**.

Mannitol (1.0 g) and aqueous potassium hydroxide (10%, 10 mL) were added to the remaining suspension, and the mixture was stirred overnight at room temperature. The aqueous layer was extracted with methylene chloride (3 × 5 mL), and the combined organic layers were subsequently dried over anhydrous potassium carbonate. Evaporation of the solvent under reduced pressure followed by preparative TLC (methylene chloride) afforded **5** as a colorless viscous oil (58 mg, 0.30 mmol): ^1H NMR δ 1.09 (s, 3 H), 1.11 (s, 3 H), 1.31 (s, 3 H), 1.35 (s, 3 H), 3.54 (broad s, 2 H), 4.67 (s, 1 H), and 4.87 (s, 1 H); IR 1650 and 3400 (broad) cm^{-1}; MS Calcd exact mass, *m/e* 194.131 (M$^+$); MS Found, *m/e* 194.135. When pyridine was omitted no **5** could be obtained.

$^1O_2$ Addition to Diene 1. A solution of diene **1** (1.60 g, 10.0 mmol) and methylene blue (50 mg) in methylene chloride (150 mL) continuously saturated with oxygen was irradiated at room temperature for 48 h with a high-pressure mercury arc (Hanau S81) using a saturated aqueous solution of potassium bichromate as a filter. Diene **1** was completely recovered upon filtration through Al$_2$O$_3$ followed by evaporation of the solvent. When the reaction was carried out at −70 °C no spectroscopic indication (^1H NMR) for the presence of **7** in the reaction mixture could be obtained. In the presence of AgClO$_4$ (41 mg, 0.20 mmol) and Na$_2$CO$_3$ (1.0 g) the experiment was repeated at room temperature under otherwise identical conditions. After 90 min **1** was completely converted. The usual workup followed by crystallization from *n*-pentane afforded **6** (1.78 g, 9.27 mmol; 93%): mp 160.5–161.5 °C; H NMR δ 2.08 (s, 6 H), 2.22 (s, 6 H), and 5.09 (s, 4 H); IR 800, 970, 995, and 1045 cm^{-1}; MS *m/e* 192 (M$^+$). Anal. Calcd for C$_{12}$H$_{16}$O$_2$: C, 74.97; H, 8.39. Found: C, 74.61; H, 8.29.

When acetic acid (0.12 g, 2.0 mmol) was added to the solution instead of AgClO$_4$/Na$_2$CO$_3$, diene **1** was found to be completely transformed to homofulvene **8** within 2.5 h under otherwise identical conditions. Compound **8** was purified by preparative TLC (*n*-pentane): ^1H NMR δ 0.92 (distorted q, *J* = 6 Hz, 1 H), 1.03 (distorted d, *J* = 6 Hz, 3 H), 1.10 (s, 3 H), 1.20 (s, 3 H), and 4.67–4.83 (6 H); IR 890, 990, and 1600 cm^{-1}; MS Calcd exact mass, *m/e* 192.115 (M$^+$); MS Found, *m/e* 192.116.

When cyclohexadiene or bicyclic diene **9** was allowed to react with $^1O_2$ at room temperature under the conditions mentioned above, it was found that the presence of AgClO$_4$/Na$_2$CO$_3$ did not alter the reaction rates of the $^1O_2$ addition.[21,37]

Synthesis of 1,2,5,6-Tetramethyl-4-methylenetricyclo[3.1.0.0^{2,6}]hexan-3-one (2). Procedure I. At room temperature ozone was added at a rate of 1.5 g/h (oxygen flow of 20 L/h through a Fischer OZ III "Ozone Generator") to a stirred solution of **1** (0.800 g, 5.00 mmol) in CHCl$_3$ (10 mL) until no ^1H NMR signals due to olefinic protons of the diene could be observed anymore. Two products were formed in a 1:4 ratio (^1H NMR), isolated (GLC; SE-30 column all temperatures below 200 °C), and identified as **2** and **11**, respectively. Enone **2**: mp 45.0–45.5 °C; ^1H NMR δ 1.16 (s, 3 H), 1.27 (s, 3 H), 1.51 (s, 6 H), 4.94 (s, 1 H), and 5.67 (s, 1 H); ^{13}C NMR δ 3.3, 4.4, 7.2, 30.9, 41.3, 50.9, 106.1, 149.3, and 210.3; IR 1650 and 1720 cm^{-1}; MS *m/e* 178 (M$^+$); UV (ethanol) λ_{max} 215 nm (log ϵ 3.7) and 314 (1.3). Anal. Calcd for C$_{11}$H$_{14}$O: C, 81.48; H, 8.64. Found: C, 81.00; H, 8.62.

Lactone **11**: mp 55.0–56.0 °C; ^1H NMR δ 1.22 (s, 3 H), 1.38 (s, 3 H), 1.55 (broad s, 6 H), 5.53 (s, 1 H), and 6.28 (s, 1 H); ^{13}C NMR δ 7.9, 8.5, 15.0 (2C), 53.4, 87.8, 120.3, 141.0, 142.1, 143.6, and 170.5; IR 1650 and 1750 cm^{-1}; MS *m/e* 178 (M$^+$). Anal. Calcd for C$_{11}$H$_{14}$O$_2$: C, 74.16; H, 7.87. Found: C, 74.00; H, 7.92.

Procedure II. When the ozonolysis was carried out in the presence of Na$_2$CO$_3$ (1.0 g) under otherwise identical conditions, the ratio of compounds **2** and **11** changed to 1:1 (^1H NMR).

Procedure III. Addition of pyridine (1.0 mL) instead of Na$_2$CO$_3$ (procedure II) afforded **2** as the major product (the ratio of compounds **2** and **11** was 4:1, respectively), as determined by ^1H NMR spectroscopy.

Procedure IV. Diene **1** (28.8 g, 180 mmol) dissolved in CH$_2$Cl$_2$ (750 mL) containing pyridine (36 mL) was ozonolyzed (O$_2$ flow >80 L/h) at −60 °C for 2 h and 53 min under vigorous mechanical stirring. The solution was allowed to warm to room temperature overnight, and subsequently methylene chloride and pyridine were removed by evaporation under reduced pressure. *n*-Hexane (100 mL) was added to the residue, the mixture was stirred for 2 h, and water (50 mL) was introduced. The reaction mixture was filtered through Celite-535, the layers were separated, and the organic phase was washed with water (3 × 10 mL) and a saturated aqueous solution of NaCl (2 × 10 mL) and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent under reduced pressure afforded crude **2** (29.7 g), which was estimated to be about 60% pure (^1H NMR). Enone **2** was purified by distillation under reduced pressure (30–40 °C, 0.01 mm): yield 53% (15.5 g, 95.7 mmol), purity 85% (^1H NMR). Analytically pure enone **2** was obtained by crystallization from *n*-pentane followed by sublimation at 35 °C. The fact that none or at the most only negligible amounts of **11** are formed makes this procedure the one of choice for the synthesis of **2**.

Procedure V. According to the method reported by Thompson,[38] the concept of reductive decomposition of the trioxolane at low temperatures was investigated. Employing triphenylphosphine or dimethyl sulfide, no improvements concerning the yield of **2** or the workup procedure were made compared with procedure IV.[39]

Preparation of 1,2,5,6-Tetramethyltricyclo[3.1.0.0^{2,6}]hexane-3,4-dione (3). Procedure I. Analogous to procedure III, enone **2** (0.810 g, 5.00 mmol) was ozonolyzed in CHCl$_3$ (10 mL) containing pyridine (1.0 mL). Two products were formed, isolated (repeated fractional crystallizations from ether followed by sublimations), and identified as α-diketone **3** and anhydride **12**, which were present in the reaction mixture in a 9:2 ratio, respectively. Diketone **3**: mp 142.5–143.0 °C; ^1H NMR δ 1.30 (s, 6 H) and 1.67 (s, 6 H); ^{13}C NMR δ 3.5, 4.6, 28.7, 51.6, and 194.6; IR 1750 cm^{-1}; UV-vis (ethanol) λ_{max} 272 nm (log ϵ 1.1) and 436 (1.4); MS *m/e* 164 (M$^+$). Anal. Calcd for C$_{10}$H$_{12}$O$_2$: C, 73.06; H, 7.36. Found: C, 72.92; H, 7.33.

Anhydride **12**: mp 154.0–155.0 °C; ^1H NMR δ 1.30 (s, 6 H) and 1.54 (s, 6 H); ^{13}C NMR δ 3.7, 10.0, 31.6, 41.9, and 169.6; IR 1770 and 1800 cm^{-1}; MS *m/e* 180 (M$^+$). Anal. Calcd for C$_{10}$H$_{12}$O$_3$: C, 66.73; H, 6.72. Found: C, 66.68; H, 6.71.

Procedure II. Enone **2** (4.82 g, 30.0 mmol) dissolved in dry methanol (125 mL) was ozonolyzed (O$_2$ flow 10 L/h; i.e., 1.2 g of O$_3$ per hour) at room temperature for 72 min. Subsequently ozone was removed by a stream of nitrogen, and dimethyl sulfide (3.0 mL) was added to the solution. Stirring was continued for 1 h. Evaporation of the solvent under reduced pressure ($T \leq 40$ °C) followed by column (diameter = 2.5 cm) chromatography (Merck, activity II–III, 50 g of Al_2O_3; ether,) of crude **3** (dissolved in CH_2Cl_2) afforded **3**, which was crystallized from ether, yield 43% (2.13 g, 13.0 mmol). This procedure constitutes the best method for the synthesis of **3**, with no **12** being formed.

Syntheses of 11 and 12. When **2** (0.162 g) or **3** (0.164 g) dissolved in $CHCl_3$ (5 mL) was treated with *m*-chloroperbenzoic acid (0.150 g) in the presence of Na_2CO_3 (1.0 g) at room temperature, the exclusive formation of **11** and **12**, respectively, was observed (^{1}H NMR).

Wittig Reactions: General Procedures. Method A. To a stirred suspension of phosphonium salt (5.00 mmol) in dry THF (50 mL) was added *n*-BuLi (2.8 mL, 1.8 N in *n*-hexane) under a nitrogen atmosphere at room temperature. A solution of the substrate (5.00 mmol) in THF (2 mL) was subsequently introduced. The workup procedure consisted of addition of water (100 mL), extraction with *n*-pentane (2 × 50 mL), drying of the combined organic layers over anhydrous potassium carbonate, filtration, evaporation of the solvent under reduced pressure, and preparative TLC (*n*-pentane).

Method B. In this case the ylide was added to the organic substrate in THF (30 mL). The workup was according to method A above.

Tetracyanoethylene (TCNE) Adducts. All newly synthesized dienes were for analytical purposes converted to their polycyclic TCNE adducts, which isomerized to aromatic compounds prior to melting.[8,19] General procedure: to a solution of the diene (0.20 mmol) in chloroform (5 mL) was added TCNE (0.025 g, 0.20 mmol) at room temperature; after stirring for 10 min the solvent was evaporated, and the obtained solid material was crystallized from ether; the polycyclic TCNE adduct was heated as such at 100 °C for 15 min, followed by crystallization from ether.

Ozonolysis of Substituted Enones. In a way essentially analogous to the one reported for the synthesis of **3** from **2** according to procedure II, all newly prepared enones were ozonolyzed to **3**, in qualitative experiments, in order to obtain confirmable information about their polycyclic skeleton.

Synthesis of 13 from 2 (Method A). Reaction time: 30 min at room temperature. Using the phosphonium bromide, compound **13** was isolated in 73% yield as a colorless liquid (0.635 g, 3.65 mmol): ^{1}H NMR δ 1.10 (s, 3 H), 1.36 (s, 9 H), 1.83 (d, J = 7 Hz, 3 H), 4.40 (s, 1 H), 4.86 (s, 1 H), and 5.68 (q, J = 7 Hz, 1 H); IR 1640 and 3080 cm^{-1}; MS *m/e* (M$^+$) 174.

Polycyclic TCNE adduct: ^{1}H NMR δ 1.06 (s, 3 H), 1.15 (s, 3 H), 1.45 (s, 3 H), 1.47 (s, 3 H), 1.62 (d, J = 7 Hz, 3 H), and 3.0–3.5 (m, 3 H); IR 1660 and 2240 cm^{-1}.

Aromatic TCNE adduct: mp 190.5–191.5 °C; ^{1}H NMR δ 1.68 (d, J = 7 Hz, 3 H), 2.17 (s, 3 H), 2.20 (s, 9 H), 3.54 and 3.74 (AB system, J_{AB} = 17 Hz, 2 H), and 3.95 (q, J = 7 Hz, 1 H); IR 2250 cm^{-1}; MS *m/e* 302 (M$^+$). Anal. Calcd for $C_{19}H_{18}N_4$: C, 75.47; H, 6.00. Found: C, 75.39; H, 5.98.

Synthesis of 14 from 3 (Method B). Reaction time: 15 min at room temperature. An 81% yield of **14** as a viscous oil (0.717 g, 4.07 mmol) was obtained using the phosphonium bromide: ^{1}H NMR δ 1.05 (s, 3 H), 1.45 (s, 3 H), 1.51 (s, 6 H), 1.84 (d, J = 8 Hz, 3 H), and 6.05 (q, J = 8 Hz, 1 H); IR 1650 and 1710 cm^{-1}; MS *m/e* 176 (M$^+$). Induced downfield shifts varied linearly with the ratio [Eu(fod)$_3$]/[**14**] in the range 0.0–0.7, $\Delta\delta_H$ = 7.0 ppm and $\Delta\delta_{CH_3}$ = 2.0 ppm at [Eu(fod)$_3$]/[**14**] = 0.7 (H and CH_3 are the substituents of the terminal sp^2 carbon atom), in agreement with the presence of the CH_3 group in the syn position in **14**.

Preparation of 13 from 14 (Method A). Reaction time: 15 min at room temperature. Using the phosphonium iodide, compound **13** was isolated in 69% yield (0.598 g, 3.44 mmol). The spectroscopic data were in agreement with those of material obtained using **2** as the starting material.

Synthesis of 15 from 14 (Method A). Reaction time: 1 h at room temperature. A 73% yield of **15** as a colorless liquid (0.683 g, 3.63 mmol) was isolated using the phosphonium bromide: ^{1}H NMR δ 1.35 (s, 6 H), 1.38 (s, 6 H), 1.84 (d, J = 7 Hz, 6 H), and 5.53 (q, J = 7 Hz, 2 H); IR 1635 and 3040 cm^{-1}; MS *m/e* 188 (M$^+$).

Polycyclic TCNE adduct: ^{1}H NMR δ 1.12 (s, 6 H), 1.45 (s, 3 H), 1.48 (s, 3 H), 1.63 (d, J = 7 Hz, 6 H), and 3.25 (q, J = 7 Hz, 2 H); IR 1650 and 2250 cm^{-1}.

Aromatic TCNE adduct: mp 192.0–193.0 °C; ^{1}H NMR δ 1.71 (d, J = 7 Hz, 6 H), 2.25 (s, 12 H), and 4.03 (q, J = 7 Hz, 2 H); IR 2260 cm^{-1}; MS *m/e* 316 (M$^+$). Anal. Calcd for $C_{20}H_{20}N_4$: C, 75.92; H, 6.37. Found: C, 75.69; H, 6.42.

Preparation of 17 from 3 (Method B). Reaction time: 15 min at room temperature. A 79% yield of **17** as a viscous oil (0.752 g, 3.96 mmol) was obtained employing the phosphonium bromide: ^{1}H NMR δ 1.06 (s, 3 H), 1.41 (s, 3 H), 1.45 (s, 6 H), 1.88 (s, 3 H), and 2.07 (s, 3 H); IR 1650 and 1700 cm^{-1}; MS *m/e* 190 (M$^+$).

Synthesis of 16 from 17 (Method A). Reaction time: 1 h under reflux. Using the phosphonium iodide, compound **16** was isolated as a colorless liquid in 72% yield (0.679 g, 3.61 mmol): ^{1}H NMR δ 1.08 (s, 3 H), 1.33 (s, 3 H), 1.37 (s, 6 H), 1.94 (broad s, 6 H), 4.73 (s, 1 H), and 4.98 (s, 1 H); IR 1640 and 3080 cm^{-1}; MS *m/e* 188 (M$^+$).

Polycyclic TCNE adduct: ^{1}H NMR δ 1.01 (s, 3 H), 1.16 (s, 3 H), 1.44 (s, 6 H), 1.57 (s, 6 H), and 3.18 (s, 2 H); IR 1650 and 2260 cm^{-1}.

Aromatic TCNE adduct: mp 191.5–192.5 °C; ^{1}H NMR δ 1.70 (s, 6 H), 2.20 (s, 3 H), 2.25 (s, 9 H), and 3.76 (s, 2 H); IR 2260 cm^{-1}; MS *m/e* 316 (M$^+$). Anal. Calcd for $C_{20}H_{20}N_4$: C, 75.92; H, 6.37. Found: C, 75.58; H, 6.42.

Preparation of 2 from 3 (Method B). Reaction time: 15 min at room temperature. Employing the phosphonium iodide gave an 84% yield (0.684 g, 4.22 mmol). The spectroscopic data were in agreement with those of material obtained from the ozonolysis of **1**.

Synthesis of 1 from 2 (Method A). Reaction time: 15 min at room temperature. Using the phosphonium iodide, compound **1** was isolated in 78% yield (0.621 g, 3.88 mmol). The spectroscopic data were in agreement with those of authentic material.[9]

Preparation of 18 from 2 (Method A). Reaction time: 6 h under reflux. A 57% yield of **18** (0.578 g, 2.83 mmol) was isolated employing the phosphonium bromide: ^{1}H NMR δ 0.74 (s, 2 H), 1.07 (s, 6 H), 1.17 (s, 3 H), 1.21 (s, 3 H), 1.42 (s, 3 H), and 1.48 (s, 3 H); ^{13}C NMR δ 2.6, 3.5, 4.8, 10.3, 19.7, 22.9, 23.5, 25.3, 29.7, 31.9, 38.0, 38.8, 52.2, and 216.4; IR 1735 and 3050 cm^{-1}; MS Calcd exact mass, *m/e* 204.151 (M$^+$); MS Found, *m/e* 204.154. Anal. Calcd for $C_{14}H_{20}O$: C, 82.31; H, 9.87. Found: C, 82.79; H, 10.01.

Preparation of the Fe(CO)$_3$ Complex 19. Diene **13** (0.696 g, 4.00 mmol) was heated with iron pentacarbonyl (1.60 g, 8.00 mmol) at 70 °C for 24 h under a blanket of nitrogen. The mixture was cooled and filtered, and excess iron pentacarbonyl was removed by distillation under reduced pressure. Preparative TLC (*n*-pentane) afforded **19** as an orange liquid (0.347 g, 1.11 mmol; 28%): ^{1}H NMR δ 0.45 (d, J = 2.5 Hz, 1 H), 1.11 (q, J = 7.0 Hz, 1 H), 1.16 (s, 3 H), 1.37 (s, 3 H), 1.49 (s, 3 H), 1.57 (s, 3 H), 1.66 (d, J = 7.0 Hz, 3 H), and 2.05 (d, J = 2.5 Hz, 1 H); IR 1980 and 2060 cm^{-1}; MS *m/e* 314 (M$^+$) (peaks at *m/e* 286, 258, and 230 indicate the successive loss of CO ligands).

Oxidation of 19. Complex **19** (0.347 g, 1.11 mmol) was heated in benzene (5 mL) at 40 °C for 2 days in the presence of Me_3NO[35] (3.0 g) in a nitrogen atmosphere. The mixture was cooled and filtered, and the solvent was evaporated under reduced pressure. Preparative TLC (*n*-pentane) yielded only diene **13** (48 mg, 0.28 mmol; 25%).

Registry No.—**1**, 50590-86-8; **2**, 56745-77-8; **3**, 56745-78-9; **4**, 65121-37-1; **5**, 65102-61-6; **6**, 65102-62-7; **8**, 65102-63-8; **11**, 56745-76-7; **12**, 56745-79-0; **13**, 65102-64-9; **13**·TCNE, 65121-38-2; **14**, 65102-65-0; **15**, 65102-66-1; **15**·TCNE, 65102-70-7; **16**, 65102-67-2; **16**·TCNE, 65102-71-8; **17**, 65102-68-3; **18**, 65102-69-4; **19**, 65120-34-5; OsO_4, 20816-12-0; Fe(CO)$_5$, 13463-40-6; O_2, 7782-44-7

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Cyclopropane and Allene Analogues of a Bicyclobutane-Bridged Diene

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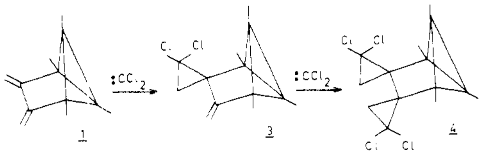
Bicyclobutane-bridged diene **1**, 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane, was used as starting material in the syntheses of cyclopropanes and allenes. These compounds were prepared by performing modifications of the butadiene moiety in **1**. First of all, dihalocarbene additions were carried out under phase-transfer conditions. Reduction of the geminal dihalocyclopropanes with sodium in liquid ammonia afforded cyclopropanes. Allenes were prepared by treating the geminal dibromocyclopropanes with methyllithium. Reactions of the allene and cyclopropane analogues of **1** with tetracyanoethylene are reported.

The bicyclobutane-bridged diene 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane, **1**,[1,2] has recently been found to be extremely reactive in Diels–Alder cycloadditions.[3] Compound **1** is also easily available in large amounts.

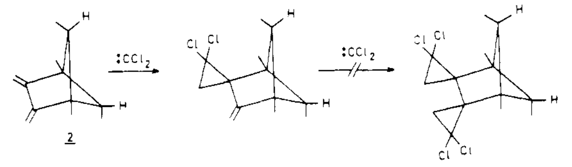


These two facts led us to consider the use of **1** as starting material in the syntheses of small ring compounds and reactive multiple bonds.

In order to minimize the risks of bicyclobutane rearrangements during modifications of the carbon–carbon double bonds of the diene moiety of **1** into allenes or cyclopropanes, it was evident that reaction paths involving the use of transition metals or acids had to be avoided. Our hope was that the transformations would occur at reasonably low temperatures and via synthesis of a common precursor or directly from the diene. Since allenes can easily be synthesized from geminal dihalocyclopropanes and alkyllithium compounds[4-8] and, moreover, reductions of geminal dihalocyclopropanes yield cyclopropanes,[4,5] geminal dihalocyclopropanes in principle constitute the desired type of precursor and our attention was drawn to their preparation.

Dihalocarbene generation under phase-transfer conditions proved to be a versatile method which facilitated the synthesis of a substantial number of geminal dihalocyclopropanes. Although the reaction of dichlorocarbene generated according to classical methods with conjugated olefins usually does not occur beyond the addition of 1 equiv, mono and multiple additions are easily accomplished with dichlorocarbene generated under phase-transfer catalysis conditions.

Dihalocarbene Additions. According to the general procedure as reported by Makosza and Warzyniewicz,[9] diene **1** was allowed to react with dichlorocarbene at room temperature under vigorous stirring. Within 1 h **1** was converted to the bis adduct (80%), of which only the trans isomer appeared to be present. This is due to the fact that one of the chlorine atoms erects a barrier at the cis side in the mono adduct. The smooth formation of the bis adduct mentioned above is in sharp contrast with the unsuccessful attempts to prepare a bis adduct in the case of diene **2**,[10] in which compared with **1** the central bicyclobutane C–C bond has been opened, therewith in principle allowing the methyl groups in question to exert more steric influence on chemical events at the diene moiety.



A modification of the organic phase, *n*-pentane and chloroform in a 3:1 ratio, made it possible to synthesize and isolate the mono adduct **3** (76%) of dichlorocarbene and diene **1** under otherwise identical conditions.

The same method allows the generation of the dibromocarbene adducts. The yields of the adducts are lower than those achieved in the corresponding dichlorocarbene reactions. Furthermore, the mono and bis adducts of dibromocarbene and **1** (compounds **5** (38%) and **6** (28%), respectively) were found to be less stable than their chloro analogues. Thermal disrotatory ring opening[11,12] takes place very easily, especially in the case of **6**, leading to a compound which we tentatively assign as structure **7**.

Synthesis of a Mono- and Bisallene. The treatment of geminal dibromocyclopropanes with methyllithium is known to provide a widely applicable route to allenes.[4,8] Intramo-

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