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Tricyclo[2.1.0.0^{2,5}]pentane and Its Derivatives

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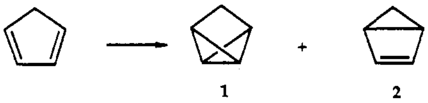
Contents

Introduction

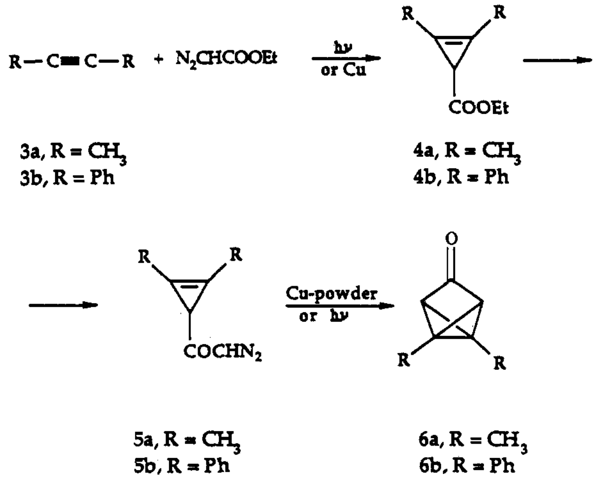
The tricyclo[2.1.0.0^{2,5}]pentanes may be viewed as rigidly fixed bicyclobutanes, distorted bicyclo[1.1.1]-pentanes, or bridged, twisted bicyclo[2.1.0]pentanes (housanes). From any standpoint the tricyclo[2.1.0.0^{2,5}]pentanes are strained, highly condensed ring systems. The parent tricyclo[2.1.0.0^{2,5}]pentane (**1**) was characterized by Andrews and Baldwin,[1] who photolyzed cyclopentadiene and isolated the desired tricyclopentane **1** from a mixture of **1** and bicyclo[2.1.0]-pent-2-ene (**2**).



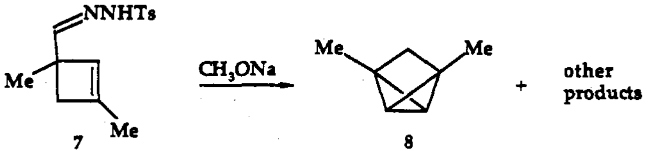
The first members of the tricyclo[2.1.0.0^{2,5}]pentane series were discovered in 1964. Doering and Pomerantz[2] synthesized 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (**6a**), and Masamune[3] prepared 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one (**6b**). Both research groups used the intramolecular insertion of a diazo ketone into a cyclopropene double bond (Scheme I) to accomplish the synthesis.

Thus, 2-butyne (**3a**)[2] or diphenylacetylene (**3b**)[3] was treated with ethyl diazoacetate in the presence of copper powder, producing cyclopropene esters **4**. Hydrolysis, conversion to the acid chloride, and condensation with diazomethane yielded diazo ketones **5**. Ring closure to the desired tricyclopentanones **6** was effected by treatment with copper (Doering and Pomerantz[2]) or by photochemical means (Masamune[3]).

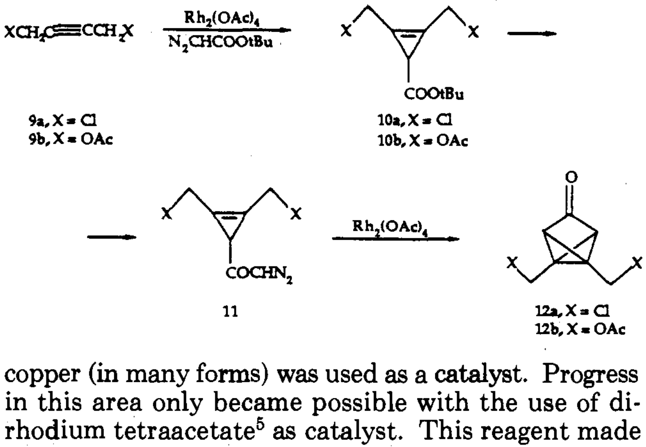
SCHEME I



SCHEME II



Closs and Larrabee[4] took a related approach to the bicyclopentane ring system (Scheme II). Upon treatment with sodium methoxide, tosylhydrazone **7** decomposes with insertion of the carbene into the double bond, resulting in the formation of tricyclopentane **8** together with a mixture of dimethylcyclopentadienes and a methylspiro[2.3]hexene.



Functionally substituted derivatives have been prepared along similar lines, but when electron-withdrawing groups are present, peculiar aspects of reactivity intrude. Thus, attempts to prepare substituted cyclopropene esters **10a** and **10b** were unsuccessful when copper (in many forms) was used as a catalyst. Progress in this area only became possible with the use of dirhodium tetraacetate[5] as catalyst. This reagent made attainable good yields of the substituted cyclopropenes

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Paul Dowd was born on April 11, 1936, in Brockton, MA. He received his A.B. degree in chemistry from Harvard College in 1958 and, in 1962, his Ph.D. from Columbia University, where he worked with Professor Ronald Breslow. Following a year of postdoctoral work in the laboratory of Professor R. B. Woodward, he remained at Harvard as instructor, lecturer, and assistant professor. In 1970, he joined the faculty of the University of Pittsburgh, where he is now Professor of Chemistry. With his observation of trimethylenemethane and tetramethyleneethane, he opened the non-Kekulé and open-chain diradical fields. Later work provided the first working model for the mechanism of action of vitamin B_{12}. Other interests include strained rings, free radicals, and photochemistry.

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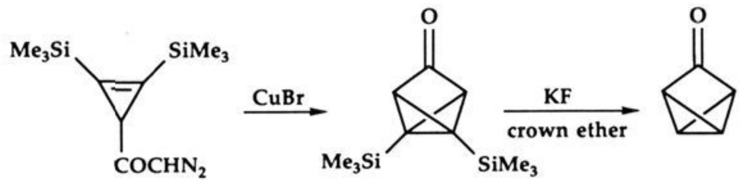
10,[6] and, after conversion to diazo ketone **11**, the same catalyst gave a much improved yield (20–30%) of tricyclopentanone products **12a** and **12b**.[7] This was also the first application of the dirhodium tetraacetate catalyst to an intramolecular diazo ketone cycloaddition.[8]

The parent tricyclo[2.1.0.0^{2,5}]pentanone (**15**) has recently been prepared by Maier,[9] who made use of blocking trimethylsilyl groups to control the cyclopropene reactivity. Thus, cyclopropenyl diazo ketone **13** was converted with cuprous bromide to bis(trimethylsilyl)tricyclopentanone (**14**), and the latter when treated with KF yielded unsubstituted tricyclic ketone **15**.

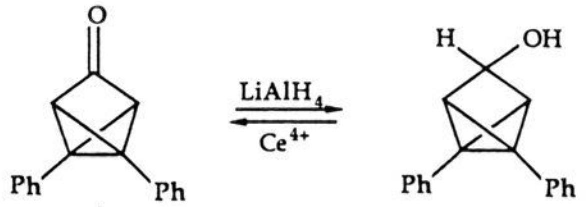


13 **14** **15**

Synthetic Elaboration

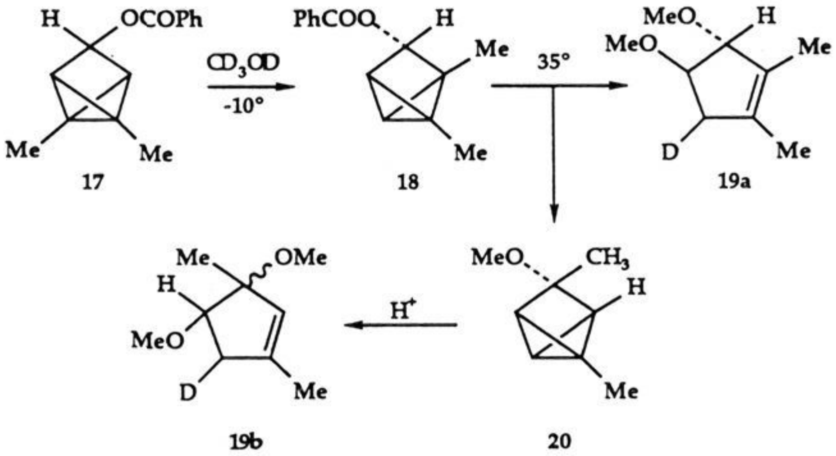
In addition to their strain-related reactivity and structure, the tricyclo[2.1.0.0^{2,5}]pentanones constitute an important crossroads providing synthetic access to a variety of other reactive intermediates. Accordingly, synthetic development of the tricyclopentanone system has often been carried out in connection with other synthetic objectives.

Masamune[10] reduced diphenyltricyclopentanone **6b** with lithium aluminum hydride to alcohol **16** and reoxidized **16** with ceric ammonium sulfate to the original ketone **6b**. The structure of the *p*-bromobenzoate derivative of **16** was established by Trotter et al.[10c] by X-ray crystallography.



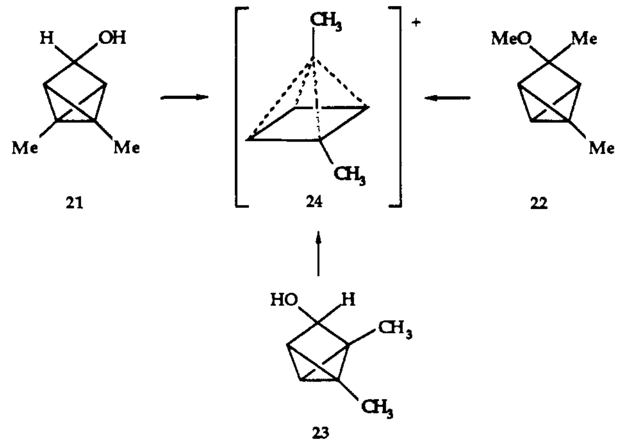
6b **16**

Derivatives of alcohol **16** are extremely reactive in a solvolytic context.[10] Solvolysis of benzoate **17** in aprotic solvents led to clean first-order rearrangement to **18**; no further rearrangement of **18** occurred even after prolonged heating. By contrast, rearrangement of **17** in CD_3OD yielded first **18** at −10 °C and then **19a** and **19b** when the temperature was raised to 35 °C. The second product (**19b**) was formed in an acid-catalyzed rearrangement of **20**; the rearrangement to **19b** was quenched by the addition of pyridine or triethylamine. These results were ascribed to the involvement of cyclopropylcarbinyl cation intermediates. A most interesting possible intermediate, the square-pyramidal cation dimethyl-$(CH)_5{}^+$ species **24**,[12] was not invoked here.[10a]

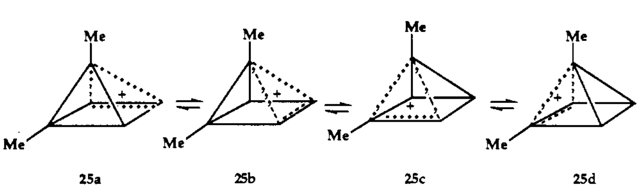


17 **18** **19a** **19b** **20**

However, treatment[10b] of the set of isomeric bicyclopentanones **21**, **22**, or **23** with FSO_3H in SO_2ClF at −78 °C, under Olah conditions,[11] yielded proton and carbon-13 NMR spectra consistent with the fully delocalized dimethyl-$(CH)_5{}^+$ structure **24** of Stohrer and Hoffmann[12] or with the equilibrating structures **25a–d**.

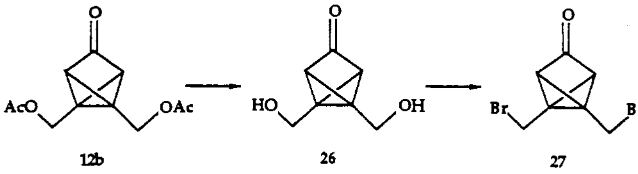


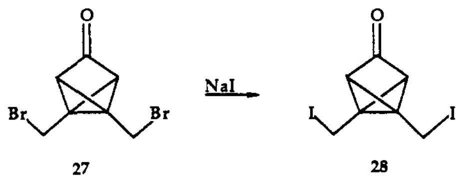
The NMR spectrum resulting from dissolution of **21** in SbF_5/SO_2ClF was also observed at an early date by Wilke.[10f] A homo-$(CH)_5^+$ has been studied by Hogeveen[13a] and by Paquette et al.,[13b] and bishomo analogues of $(CH)_5^+$ have been explored by a number of authors.[13c–i]



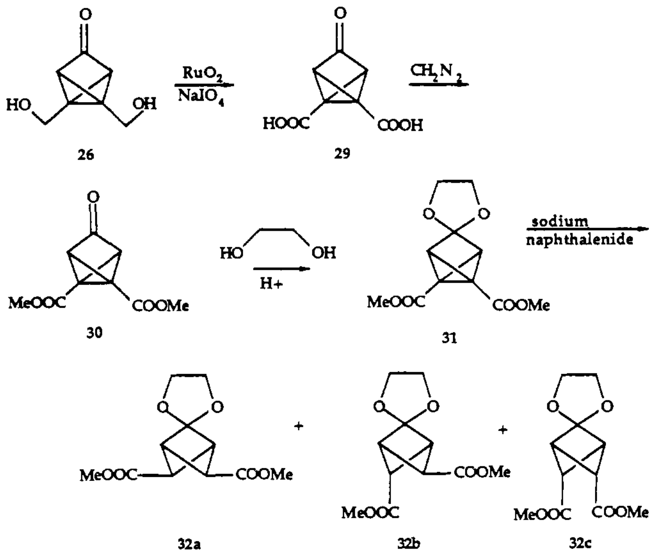
Because of the ease of formation of the apical carbonium ion and rearrangements such as those described above, the members of the tricyclo[2.1.0.0^{2,5}]pentanone series are somewhat sensitive to acid. In most other respects, synthetic transformations, including acid-catalyzed ketal formation, are quite easily carried out.

Hydrolysis of the acetate groups in **12b** with Na_2CO_3 in MeOH yields diol **26**. The latter is a central synthetic intermediate from which many other derivatives can be prepared. Thus, treatment with triphenylphosphine and carbon tetrabromide yields dibromo ketone **27**.[7,14] Treatment of dibromide **27** under Finkelstein conditions produces diiodide **28**. The latter is quite unstable and subject to sudden decomposition with evolution of iodine.[7]

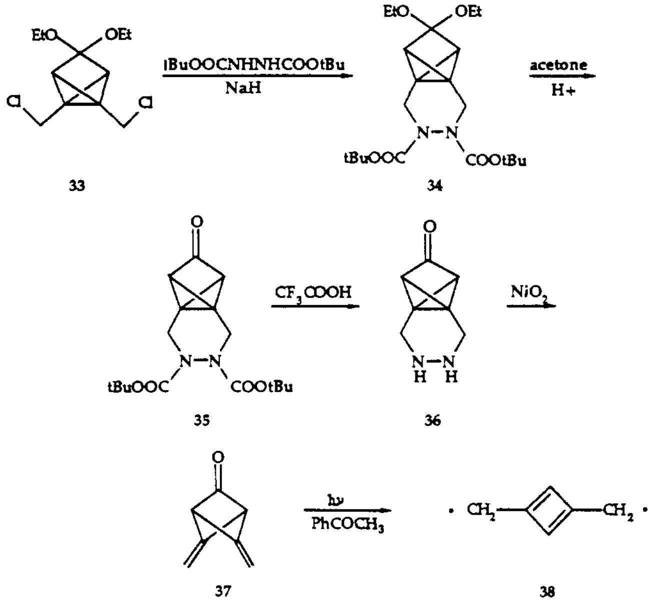




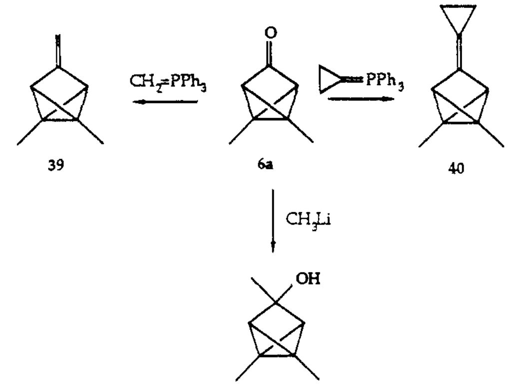
Oxidation of diol **26** with ruthenium dioxide in the presence of sodium periodate yielded diacid **29**, which was esterified with diazomethane to dimethyl ester **30**. Following protection of the ketone as the ketal **31**, the tricyclopentanone ring system was opened by reduction with sodium naphthalenide to bicyclo[1.1.1]pentane diesters **32a–c**, whose structures have been established by X-ray crystallography.[15]



From the dihalides, one can build more highly condensed ring systems. Thus, treatment of ketal dichloride **33** with di-*tert*-butyl hydrazodicarboxylate in the presence of sodium hydride yielded tetracyclic adduct **34**.[16] Because of the unusual ease of formation of the apical carbonium ion, the ketal group in **34** can be removed by acid-catalyzed exchange with acetone without disturbing the *t*-BOC groups. The aim of this series of transformations was the non-Kekulé diradical **38**. Thus, the *t*-BOC groups were removed by treatment with trifluoroacetic acid. Nickel peroxide oxidation led to the dimethylenebicyclo[1.1.1]butanone **37**, following spontaneous extrusion of nitrogen.[16] Acetophenone-sensitized photolysis of **37** yielded the desired dimethylenecyclobutadiene **38**.[17]



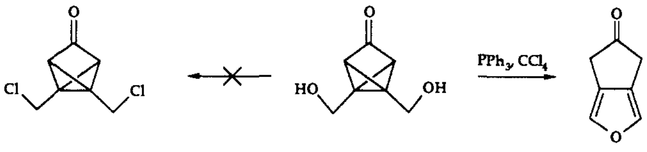
The carbonyl group of the tricyclo[2.1.0.0^{2,5}]pentanone nucleus can be transformed to the corresponding olefins by Wittig reaction as illustrated in the following, where dimethyl ketone **6a** yields olefins **39** and **40**.[18a] The *exo*-methylene derivative **39** yields a trimethyl derivative of $(CH)_5^+$ when treated with an excess of fluorosulfonic acid in liquid sulfur dioxide, as does the carbinol, 1,3,5-trimethyltricyclo[2.1.0.0^{2,5}]pentan-3-ol (**6a′**), derived from methyllithium treatment of **6a**.[18b]

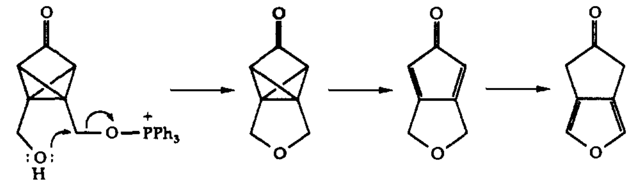


Rearrangements and Isomerizations

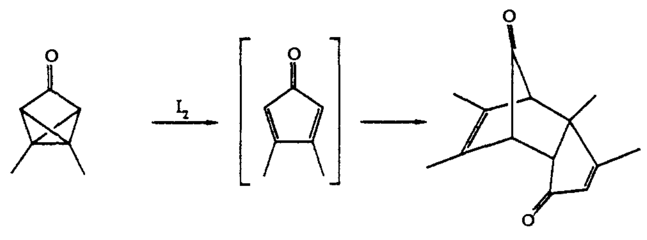
The tricyclopentanone system is highly prone to rearrangement as illustrated by the isomerization reactions in the Masamune series.[10]

An unusual rearrangement was observed in the halomethyl series described above.[7,14] Thus, no difficulty was experienced in preparing dibromide **27** from diol **26**, but when carbon tetrachloride was used in place of carbon tetrabromide in an analogous reaction, furan **41** was isolated and only small amounts of dichloride **12a** were detected. A tentative mechanism has been suggested whereby intramolecular displacement of the first-formed oxaphosphonium ion intermediate **42** by the adjacent hydroxyl group leads to the [3.1.1]propellane intermediate **43**.[19] This tricyclopentanone is highly strained and undergoes a bicyclobutane to butadiene isomerization reaction.[20] Since the product **44** of that change is a cyclopentadienone, it is also unstable and escapes by tautomerization to the final furan product **41**. The structure of furan **41** was confirmed by independent synthesis of an authentic sample.[7]

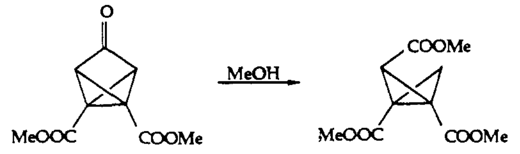


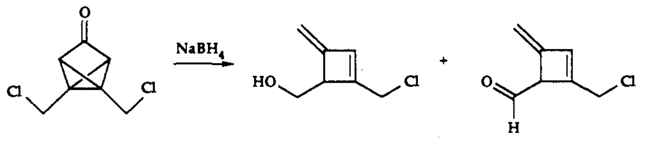


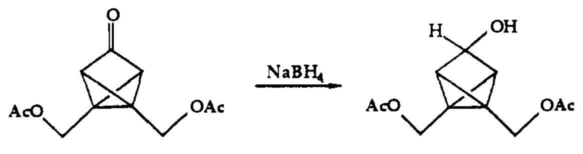
A bicyclobutane to butadiene transformation also occurs in an iodine-catalyzed reaction of the dimethyltricyclo[2.1.0.0^{2,5}]pentanone **6a**. In this instance, there is no convenient escape for the cyclopentadienone intermediate **45**, so it dimerizes to the product **46**.[7,14] The iodine may promote the rearrangement by electron transfer through the carbonyl group. The same ring-opening and dimerization reaction occurs when the tricyclopentanone **6a** is treated with $PdCl_2(C_6H_5CN)_2$.[21]



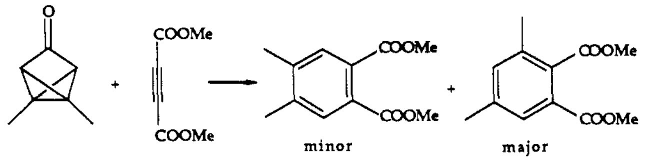
With electron-withdrawing ester groups attached to the bicyclopentanone nucleus, the bridging carbonyl becomes very susceptible to nucleophilic attack followed by ring opening and/or rearrangement.[22] Thus, when keto diester **47** is dissolved in MeOH, ring opening to bicyclobutane triester **48** is complete in 3 h at room temperature.[22] When an attempt was made to reduce dichloro ketone **12a** with sodium borohydride, ring opening also occurred, yielding methylenecyclobutenes **49** and **50**.[22] With the poorer acetate leaving group, the reduction of **12b** takes its normal course to alcohol **51**,

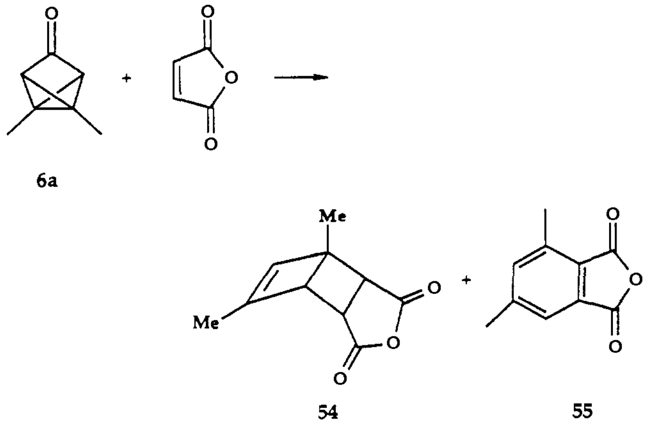




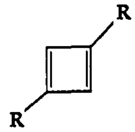


Pyrolysis of dimethyltricyclopentanone **6a** in the presence of dimethyl acetylenedicarboxylate yielded, as a minor product, dimethyl 4,5-dimethylphthalate (**52**), presumed to arise by trapping of the ring-opened cyclopentadienone **45** followed by extrusion of carbon monoxide.[23] The major product from this reaction was dimethyl 3,5-dimethylphthalate (**53**). The ratio of the two products was sensitive to temperature, with the 3,5-dimethyl isomer **53** becoming the only isomer as the temperature was lowered to 100 °C and below.[23] Masamune[24] carried out further trapping experiments with maleic anhydride and isolated adduct **54**. This was





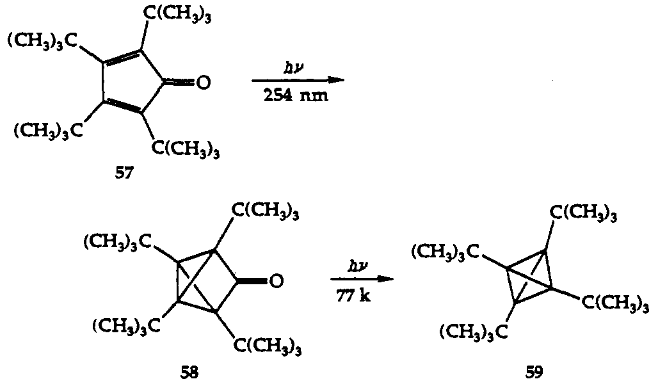
interpreted as evidence for a decarbonylation reaction leading to 1,3-dimethylcyclobutadiene (**56a**) trapped as adduct **54**.[24]



56a, R=Me
56b, R=Ph

Decarbonylation of the tricyclo[2.1.0.0^{2,5}]pentanones can also be effected by treatment in benzene with $AgClO_4$. Dimethyl and diphenyl derivatives **6a** and **6b** yielded adducts of the corresponding cyclobutadienes **56a** and **56b** in the presence of maleic anhydride.[21a] Photolysis of diphenyl derivative **6a** yields either *p*-terphenyl or a mixture of 1,3,5,7-tetraphenylcyclooctatetraene and 1,3,4,6-tetraphenylcyclooctatetraene; diphenyltetrahedrane is suggested as a possible intermediate.[21b]

In his spectacular quest for tetrahedrane and the successful completion of the work leading to the tetra-*tert*-butyl derivative of that elusive substance, Maier[25a–c] made extensive use of the tricyclo[2.1.0.0^{2,5}]pentanones and explored a number of them in detail. Thus, a key element of the tetra-*tert*-butyl series was the photochemical conversion at 254 nm of tetra-*tert*-butylcyclopentadienone (**57**) to tetra-*tert*-butyltricyclopentanone (**58**), which was then transformed photochemically[25a–c] at liquid nitrogen temperatures to tetra-*tert*-butyltetrahedrane (**59**).[26] The latter step is also accompanied by slow photochemical formation of ketene **60**.



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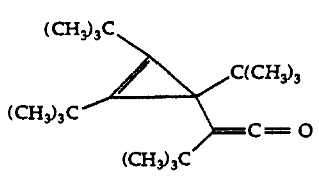
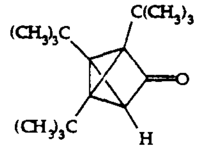
58

59

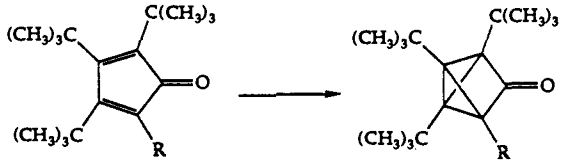


60

The factors leading to the successful tetrahedrane synthesis involve subtle interplay of steric factors. Masamune[25d] showed that tri-*tert*-butyl analogue **61** is photochemically stable, and in the course of Maier's work, the properties of several other tricyclopentanones, including the parent **15**, were explored. Tri-*tert*-butylcyclopentadienones **62a–c** yielded tricyclopentanones **63a–c** on photolysis; however, none of the tricyclopentanones **62a–c** yielded a tetrahedrane product.[25a] Similarly, the parent, unsubstituted tricyclopentanone **15** does not yield tetrahedrane upon photolysis; instead cyclobutadiene is produced.[25a]

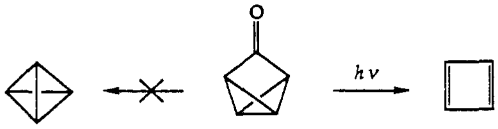


61



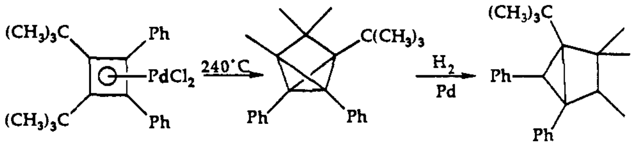
62a, R = ethyl
62b, R = isopropyl
62c, R = 1-adamantyl

63a, R = ethyl
63b, R = isopropyl
63c, R= 1-adamantyl



15

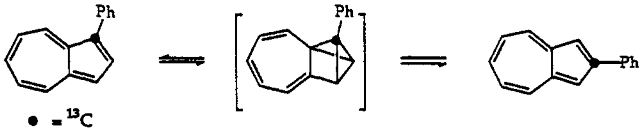
A reaction in the opposite sense, **64** → **65**, was reported by Moritani,[27a] who heated (1,2-di-*tert*-butyl-3,4-diphenylcyclobutadiene)palladium chloride (**64**), transforming it to tricyclo[2.1.0.0^{2,5}]pentane **65**. The latter was hydrogenated to bicyclo[2.1.0]pentane **66**. A diene to tricyclo[2.1.0.0^{2,5}]pentane transformation was postulated by Zeller[27b] to explain the carbon-13 labeling result observed in the thermal rearrangement of 1-phenyl- to 2-phenylazulene shown.



64

65

66

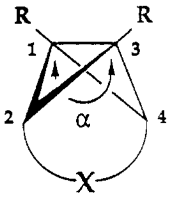


• = ^{13}C

On a speculative note, it has been suggested[27c,d] on the basis of MINDO/3 calculations that tricyclo[2.1.0.0^{2,5}]pentylidene might provide access to the fascinating hydrocarbon pyramidane shown.

Structure

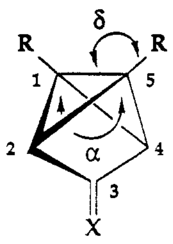
In bicyclo[1,1.0]butanes, the length of the central bond depends on the interplanar angle α between the three-membered rings. This structural feature has been established by X-ray analysis of bicyclobutane derivatives with bridges X (structure **67**) of different lengths spanning the 2- and 4-positions and serving to vary the interplanar angle α.[28] With increasing angle α the



67

central bond C1–C3 becomes longer, and, to a lesser extent, the side bonds become shorter. Additional X-ray analyses[30-35] and theoretical studies have confirmed and expanded this observation, and this result has been successfully simulated by ab initio calculations.[29]

To separate the electronic effects of substituents from geometrical factors, the interplanar angle α must be fixed. Tricyclo[2.1,0.0^{2,5}]pentane derivatives may be viewed as rigidly fixed bicyclobutanes with a one-carbon bridge in the 2- and 4-positions (structure 68). The average interplanar angle α is 97° for tricyclo[2.1.0.0^{2,5}]pentane derivatives **6a**, **6b**, **12b**, **30**, **31**, **69**, **70**, and **71**, whose structures have been determined by X-ray structure analysis (Scheme III and Table I). Stereoscopic representations of these molecules are shown in Figure 1. Unbridged bicyclobutanes have angles α ranging from 113 to 130°.

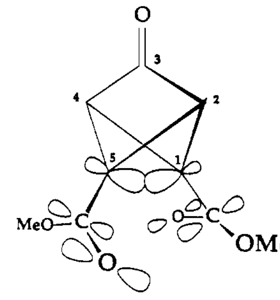


68

In tricyclo[2,1.0.0^{2,5}]pentanes the C1–C5 central bond (structure **68**) is very short as a consequence of the interaction between the folding angle α and the central bond length. Of the structures in Scheme III, the average central bond length of 1.44 Å is significantly shorter than the 1.52-Å length of the lateral bonds or the central C1–C3 bond in bicyclobutane (1.50 Å).[33] Propellane **70** is an exception to be discussed later. The exocyclic bonds from the bridgehead carbon atoms to the substituents are also short (1.47 Å) compared to ordinary carbon–carbon single bonds.

The unusual properties of the tricyclo[2,1.0.0^{2,5}]pentanes are produced by steric strain, which is most apparent at the C1 and C5 bridgehead carbon atoms (structure **68**). The hybridization of these carbon atoms is expected to deviate sharply from the normal sp^3 state. The orbitals of the exocyclic bonds have a high degree of s character according to theoretical calculations and NMR measurements (vide infra).[4] This is also reflected in the length of the exocyclic single bonds in the tricyclo[2,1.0.0^{2,5}]pentanes, which is comparable to that of the single bonds in 2-butyne (1.46 Å).[36]

The bonding orbitals of the C1–C5 bridging bond have substantial p character, so that substituents with π-accepting properties interact efficiently with the tricyclo[2.1.0.0^{2,5}]pentane system. The electronic influence of substituents has been investigated by structure determination of substituted derivatives (Figure 2). Ketal diacetate **69** may be designated the reference system having no conjugating substituents; the bridging C1–C5 bond in **69** has the characteristic short distance (for this series) of 1,455 Å (Figure 2).[37] If π-accepting carboxylate groups are attached to the bridgehead carbon atoms, the central C1–C5 bond in **31** is lengthened by 0.030 Å to 1.485 Å (Figure 2).[38] The angle between the carboxylate plane and the plane bisecting the C2–C5–C4 angle of the four-membered ring is close to 90°. The carboxyl groups are in optimal orientation for interaction with the Walsh orbitals of the bicyclobutane (**72** and Figure 1).[33] The bridging carbonyl group (C3) linking the 2- and 4-positions in **30** has the opposite effect and shortens the central bond by the same amount (0.032 Å) to 1.453 Å (Figure 2). The shortening effect of a carbonyl group on the distal bond of ordinary cyclopropanes (0.026 Å) is not as great.[39] The substituent effects on the central bond length of **30** neutralize each other. In **12b**[6,40] the shortening effect of the bridging carbonyl group is felt and the length of the central bond is reduced by 0.039 Å. A similar effect is observed on comparing **31** to **30** and **69** to **6a**[28] (Figure 2). Compounds **6a** and **12b** are electronically comparable. Both compounds have the shortest bonds (1,408 and 1.416 Å) in this series. These bonds are most striking; they are comparable in length to aromatic carbon–carbon bonds. The bond shortening is ascribed to the highly favorable overlap of the hybrid orbitals on carbons C1 and C5,[29]



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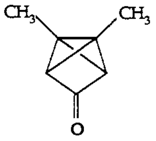
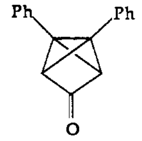


6a



6b

The phenyl substituents in **6b**[28] have optimal orientation for interaction with the central bond (Figure 1) and have an effect similar to that of the carboxyl groups in **30**. The central bond length of **6b** (Table I) corresponds to that of **30**. In general, the substitution of carboxylate or phenyl groups on the bridgehead carbon atoms gives rise to a lengthening of the central bond by 0.035 Å, and introduction of a bridging crbonyl group at C3 shortens the central C1–C5 bond by 0,040 Å. Compound **71**[10c,41] also exhibits the main features established for the tricyclopentanes (Table I) within the limits of resolution available at that time. Substituent effects on the four lateral bonds C1–C2, C1–C4, C2–C5, and C4–C5 are smaller than those on the central bond and are opposite in direction (Figure 2, numbers in square brackets). From the results shown in Figure 2 and a comparison of **6a** to **12b** and **6b** to **30**, we observe on the average a shortening by 0.010 Å of the lateral bonds produced by the electronic influence of carbox-

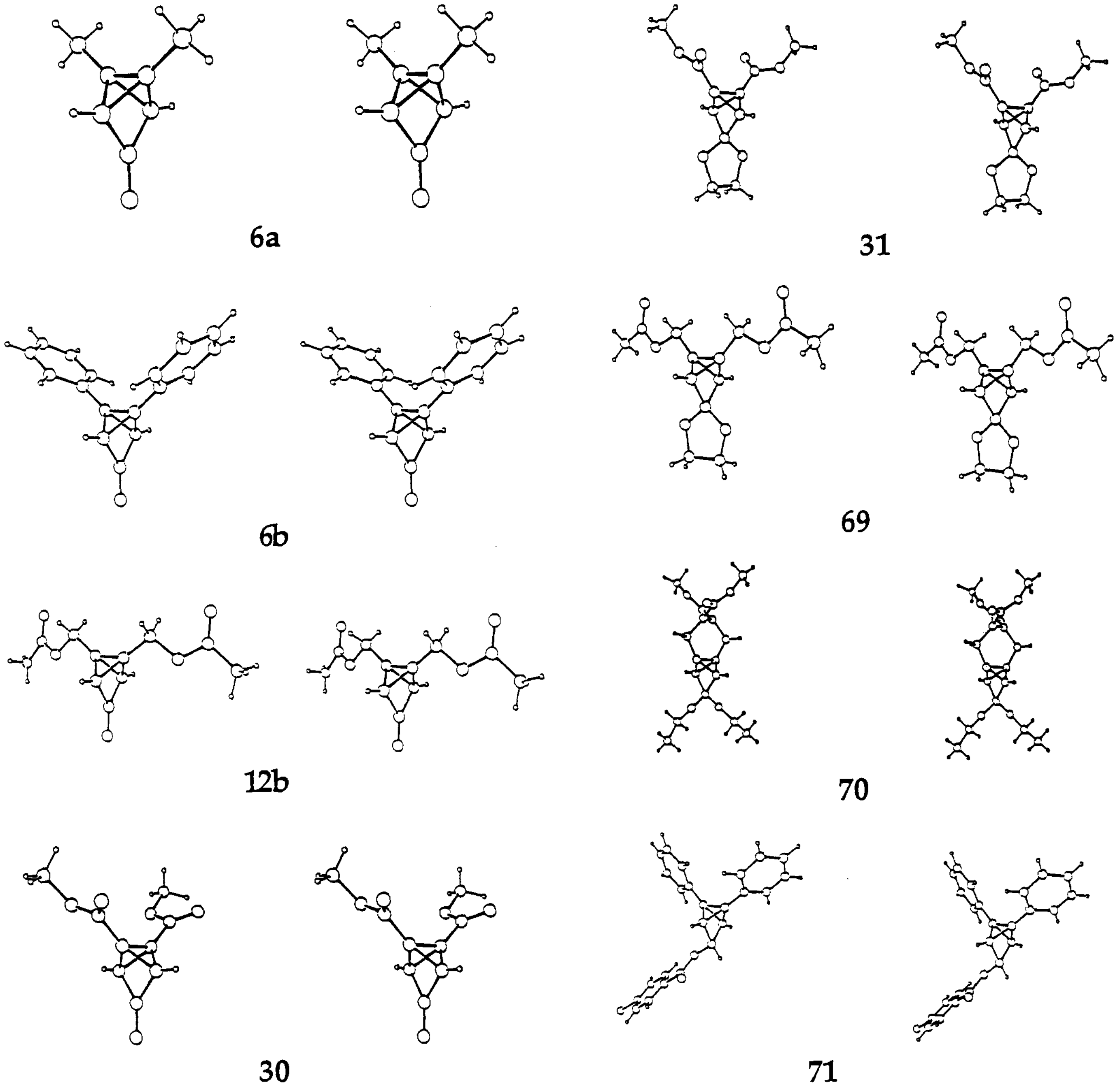
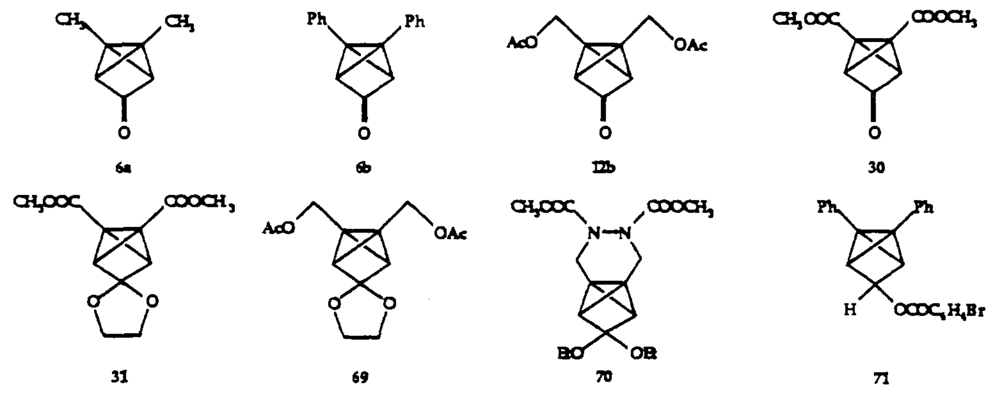


Figure 1. Stereoscopic drawings of the structures of tricyclo[2.1.0.0^{2,5}]pentane derivatives determined by X-ray structure analysis.

SCHEME III



ylate or phenyl groups substituted on the bridgehead carbon atoms. The C3 carbonyl group bridging the 2- and 4-positions gives rise to a lengthening by 0.017 Å of the lateral bonds.

Correlation also exists between the central C1–C5 bond distance and the angles δ (see structure **68**) between the central bond and exocyclic bonds. The angles δ of most of the tricyclo[2.1.0.0^{2,5}]pentanes examined

TABLE I. Molecular Parameters of Tricyclo[2.1.0.0^{2,5}]pentane Derivatives

	C1–C5, Å	C1–C2, Å	C–R, Å	C3–C, Å	α, deg	δ, deg	C2⋯C4, Å	ref
6a (298 K)	1.408	1.539	1.489	1.498	94.1	144.5	2.003	28
6a (118 K)	1.417	1.545	1.484	1.507	95.0	145.0	2.024	43
6b	1.444	1.526	1.453	1.506	96.1	142.1	2.001	28
12b	1.416	1.528	1.470	1.499	95.7	144.1	2.006	6, 40
30	1.453	1.521	1.466	1.527	98.9	137.9	2.031	38
31	1.485	1.509	1.453	1.536	98.7	131.4	1.993	38
69	1.455	1.515	1.464	1.520	96.8	132.9	1.987	37
70	1.509	1.511	1.490	1.536	98.6	120.0	1.986	42
71	1.44	1.53	1.46	1.52	95	139	1.99	41

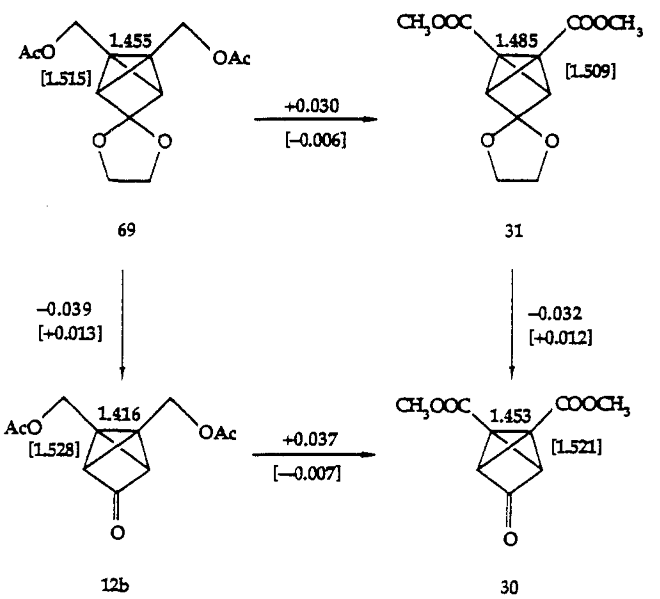
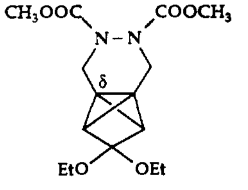


Figure 2. Substituent effects on the bond length of tricyclo[2.1.0.0^{2,5}]pentane. Averaged values for the lateral bonds of the bicyclobutanes are given in square brackets. Reprinted from ref 38; copyright 1988 Munksgaard.

are very large (131–145°, Table I). The exception is compound **70**.[42]



70

The substituents on the bridgehead carbon atoms of **70** are incorporated into a six-membered ring, and the angle δ is compressed to 120°. Since the bridging C1–C5 bond (1.509 Å) in **70** is significantly longer than the corresponding bond (1.455 Å) in **69**, the difference must be a consequence of the external bond angle δ. Compound **70** is a propellane. Other [4.1.1]propellanes[44–47] show bond lengths between the bridgehead carbon atoms ranging from 1.541 to 1.573 Å. This is longer than the bridging bond length in compound **70**, because the propellane interplanar angles α are larger (133.3–121.9°) than those in **70**, and the δ values are usually smaller. Both factors cause a lengthening of the central propellane bond.

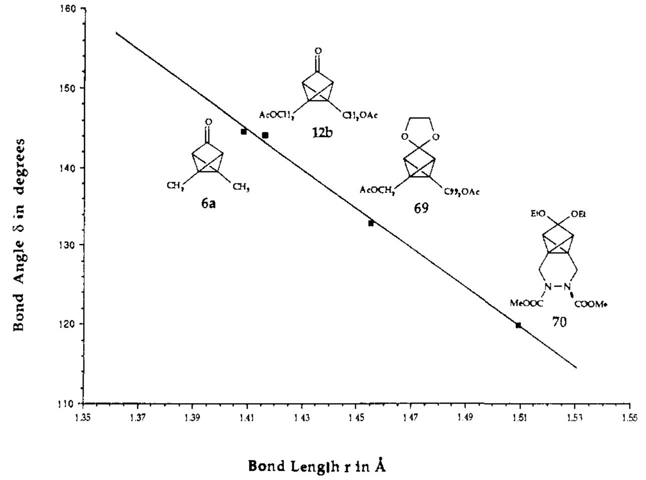


Figure 3. Plot of the C1–C5 bond length r versus external angle δ in tricyclo[2.1.0.0^{2,5}]pentane derivatives. Reprinted from ref 42; copyright 1987 American Chemical Society.

Ketones **12b**[6,40] and **6a**[28] have the same conformationally rigid tricyclo[2.1.0.0^{2,5}]pentane carbon framework system as ketals **70** and **69**. The bridging bond lengths in **6a** and **12b** are shortened by the electronic effect of the carbonyl group, but superimposed on this effect is a striking dependence of the C1–C5 bond length on the angle δ.[42] The inverse relationship between the central bond length C1–C5 and the bridgehead substituent angle δ is apparent in the linear correlation between the length of the bridging C1–C5 bond and the angle δ (Figure 3).[42] This plot constitutes direct confirmation of the theoretical prediction[29] and the qualitative suggestion[33] that the angle δ is a direct determinant of the bridging bond length in bicyclobutanes.

Deformation Density

The electron density distribution in the bonds of a tricyclo[2,1.0.0^{2,5}]pentan-3-one has been determined by low-temperature (118 K) X-ray analysis of compound **6a** by the X–X method.[43] All the electron density maxima in the bonds of the tricyclopentane framework of **6a** (Figure 4) are displaced outward from the bond axes; hence this system consists only of bent bonds. The density maximum of the central bond is shifted by 0.37 Å from the bond axis, corresponding to an extreme bending of 28°. Among polycyclic systems this bending is one of the largest known (bicyclobutane[30] is 0.2 Å, estimated from its density map; tetrahedrane[48] is 0.37 Å, equivalent to 26° bending). The density maxima of the three-membered rings in **6a** do not lie in the plane of the rings. The bonds not only are bent within the plane of the three-membered ring but are also twisted out of this plane. If the bond angle δ (145.0°) is not measured between the nuclear positions but between both density maxima at the bridgehead atom, a reduced bonding angle of 117° is obtained. Likewise, the bond length of the central bond in **6a** (1.417 Å, Table I) measured along a bow proceeding from the bridgehead atoms and passing through the density maximum

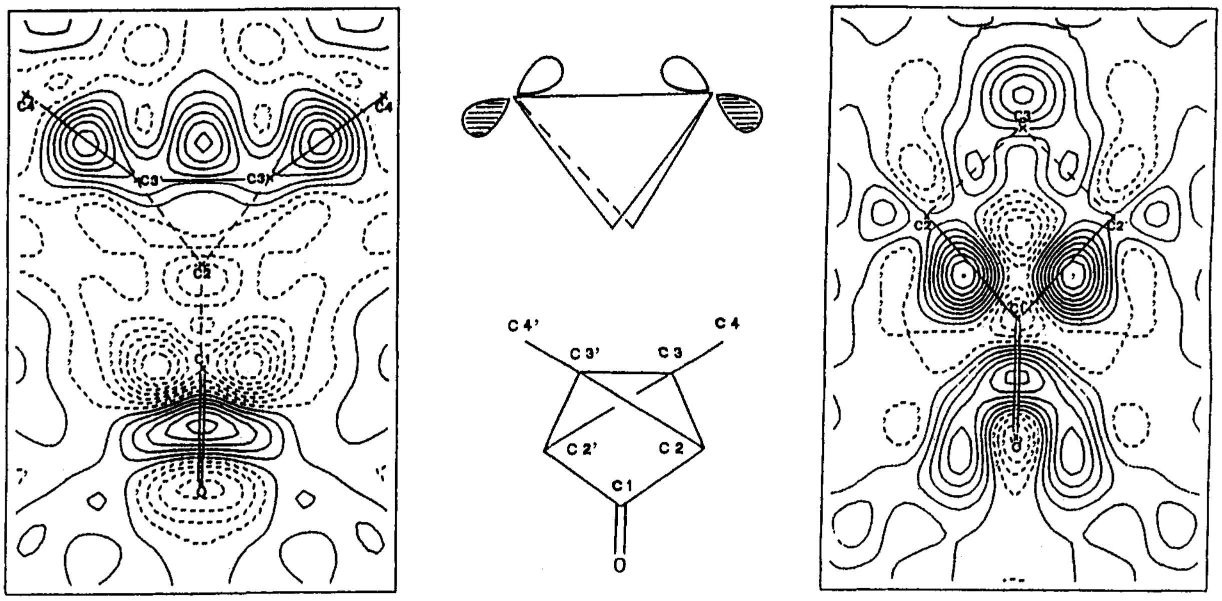


Figure 4. Electron density distribution in the bonds of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (**6a**) from low-temperature (118 K) X-ray data obtained with the *X*–*X* method. Contours are drawn at intervals of 0.05 e Å^{-3}. Left: Section through the plane of the atoms C1, C3, C3′, C4, C4′, and O, bisecting the interplanar angle α between the three-membered rings. Right: Section through the plane of the atoms C1, C2, C2′, and O. Reprinted from ref 43; copyright 1982 VCH Verlagsgesellschaft mbH.

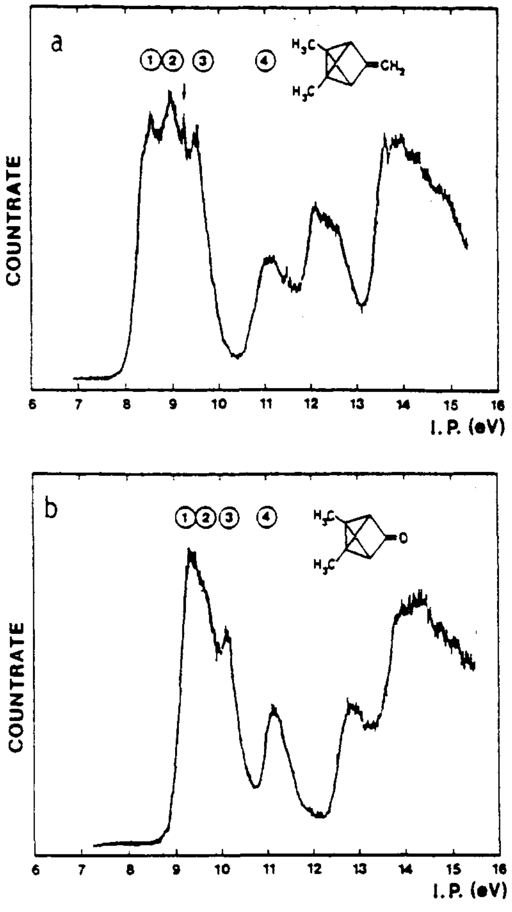


Figure 5. He I photoelectron spectra of (a) 1,5-dimethyl-3-methylenetricyclo[2.1.0.0^{2,5}]pentane (**39**) (the arrow marks a trace of benzene) and (b) 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (**6a**). Reprinted from ref 50; copyright 1984 American Chemical Society.

amounts to 1.66 Å, quite a long bond. The experimental results are supported by theoretical calculations.[30] Recent quantum mechanical calculations of the Laplacian of the electronic charge density in polycyclic compounds also yield bent bond paths.[49]

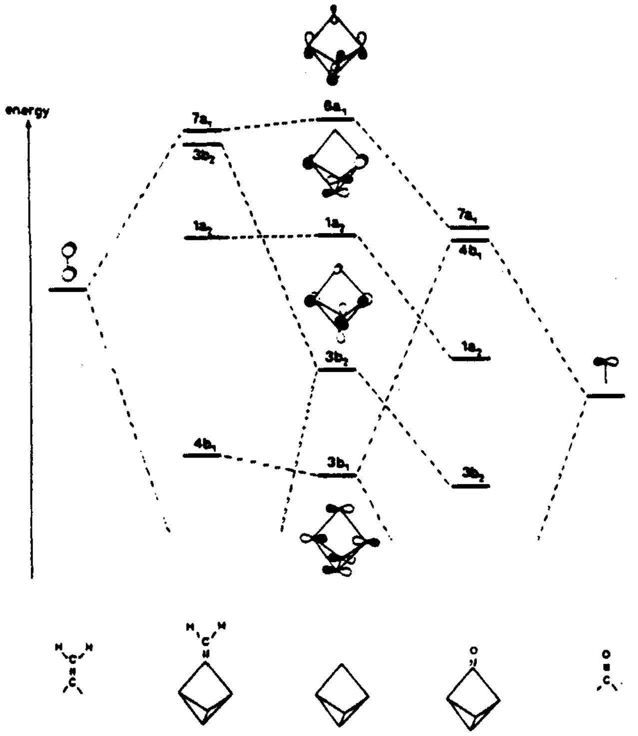
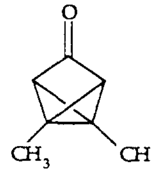


Figure 6. Qualitative correlation diagram between the highest occupied MOs of tricyclo[2.1.0.0^{2,5}]pentane (**1**) and a double bond to yield 3-methylenetricyclo[2.1.0.0^{2,5}]pentane (left) and a 2p orbital on oxygen to yield tricyclo[2.1.0.0^{2,5}]pentan-3-one (**15**) (right). Reprinted from ref 50; copyright 1984 American Chemical Society.

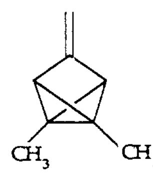
Spectroscopic Investigation of Structure

Photoelectron Spectroscopy

The direct X-ray structural investigations of Irngartinger[6,28,37,38,40,42,43] and Trotter[10c,41] are complemented by spectroscopic investigation of molecular properties. Gleiter et al.[50] have examined the photoelectron spectra of ketone **6a** and derived olefin **39**.[18] The photoelectron spectrum of **39** consists of overlapping bands at 8.54, 8.96, and 9.53 eV, well separated from a single peak at



6a

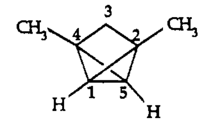


39

11.1 eV (Figure 5a). MINDO/3 calculations[51] predict three energetically similar orbitals (9a$_1$, 5b$_2$, and 2a$_2$) followed by a fourth (5b$_1$) (Figure 6). The tricyclo[2.1.0.0^{2,5}]pentane orbitals in Figure 6 are constructed by combining the orbitals of a bicyclobutane having a fixed 90° flap angle with the valence orbitals of a CH_2 group. Combining the tricyclopentane orbitals with the valence orbitals of a methylene group yields the one low-lying and three high-lying orbitals shown in the second column of Figure 6, in agreement with the spectral result. Similarly, the spectral properties of ketone **6a** (Figure 5b) are predicted by MINDO/3 using the highest occupied orbitals of the parent tricyclo[2.1.0.0^{2,5}]pentane (**1**) (Figure 6, center) in conjunction with the oxygen nonbonding p orbital. In agreement with the analysis of others, the authors suggest that interaction of the 3b$_2$ orbital with the antibonding π^* orbital of the carbonyl group will result in transfer of density from 3b$_2$, reducing the antibonding contribution of 3b$_2$ and resulting in a shorter bond.

NMR Studies

Angular distortion in tricyclo[2.1.0,0^{2,5}]pentanes has been investigated by carbon-13 NMR spectroscopy. Closs and Larrabee[4] reported $^1J_{CH}$ = 206 Hz for the C1–H and C5–H bonds of tricyclopentane **8**, indicating that the bridgehead carbons, C1 and C5, are substantially rehybridized.



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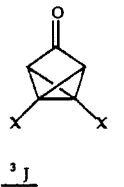
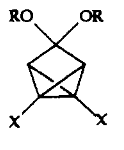
Making use of an empirical relationship derived from 30 hydrocarbon data points, Szalontai[52a] rationalized the rehydridization at C1 and C5 in **8** in terms of three distorted bond angles calculated with molecular mechanics. The internuclear angles obtained are as follows: C1–C4–C5, 80.66°; C5–C1–C4, 60.54°. The value of 80.66° corresponds to a flap angle of 94°. This agrees well with the value of 94.1° from X-ray analysis of ketone **6a** since the angle may be somewhat compressed with an sp^3 carbon at the C3 bridge in **8**, instead of the sp^2 carbon in **6a**.

Carbon-13 NMR studies also reveal a strong $^3J_{CH}$ coupling with the bridgehead carbon across the ring. In the ketones the long-range couplings are close to 15 Hz, while in the ketal series the value drops to 10 Hz.

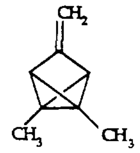


^3J	
14.7	X = CH_2OAc
14.7	X = CH_2Br
14.8	X - COOMe



^3J	
10.8	X = CH_2OAc, R = Et
10.5	X = CH_2OH, R = Et
10.5	X - CH_2OAc, R = $-CH_2CH_2-$

Proton and carbon-13 NMR examination of olefin **39**[52b] reveals an upfield chemical shift of the exocyclic methylene group relative to 7-methylenenorbornane, and it is suggested[52b] that this supports an across-the-ring or longicyclic form of conjugation.



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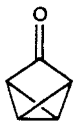
Theoretical Studies

The tricyclo[2.1.0.0^{2,5}]pentanes have been examined from a wide variety of theoretical viewpoints. Early CNDO/2 and extended-Hückel calculations by Stohrer and Hoffmann[12] focused on the tricyclopentanones and the possible relationship to the $(CH)_5^+$ cation. Speculation revolved about the possible duality of structures of the tricyclopentanone system with two minima corresponding to structures **15** and **15a**. Structure **15a** is described as a diradical or as a "bond stretch" isomer. Both extended-Hückel and CNDO/2 calculations concur in finding that structure **15** is the more stable of the two, but only by 7–8 kcal/mol. At the equilibrium geometry, the C1–C5 bond length for **15** is estimated to be 1.51 Å (extended Hückel) or 1.48 Å (CNDO/2), substantially longer than the value measured by X-ray analysis for **6a** and **12b**. However, the C1–C5 bond length was not the principal focus of these calculations.



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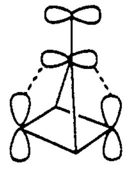
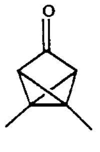
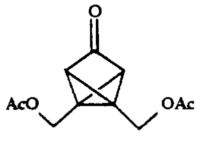


15a



6a

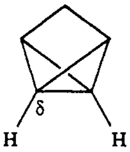


12b

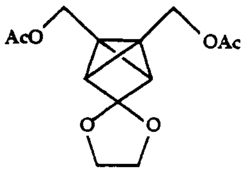
Extended-Hückel theory was also used to compare the relative HOMO and LUMO energies of a series of bicyclobutanes comprising tetrahedrane, tricyclo[2.1.0.0^{2,5}]pentane, and tricyclo[3.1.0.0^{2,6}]hexane,[53] This study revealed a narrowed HOMO–LUMO energy gap in comparison with cyclopropane; longer wavelength ultraviolet absorption and greater conjugative power in comparison with cyclopropane was predicted. In commenting on the bonding, the authors[53] suggest that the central bond is composed of a π-type overlap of p_z orbitals. They suggest that this is compatible with the general reactivity of this bond. However, no estimates of bond length are presented and it is difficult to com-

pare these ideas with experiment.

Once the substantial bond length contraction was established experimentally, it became worthwhile to attempt to understand the bonding in theoretical terms. Ab initio calculations[29] using the STO-3G basis set gave a good accounting of the variation in the C1–C5 bond length as a function of angle. The bonding can be described as σ-bonding, and the favorable bond formation is the result of the overlap of the sp^x hybrids from the pyramidalized carbons making up the C1–C5 bond. The model for this bonding picture considers the bridgehead carbons, C1 and C5, as formal radical centers and computes the effect of angle compression on the degree of pyramidalization of the radical centers, Thus, the pyramidalization at the bridgehead carbons is a consequence of the bending of the bicyclobutane part of the tricyclopentane enforced by the one-carbon bridge. Bending in the opposite direction, opening of the bicyclobutane, leads to a lengthening of the central C1–C5 bond. Likewise, bending inward of the angle δ



will cause pyramidalization in the outward direction, weakening the central bond. An extreme example of this is provided by the calculations[54] which yielded a central bond length of 1,6Å for [1,1.1]propellane. An example, discussed earlier, is provided by propellane **70**, whose C1–C5 bond length of 1.5Å is substantially longer than that of open ketal **69**.



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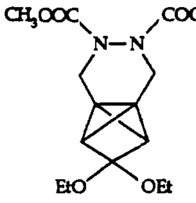

70

The consequences of pyramidalization can be placed on a semiquantitative basis (Figure 7) by examining the shape of the bridgehead carbons. In propellane **70** C1 and C5 are inverted in the sense that all four bond vectors point into one hemisphere.[55] The deviation d (Figure 7) of a bridgehead carbon atom from the plane of its three ligands is negative for the inverted centers in **70**, and this corresponds to a long bond. In the other tricyclo[2.1.0.0^{2,5}]pentane derivatives (**6a**, **12b**, **6b**, **71**, **30**, and **69**) d is positive, corresponding to pyramidalization in the direction favorable to bond shortening; the nearly linear relationship is clear in Figure 7, The zero point in Figure 7 is provided by compound **31**, in which the C1 and C5 carbon atoms are planar.

Subsequent application[56] of MINDO/3 calculations to bicyclobutane and tricyclic systems containing bicyclobutanes of various degrees of bend confirms the earlier ab initio calculations. An estimate of strain of 107.9 and 94.6 kcal/mol for the parent **1** and ketone **15** is suggested.

Additional MINDO/3 calculations[57] have provided an estimate of the dipole moment for **15** of 3.0 D. This large value is ascribed to charge transfer between the ring system and the carbonyl group,

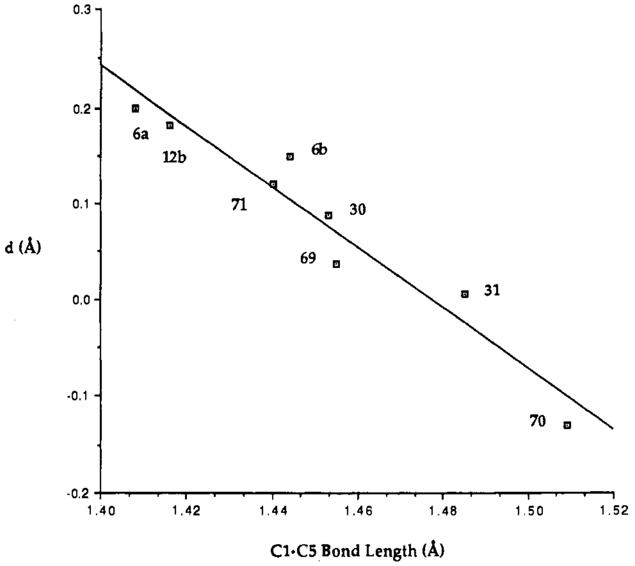

Figure 7. Plot of the C1–C5 bond length (Å) versus the inversion parameter d (Å) of the bridgehead carbon atoms, C1 and C5. The parameter d is the distance of the bridgehead carbon atom C1 (structure **68**) from the plane through C2, C4, and C(R, C1) and of C5 from the plane C2, C4, and C(R, C5); d is negative for inverted carbon atoms.

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