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Cyclopropane and Allene Analogues of a Bicyclobutane-Bridged Diene

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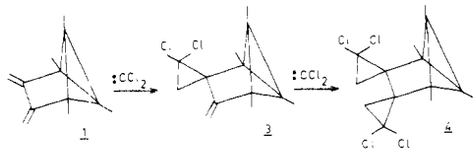
Bicyclobutane-bridged diene **1**, 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane, was used as starting material in the syntheses of cyclopropanes and allenes. These compounds were prepared by performing modifications of the butadiene moiety in **1**. First of all, dihalocarbene additions 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.

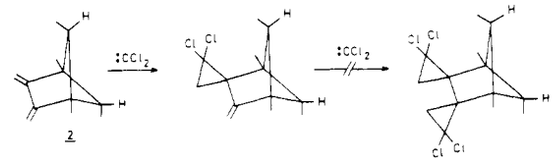


These two facts led us to consider the use of **1** as starting material in the syntheses of small ring compounds and reactive multiple bonds.

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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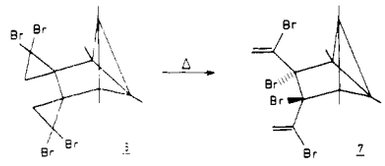
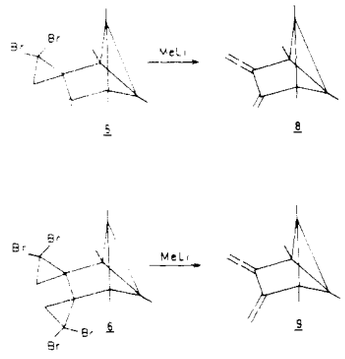


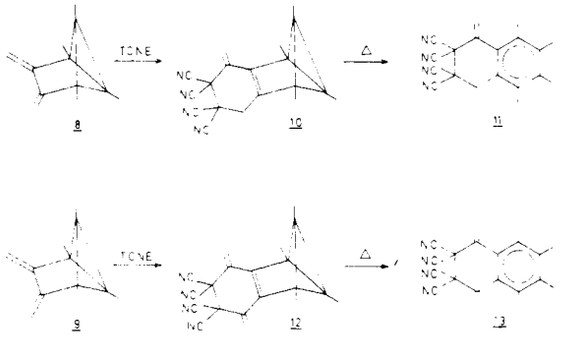
lecular reactions may cause complications, however, when the bromides involved are derivatives of vinylcyclopropane or bicyclopropane: Skattebøl obtained cyclopentadienes in the former and fulvenes in the latter case as the major products.[8]

Because of these findings a risk of intramolecular mishaps existed also in the planned conversion of **5** to monoallene **8** and

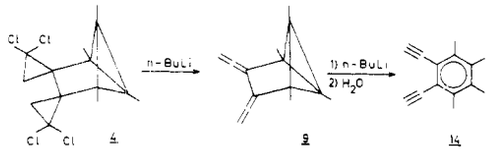


of **6** to bisallene **9**. However, when methyllithium was added at low temperature (−50 °C) to ether solutions of either **5** or **6** followed by workup at room temperature, the allenes **8** and **9** were isolated as the major product. Although the formation of minor amounts of a cyclopentadiene and a fulvene, respectively, cannot rigorously be excluded, there were no spectroscopic indications for their presence in the reaction mixtures immediately after workup.

The allenes were allowed to react with tetracyanoethylene (TCNE) at room temperature, and after isomerization of the bicyclobutane moieties the aromatic cycloadducts **11** and **13** were subjected to elemental analyses.

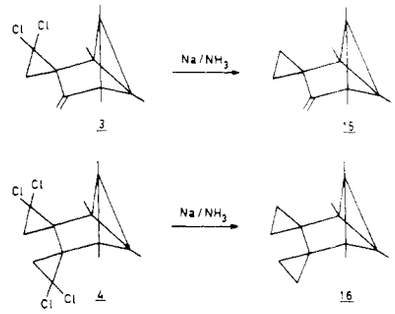


When the chloro analogues **3** and **4** were treated likewise with methyllithium, the starting materials were recovered unchanged. Neither was compound **8** formed from **3** using *n*-butyllithium. However, bis adduct **4** did undergo the desired reaction on addition of *n*-butyllithium, but the reaction mixture consisted of **4**, bisallene **9**, and *o*-diethynylbenzene derivative **14**. The intermediacy of **9** in the conversion of **4** to

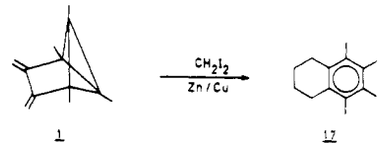


14 was shown by an experiment in which a large excess of *n*-butyllithium was added to a sample of pure bisallene **9**, prepared from **6**, affording exclusively **14**.[13] The allene–acetylene equilibrium can be set up by the use of catalytic amounts of strong bases. No equilibrium is obtained when large quantities of base are used, but all the material is tied up as the alkali salt of the terminal acetylene.[14]

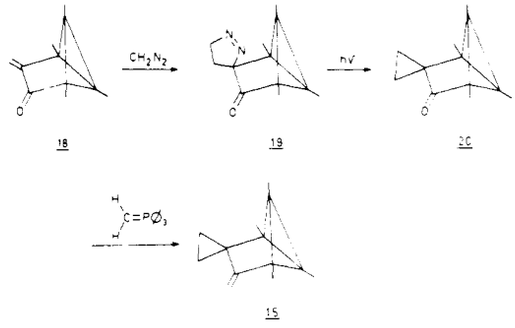
Synthesis of a Mono- and Bicyclopropane. The Na/NH_3 type of reduction[15] was tried on **3**, **4**, **5**, and **6**. This approach turned out to be successful in all cases, and both the bicyclobutane-bridged vinylcyclopropane **15** and bicyclopropane **16** were isolated. Since these compounds can be synthesized in higher yields and, moreover, are easier to handle, the geminal dichlorocyclopropanes **3** and **4** are preferable to the corresponding dibromo compounds **5** and **6** as starting materials.



Attempts to prepare **15** and **16** directly from diene **1** according to the method published by Simmons and Smith[16] failed due to isomerization of the bicyclobutane moiety. The tetraline derivative **17** was isolated in spite of the presence of dimethoxyethane, which was recommended to prevent Lewis acid catalyzed rearrangements under the prevailing conditions (Simmons–Smith reagent/diene **1**, 3:1).

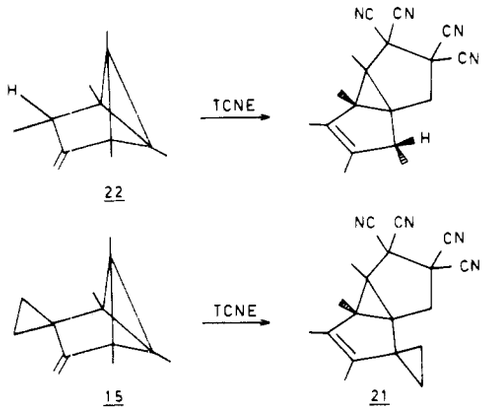


Diazomethane addition to unsaturated ketone **18**[21] followed by the photochemically induced loss of nitrogen and a Wittig reaction provides another route to **15** which proceeds in a high

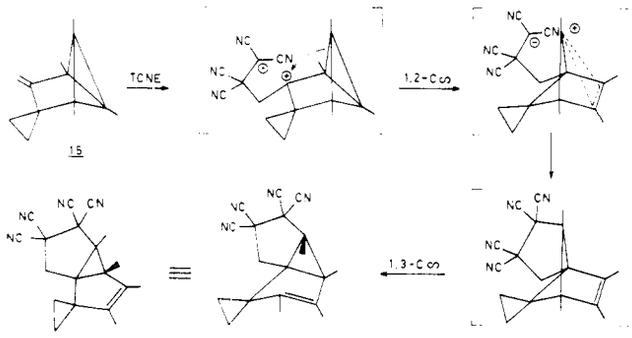


overall yield;[17] the method described earlier is, however, superior for reasons of simplicity.

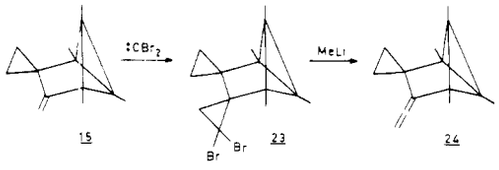
In the literature[18] the initial formation of a [2 + 2] adduct from vinylcyclopropane and TCNE has been reported; the product isomerizes thermally to a seven-membered ring. Although **15** contains a vinylcyclopropane moiety, its reaction with TCNE takes a different course involving a rearrangement of the bicyclobutane skeleton. In chloroform the conversion of **15** to **21** is complete within 3 min at room temperature. The behavior of **15** toward TCNE bears a close resemblance to that of **22**.[19] Although in contrast to the latter reaction an intermediate adduct was not observed by NMR spectroscopy, the addition of TCNE to **15** leading to **21** is likely to occur along an analogous pathway.



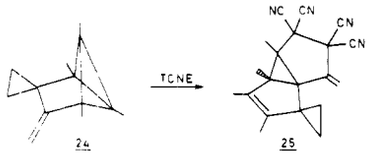
No reaction between TCNE and **16** was observed at temperatures up to 150 °C.



Synthesis of a Cyclopropylallene. In order to complete the class of allene and cyclopropane modifications of **1**, the synthesis of the cyclopropylallene **24** starting from **15** via the dibromocarbene adduct **23** was attempted. No attempts were made to purify and completely characterize **23.** Compound



24 could actually be isolated after addition of methyllithium to a solution of crude **23,** but difficulties were encountered in its reaction with TCNE. The immediate addition of TCNE did take place at −20 °C, but the 1:1 adduct which is thought to have structure **25** decomposed during workup.



Conclusion

Of the newly prepared compounds, allenes **8** and **9** decompose rapidly within a few days at room temperature and, moreover, are difficult to purify. However, compounds **15** and **16** deserve further experimental and theoretical attention since they possess a considerable amount of strain energy, are easily synthesized, and are fairly stable at room temperature. Experiments to exploit their chemical reactivity are being performed.

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. ^{1}H NMR spectra were taken with a Jeol C-60 HL spectrometer with deuteriochloroform as the solvent and Me_4Si as an internal reference. ^{13}C NMR spectra were run on a Varian XL-100 with deuteriochloroform as the solvent and Me_4Si as an internal reference. Preparative TLC was performed with aluminium oxide (Merck; 10–40 μm, not activated).

Synthesis of Spiro[2,2-dichlorocyclopropane-1,3′-1′,2′,5′,6′-tetramethyl-4′-methylenetricyclo[3.1.0.0^{2,6}]hexane] (3). Chloroform (25 mL), *n*-pentane (75 mL), diene **1** (4.0 g, 25 mmol), a 50% aqueous solution of sodium hydroxide (100 g), and triethylbenzylammonium chloride (1.0 g) were combined and stirred vigorously at room temperature for 1 h. Then water (200 mL) and chloroform (100 mL) were added, the organic layer was separated, washed with water (3 × 20 mL), and dried over anhydrous potassium carbonate, and the solvent was evaporated. A mixture of **1** and **3** was obtained, from which **1** was removed by vacuum distillation. Compound **3** (4.6 g, 19 mmol; 76%) was pure enough to be used in further experimental work: mp 58.0–59.0 °C; ^{1}H NMR δ 1.07 (s, 3 H), 1.14 (s, 3 H), 1.33 (s, 3 H), 1.45 (s, 3 H), 1.70 and 1.80 (AB system, J_{AB} = 8 Hz, 2 H), 4.48 (s, 1 H), and 4.73 (s, 1 H); ^{13}C NMR δ 2.4, 3.2, 7.5, 8.6, 26.0, 27.4, 28.7, 42.2, 45.5, 46.6, 64.7, 99.0, and 157.6; IR 1660 cm^{-1}; MS Calcd exact mass, *m/e* 242.063 (M$^+$); MS Found, *m/e* 242.065.

Preparation of *d,l*-Dispiro[2,2-dichlorocyclopropane-1,3′-1′,2′,5′,6′-tetramethyltricyclo[3.1.0.0$^{2',6'}$]hexane-4′,1″-2″,2″-dichlorocyclopropane] (4). Compound **4** was prepared analogously to the synthesis of **3.** However, instead of *n*-pentane (75 mL) additional chloroform was used (75 mL). After evaporation of the organic solvent a solid material resided which was recrystallized from *n*-pentane. An 80% yield of **4** (6.5 g, 20 mmol) was obtained: mp 140.0–140.5 °C; ^{1}H NMR δ 1.06 (s, 6 H), 1.48 (s, 6 H), and 1.81 and 2.07 (AB system, J_{AB} = 9 Hz, 4 H); ^{13}C NMR δ 3.0, 9.2, 27.0, 27.1, 44.1, 47.0, and 64.6; MS (M$^+$) *m/e* 324, 326, 328, 330, and 332. Anal. Calcd for $C_{14}H_{16}Cl_4$: C, 51.56; H, 4.95; Cl, 43.49. Found: C, 51.48; H, 4.95; Cl, 43.55.

Synthesis of Spiro[2,2-dibromocyclopropane-1,3′-1′,2′,5′,6′-tetramethyl-4′-methylenetricyclo[3.1.0.0$^{2',6'}$]hexane] (5). Mono adduct **5** was prepared in a similar manner as **3.** Instead of chloroform (25 mL) bromoform (25 mL) was used. Both **1** and excess bromoform were removed by distillation (T < 35 °C) under reduced pressure. For reasons of stability crude **5** (viscous oil) was stored in the dark while cool, yield 38% (2.4 g, 9.5 mmol): ^{1}H NMR δ 1.11 (s, 3 H), 1.15 (s, 3 H), 1.33 (s, 3 H), 1.46 (s, 3 H), 1.90 and 2.36 (AB system, J_{AB} = 7 Hz, 2 H), 4.47 (s, 1 H), and 4.75 (s, 1 H); IR 1650 cm^{-1}; MS (M$^+$) *m/e* 330, 332, and 334.

Preparation of *d,l*-Dispiro[2,2-dibromocyclopropane-1,3′-1′,2′,5′,6′-tetramethyltricyclo[3.1.0.0$^{2',6'}$]hexane-4′,1″-2″,2″-dibromocyclopropane] (6). Bis adduct **6** was synthesized in a way analogous to the preparation of **4.** Instead of chloroform (100 mL) bromoform (100 mL) was used. Excess bromoform was removed by distillation under reduced pressure (T < 35 °C). After crystallization from *n*-pentane **6** was obtained in 28% yield (3.5 g, 6.9 mmol): ^{1}H NMR δ 1.12 (s, 6 H), 1.55 (s, 6 H), and 2.04 and 2.42 (AB system, J_{AB} = 9 Hz, 4 H); MS (M$^+$) *m/e* 500, 502, 504, 506, and 508.

Prior to melting, compound **6** underwent ring opening on heating at 60 °C for 5 min, affording **7** as a viscous oil: ^{1}H NMR δ 1.03 (s, 6 H), 1.36 (s, 6 H), 4.78 (s, 2 H), and 5.33 (s, 2 H); MS (M$^+$) *m/e* 500, 502, 504, 506, and 508.

Synthesis of 1,2,5,6-Tetramethyl-3-methylene-4-vinylidenetricyclo[3.1.0.0^{2,6}]hexane (8) from 5. A solution of **5** (0.664 g, 2.00 mmol) in ether (25 mL) kept under a nitrogen atmosphere was cooled (−50 °C), and subsequently methyllithium (1.4 mL, 1.5 N in ether) was added by means of a syringe. Then the mixture was allowed to warm to room temperature and water (25 mL) was added. The two layers were separated, and the organic layer was collected, dried over anhydrous potassium carbonate, and evaporated, leaving crude allene **8** which was purified by preparative TLC (*n*-pentane). An isolated yield of 27% of **8** (0.083 g, 0.54 mmol) was obtained. For reasons of stability compound **8,** a colorless mobile oil, was used immediately or stored at low temperature in the dark: ^{1}H NMR δ 1.16 (s, 6 H), 1.43 (s, 6 H), 4.96 (s, 1 H), and 5.21 and 5.25 (two partially overlapping s, 3 H); IR 1650 and 1960 cm^{-1}; MS *m/e* 172 (M$^+$).

Preparation of 10. To a solution of **8** (0.070 g, 0.41 mmol) in chloroform (10 mL) was added TCNE (0.051 g, 0.40 mmol) at room temperature. After stirring for 10 min the solvent was evaporated (T < 35 °C) and the residing solid was crystallized from *n*-pentane. Adduct **10** (0.097 g, 0.32 mmol) was isolated in 80% yield; it rearranged to compound **11** before melting: ^{1}H NMR δ 1.13 (s, 3 H), 1.35 (s, 3 H), 1.55 (s, 6 H), 3.37 (s, 2 H), and 5.88 (apparent s, 2 H); IR 1625 and 2260 cm^{-1}.

Synthesis of 11. When **10** (0.097 g, 0.32 mmol) was heated at 100 °C a rearrangement took place which was complete within 5 min and afforded **11** in a quantitative yield: ^{1}H NMR δ 2.22 (s, 3 H), 2.31 (s, 6 H), 2.42 (s, 3 H), 3.77 (s, 2 H), 5.87 (d, J = 2 Hz, 1 H), and 6.46 (d, J = 2 Hz, 1 H); IR 1625 and 2260 cm^{-1}; MS m/e 300 (M^+). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.76; H, 5.42; N, 18.79. Compound **11** decomposed at temperatures above 225 °C.

Synthesis of 1,2,5,6-Tetramethyl-3,4-divinylidenetricyclo[3.1.0.0^{2,6}]hexane (9) from 6. Both the preparation and the purification of **9** were carried out according to the procedures described previously for monoallene **8**. Using **6** (1.000 g, 1.984 mmol) as the starting material, bisallene **9** (0.212 g, 1.15 mmol) was isolated as a colorless mobile oil in a 58% yield and for reasons of stability it was used immediately or stored at low temperature in the dark: ^{1}H NMR δ 1.12 (s, 6 H), 1.41 (s, 6 H), and 5.06 (s, 4 H); IR 1970 cm^{-1}; MS m/e 184 (M^+).

Preparation of 12. Starting from **9** (0.212 g, 1.15 mmol), adduct **12** (0.281 g, 0.901 mmol) was prepared and purified in the way mentioned in the case of **10** (80% yield); **12** rearranged to **13** prior to melting; ^{1}H NMR δ 1.34 (s, 6 H), 1.57 (s, 6 H), and 5.90 (apparent s, 4 H); IR 1620 and 2260 cm^{-1}.

Synthesis of 13. Compound **12** (0.281 g, 0.901 mmol) isomerized on heating at 100 °C for 10 min. The aromatic compound **13** was isolated in quantitative yield: ^{1}H NMR δ 2.32 (s, 6 H), 2.45 (s, 6 H), 5.88 (d, J = 2 Hz, 2 H), and 6.48 (d, J = 2 Hz, 2 H); IR 1625 and 2260 cm^{-1}; MS m/e 312 (M^+). Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.61; H, 5.10; N, 18.06. Compound **13** decomposed at temperatures above 225 °C.

Formation of 1,2-Diethynyl-3,4,5,6-tetramethylbenzene (14). To a cold (−50 °C) solution of **4** (1.63 g, 5.00 mmol) in ether (25 mL) kept under a nitrogen atmosphere was added n-butyllithium (6.0 mL, 1.8 N in n-hexane). After warming to room temperature water (25 mL) was introduced and the organic layer was collected and evaporated. ^{1}H NMR spectroscopy indicated the presence of **9** and **14** (1:2 ratio) and starting material (30%).

When pure **9** (0.184 g, 1.00 mmol), prepared from **6**, was treated with an excess of n-butyllithium (10 mL, 1.8 N in n-hexane) under otherwise identical conditions, only **14** could be observed by ^{1}H NMR spectroscopy after workup. Compound **14** was purified by preparative TLC (n-pentane) followed by crystallization from n-pentane. A 73% yield of **14** (0.133 g, 0.731 mmol) was isolated: ^{1}H NMR δ 2.12 (s, 6 H), 2.35 (s, 6 H), and 3.40 (s, 2 H); IR 2120 cm^{-1} MS m/e 182 (M^+). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.74. After melting at 114.5–115.5 °C, compound **14** decomposed at a slightly higher temperature.

Synthesis of Spiro[cyclopropane-1,3′-1′,2′,5′,6′-tetramethyl-4′-methylenetricyclo[3.1.0.0$^{2',6'}$]hexane] (15). Ammonia (250 mL) was condensed at −50 °C in a dry reaction vessel containing **3** (4.86 g, 20.0 mmol), and the vessel was equipped with a cold-finger condenser. The ammonia inlet was replaced with a stopper, and sodium (1.84 g, 80.0 mg-atom), cut into small pieces, was introduced in portions throughout the reaction. After addition of the total amount of sodium the reaction mixture was stirred at −50 °C until the solution decolorized. Then the condenser was removed and the ammonia allowed to evaporate. Ether (100 mL) and water (100 mL) were added, and the aqueous layer was extracted with ether (2 × 200 mL). The organic layers were combined and dried over anhydrous potassium carbonate, and the solvent was subsequently evaporated, leaving crude **15** which was distilled under reduced pressure at 28–33 °C (1.0 mm). A 76% yield of **15**, a colorless liquid (2.64 g, 15.2 mmol), was obtained: ^{1}H NMR δ 0.40 (m, 2 H), 0.68 (m, 2 H), 0.76 (s, 3 H), 1.13 (s, 3 H), 1.38 (s, 6 H), 4.07 (s, 1 H), and 4.38 (s, 1 H); ^{13}C NMR δ 2.6, 4.9, 7.1, 9.4, 25.7, 30.1, 40.1, 46.1, 89.9, and 164.2; IR 1650 and 3050 cm^{-1}; MS m/e 174 (M^+).

Since no satisfactory elemental analysis could be obtained, compound **15** was also synthesized in an independent way using diazomethane (see below).

Preparation of Dispiro[cyclopropane-1,3′-1′,2′,5′,6′-tetramethyltricyclo[3.1.0.0$^{2',6'}$]hexane-4′,1″-cyclopropane] (16). In the manner described for the conversion of **3** to **15**, compound **4** (6.52 g, 20.0 mmol) afforded **16** upon reduction with sodium (3.68 g, 160 mg-atom) in liquid ammonia at −50 °C. An 84% yield of **16**, a colorless liquid (3.14 g, 16.7 mmol), was isolated after distillation under reduced pressure at 30–35 °C (1.0 mm): ^{1}H NMR δ −0.17 (m, 4 H), 0.28 (m, 4 H), 0.72 (s, 6 H), and 1.32 (s, 6 H); ^{13}C NMR δ 3.0, 3.5, 5.6, 21.0, 31.8, and 43.5; IR 3050 cm^{-1}. MS Calcd exact mass, m/e 188.156 (M^+); MS Found, m/e 188.158.

Na/NH$_3$ Reductions of 5 and 6. Using **5** or **6** as the starting material, **15** and **16**, respectively, were synthesized in a way essentially identical with the method described above. After distillation under reduced pressure compound **5** (0.664 g, 2.00 mmol) afforded **15** (72%) and compound **6** (0.504 g, 1.00 mmol) gave **16** (79%).

Preparation of 17. A mixture of methylene iodide (1.90 g, 7.10 mmol), a zinc–copper couple prepared according to Shank and Shechter[16] (4.68 g, 7.20 mg-atom), diene **1** (400 mg, 2.50 mmol), anhydrous ether (2.5 mL), dimethoxyethane (0.5 mL), and a crystal of iodine was heated under reflux for 6 h in a nitrogen atmosphere. The solution was then washed with a saturated ammonium chloride solution (3 mL) and water (3 mL). Evaporation of the solvent afforded a complex reaction mixture. Preparative TLC (n-pentane) made it possible to isolate and characterize one of the components (**17**); the melting point (78.0–78.5 °C) and spectroscopic data of **17** (MS, IR, and ^{1}H NMR) are in agreement with those of authentic material.[20] No indication for the presence of **15** or **16** was obtained by ^{1}H NMR spectroscopy. The yield of **17** was 24% (0.112 g, 0.596 mmol).

Alternative Synthesis of 15 Using Diazomethane. To a solution of diazomethane in ether (20 mL, 0.25 n) was added enone **18** (0.810 g, 5.00 mmol) under stirring at room temperature. After about 2 h the solution lost its characteristic color and the solvent was evaporated, leaving **19** in quantitative yield: ^{1}H NMR δ 0.93 (s, 3 H), 1.18 (s, 3 H), 1.50 (s, 3 H), 1.65 (s, 3 H), and 4.3–4.8 (ABCD system, 4 H); ^{13}C NMR δ 2.4, 3.1, 4.3, 6.0, 21.2, 26.3, 28.5, 41.5, 52.4, 77.0, 100.1, and 211.5; IR 1540 and 1730 cm^{-1}.

Using a high-pressure mercury arc, compound **19** (0.998 g, 4.89 mmol) dissolved in benzene or chloroform (150 mL) was irradiated for 3 h. Evaporation of the solvent afforded **20** (0.848 g, 4.82 mmol) as a waxy solid in quantitative yield: ^{1}H NMR δ 0.56 (s, 4 H), 0.87 (s, 3 H), 1.09 (s, 3 H), and 1.49 (s, 6 H); IR 1735 cm^{-1}; MS m/e 174 (M^+).

To a suspension of methyltriphenylphosphonium iodide (2.02 g, 5.00 mmol) in dry tetrahydrofuran (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 **20** (0.848 g, 4.82 mmol) in tetrahydrofuran (2 mL) was subsequently introduced, and the reaction mixture was stirred for 15 min at room temperature. Water (100 mL) was added and the aqueous layer was extracted with n-pentane (2 × 50 mL). The combined organic layers were dried over anhydrous potassium carbonate, and the solvent was evaporated, leaving crude **15** which was identical with the material prepared by Na/NH$_3$ reduction of **3**. Preparative TLC (n-pentane) afforded 89% of **15** (0.738 g, 4.29 mmol).

Synthesis of 21. To a stirred solution of **15** (0.696 g, 4.00 mmol) in chloroform (25 mL) was added TCNE (0.512 g, 4.00 mmol) at room temperature. After 15 min the solvent was evaporated and the resulting crude **21** was crystallized from ether, yield 83% (0.998 g, 3.30 mmol): mp 154.0–154.5 °C; ^{1}H NMR δ 0.5–1.0 (m, 4 H), 1.28 (q, J = 0.5 Hz, 3 H), 1.41 (s, 3 H), 1.65 (s, 3 H), 1.70 (q, J = 0.5 Hz, 3 H), and 2.55 and 2.75 (AB q, J_{AB} = 7.5 Hz, 2 H); ^{13}C NMR δ 5.8, 6.5, 8.4, 11.3, 12.4, 12.8, 30.8, 38.6, 41.5, 45.5, 47.2, 47.5, 52.5, 110.4, 110.9, 111.2, 112.7, 132.5, and 136.6; IR 1660 and 2240 cm^{-1}; MS m/e 302 (M^+). Anal. Calcd for $C_{19}H_{18}N_4$: C, 75.47; H, 6.00; N, 18.53. Found: C, 75.20; H, 5.92; N, 18.24.

No indication for an intermediate adduct was obtained from ^{1}H NMR spectra recorded during an experiment performed at low temperature (T = −40 °C).

Attempted Addition of TCNE to 16. Under the conditions mentioned above **16** was not found to react with TCNE. Even at higher temperatures (T < 150 °C and hexachlorobuta-1,3-diene as the solvent) no formation of an adduct was observed by ^{1}H NMR spectroscopy.

Synthesis of Spiro[cyclopropane-1,3′-1′,2′,5′,6′-tetramethyl-4′-vinylidenetricyclo[3.1.0.0$^{2',6'}$]hexane] (24). Under phase-transfer conditions dibromocarbene was allowed to react with compound **15** (0.870 g, 5.00 mmol) in the way indicated earlier (synthesis of **6**). Excess bromoform was removed by distillation under reduced pressure (T < 35 °C). By ^{1}H NMR spectroscopy signals due to olefinic protons in **15** were shown to be absent and, furthermore, absorptions due to the four methyl groups in **23** (δ 1.07, 1.27, 1.33, and 1.50) were observed. Under a nitrogen atmosphere methyllithium (4.0 mL, 1.5 N in ether) was added to a solution of **23** in ether (25 mL) at −50 °C followed by workup as reported previously (preparation of **8**). Preparative TLC (n-pentane) afforded 27% of **24** as a colorless mobile oil (0.247 g, 1.33 mmol): ^{1}H NMR δ 0.25–0.55 (m, 4 H), 0.73 (s, 3 H), 1.12 (s, 3 H), 1.38 (s, 6 H), and 4.90 (s, 2 H); IR 1965 and 3050 cm^{-1}; MS Calcd exact mass, m/e 186.141 (M^+); MS Found, m/e 186.144.

Addition of TCNE to 24. Upon addition of TCNE (0.170 g, 1.33 mmol) to a solution of **24** (0.247 g, 1.33 mmol) in chloroform (0.3 mL) kept in a NMR tube at −40 °C a reaction took place leading to a product (**25**) containing olefinic protons [δ 5.47 (d, J = 2.5 Hz) and 6.02 (d, J = 2.5 Hz)]. However, when the temperature was raised to

room temperature the adduct decomposed. Upon addition of more TCNE the formation of yet another adduct (presumably 2:1) was observed (also at −40 °C) suggesting the presence of a vinylcyclopropane moiety in the initially formed adduct **25**. Because of the encountered difficulties in workup no adduct was isolated.

Registry No.—**1**, 50590-86-8; **3**, 65103-68-6; **4**, 65103-69-7; **5**, 65103-70-0; **6**, 65103-71-1; **7**, 65103-72-2; **8**, 65103-73-3; **9**, 65103-74-4; **10**, 65103-75-5; **11**, 65103-76-6; **12**, 65103-77-7; **13**, 65103-78-8; **14**, 65103-79-9; **15**, 65103-80-2; **16**, 65103-81-3; **17**, 19063-11-7; **18**, 56745-77-8; **19**, 65103-82-4; **20**, 65103-83-5; **21**, 65103-84-6; **23**, 65103-85-7; **24**, 65103-86-8; **25**, 65103-87-9; chloroform, 67-66-3; bromoform, 75-25-2; diazomethane, 334-88-3.

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Photoinduced Decomposition of Peracetic Acid in Benzene

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The decomposition of peracetic acid in benzene, which was initiated by two light sources (at 2537 Å or over 2900 Å), showed preferential reaction of methyl radical with benzene, affording toluene, rather than reaction of hydroxyl radical, affording phenols. Analysis of simple products including methane, ethane and water showed that induced decomposition of peracid by methyl and hydroxyl radicals is the major pathway rather than aromatic radical substitution. The formation of biphenyl by phenyl radical coupling or addition of phenyl radical to benzene is not important.

The interaction between radicals and aromatic hydrocarbons may involve two reactions, i.e., radical addition and hydrogen atom abstraction, and radical addition is said to predominate in solution.[1,2] The reaction of methyl radical with benzene affords mainly toluene via addition and dehydrogenation,[1,2] while hydroxyl radical gives phenols and coupling products.[3-5]

The thermal decomposition of peracetic acid in benzene has been studied kinetically[6] but is only limited information on the decomposition mechanism and products. The photolysis of peracetic acid in cyclohexane was reported to give mainly cyclohexanol which suggests induced decomposition of peracid by cyclohexyl radical.[7]

Our previous study[8] suggested that the photolysis of peracetic acid in toluene involved the induced decomposition of peracid by CH_3·, HO·, and $PhCH_2$· radicals and the extent of the induced decomposition varied with wavelength of light.

The present paper discloses the mechanism of photoinduced decomposition of peracetic acid in benzene, where more induced decomposition occurs than in toluene.

Results

The photolysis of peracetic acid in benzene with 2537 Å or >2900 Å light afforded carbon dioxide, oxygen, methane, ethane, water, methanol, methyl acetate, toluene, phenol, and biphenyl (trace). The yield of phenol with 2537 Å light increases with a decrease in peracid concentration, while only a trace of phenol is formed at >2900 Å independent of the peracid concentration. Trace amounts of xylenes and methylbiphenyls (M^+ 168, *m/e* 152, 153, 165, 167, 168 and no peak of *m/e* 91 corresponding to $PhCH_2$)[9] were obtained in both photolyses.

Estimation of CO_2 and O_2. CO_2 (1 mol) was evolved from 1 mol of peracid decomposed with 2537 Å light, but the yield of CO_2 was 5–10% lower at >2900 Å (Tables I and II). The yield of O_2 was 5–15% of peracid decomposed at 2537 Å and >2900 Å.

Products. The time dependence of yields was studied in order to know primary products and the possibility of further reaction. These results are shown in Tables I (2537 Å) and II (>2900 Å). As is apparent from the tables, the yield of H_2O, methane, and toluene increases as the photolysis proceeds, i.e., the concentration of peracid decreases. The yield of phenol is relatively high at 2537 Å, while only a trace was detected at >2900 Å.

Analogously to toluene,[8] the yield of MeOH decreases as the photolysis proceeds. The MeOH initially formed being esterified to methyl acetate with acetic acid.

The effects of the concentrations of peracid and radicals on the yields were studied to estimate the reactivity of methyl and hydroxyl radicals, and the results are shown in Tables III (2537 Å) and IV (>2900 Å).

The effects of peracid concentration on the yields (Tables III and IV) were similar as observed in the time dependence (Tables I and II). The remarkable difference between 2537 Å and >2900 Å was observed in the yields of H_2O, CH_4, C_2H_6, and PhOH. That is, at 2537 Å, the yield of H_2O is high (relative to >2900 Å) and the yield of CH_4 is less than that of C_2H_6. Whereas at >2900 Å, the yield of H_2O is low and the yield of CH_4 is greater than that of C_2H_6. In addition, the yield of

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