washed with water, 10% Na_2CO_3, water, and brine. After drying, the solvent was removed to yield 107 mg of a pale yellow oil (**20**) whose ir spectrum indicated the absence of starting material: ir 2940 (s), 2865 (s), 1780 (m), 1730 (s), 1455 (m), 1250 (s), 1220 (s), 1165 (s), 1140 (s), and 1015 cm^{-1} (m).

Without further purification, the crude lactone mixture **20** was hydrolyzed with 5% methanolic KOH (10 ml) and water (1 ml) for 1 day. The reaction mixture was diluted with water and extracted with ether to remove neutral materials. The aqueous phase was acidified and extracted with ether. The organic extracts were dried, and solvent was removed to yield 104 mg of a white solid, mp 80–82.5°, **21**: ir (KBr) 3470 (m), 1690 cm^{-1} (s). A portion of the crude **21** (86 mg, 0.38 mmol) was esterified with diazomethane to yield 106 mg of an oil which was used without further purification: ir 3585 (m), 3410 (br), 1740 cm^{-1} (s). This hydroxy ester was oxidized with CrO_3–pyridine according to the procedure of Ratcliff and Rodehorst[21] to yield 62 mg of oil, which was purified by VPC on column C to yield **22**: ir 2920 (s), 2845 (s), 1785 (s), 1745 (s), 1460 (m), 1435 (m), 1385 (m), 1360 (m), 1245 (m), 1195 (m), 1170 (m), 1110 (m), and 1085 cm^{-1} (m); NMR (220 MHz) δ 3.61 (s, 3 H), 3.15–2.97 (m, 2 H), 2.67–2.49 (m, 2 H), 2.36–2.21 (m, 1 H), 2.22 (t, J = 6 Hz, 2 H), 1.69–1.47 (m, 4 H), 1.39–1.21 (s, 10 H).

Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.94; H, 9.89.

Registry No.—**3**, 3045-76-9; **5**, 35522-56-6; **6**, 35522-60-2; **7**, 56468-02-1; **8**, 56468-03-2; **9**, 56468-04-3; **10**, 56498-05-6; **11**, 56498-06-7; **14**, 56468-05-4; **15**, 16837-94-8; **19**, 56468-06-5; **20**, 56468-07-6; **22**, 56468-08-7; cyclododecanone, 830-13-7.

References and Notes

(1) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 4873 (1973).
(2) R. A. Cormier and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 618 (1974).
(3) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(4) K. Matsui, T. Mori, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **44**, 3440 (1971), and references cited therein.
(5) C. A. Brown and D. Barton, *Synthesis*, 434 (1974).
(6) R. Criegee, B. Marchand, and H. Wannowius, *Justus Liebigs Ann. Chem.*, **550**, 99 (1942); J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).
(7) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).
(8) The conditions employed for this small-scale reaction were those described by R. A. Cormier and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 1867 (1974).
(9) An important point in this regard is that we find that on irradiation in benzene neither **3** nor the previously investigated[2] α-methylene ketones cause isomerization of 0.05 *M cis*-piperylene [see G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961)]. This result is contrary to our earlier report.[2] Thus, while there is no quenching of these rearrangements even by 4 *M* diene, there is no evidence that any triplets are being quenched at all. These observations have no effect on the present demonstration that **3** behaves like other α-methylene ketones, and the available data still support the earlier conclusion[2] that these are singlet reactions.
(10) Examination of ir and NMR spectra of various α-methylene ketones has led to the conclusion that **3** exists largely in an s-trans conformation, which is that required for γ-hydrogen abstraction as depicted in **12**: M. Mühlstädt, L. Zach, and H. Becwar-Reinhardt, *J. Prakt. Chem.*, **29**, 158 (1965); M. Mühlstädt, H. J. Köhler, D. Porzig, and M. Scholz, *ibid.*, **312**, 292 (1970).
(11) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *J. Am. Chem. Soc.*, **93**, 1984 (1971); C. P. Casey and R. A. Boggs, *ibid.*, **94**, 6457 (1972).
(12) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971), and references cited therein.
(13) J. P. Barnier, J. M. Denis, J. Salaun, and J. M. Conia, *Tetrahedron*, **30**, 1405 (1974), and references cited therein.
(14) J. E. Baldwin and R. H. Fleming, *J. Am. Chem. Soc.*, **95**, 5261 (1973), and references cited therein.
(15) R. M. Roberts, R. M. Landolt, R. N. Greene, and E. W. Heyer, *J. Am. Chem. Soc.*, **89**, 1404 (1967), and references cited therein.
(16) In both cis and trans model ketones the cyclobutyl proton α to the carbonyl group appears as a clean, symmetrical signal at δ ~3.0 ppm. The spectrum of **14** shows this signal as a broader, unsymmetrical multiplet, which is virtually unchanged on treatment with base.
(17) T. Cuvigny and H. Normant, *Bull. Soc. Chim. Fr.*, 1872 (1965).
(18) A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Lett.*, 2251 (1974).
(19) Spectroscopic properties of **19** were in agreement with those previously reported by J. Casanova and B. Waegell, *Bull. Soc. Chim. Fr.*, 1289 (1971).
(20) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).
(21) R. Ratcliff and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

Bicyclo[4.2.1]non-3-en-2-one. A Convenient Synthesis and Evidence for a Boat Conformation in the Seven-Membered Ring[1,2]

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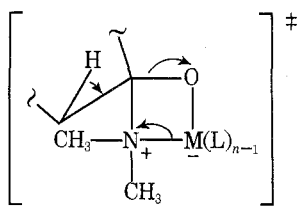
The cycloaddition reaction of 2-(*N,N*-dimethylamino)bicyclo[2.2.1]heptene, prepared from bicyclo[2.2.1]heptan-2-one and dimethylamine with stannic chloride, with ethyl propynoate in refluxing toluene produced ethyl 2-(*N,N*-dimethylamino)bicyclo[4.2.1]nona-2,4-diene-3-carboxylate. Acid hydrolysis of the amino carboxylate derivative produced bicyclo[4.2.1]non-3-en-2-one in 41% overall yield, based on bicyclo[2.2.1]heptan-2-one. The NMR data for the title compound are best understood in terms of a boat conformation in the seven-membered ring, in contrast to the evidence available for the parent hydrocarbon.

Synthetic routes into the bicyclo[4.2.1]nonane ring system are relatively few in number.[3-9] Many of these involve low-yield reactions and/or multistep sequences which are synthetically unattractive. We were particularly interested in developing an efficient route to bicyclo[4.2.1]non-3-en-2-one (**1**), an important intermediate in some of our work. Also, the four-carbon bridge of this ring system seems to us a potentially interesting scaffolding for stereochemical and mechanistic studies. The best example of the methods we wished to improve upon is the reported synthesis of the 3-bromo derivative of **1**.[8] Although the bicyclo[2.2.1]heptane system would seem to be a logical starting point for such a synthesis, there is only one report of its use in the synthesis of the [4.2.1]bicyclic system.[5] We wish to report our successful scheme, based on the commercially available bicyclo[2.2.1]heptan-2-one (2-norbornanone) (**2**).

It is well known that cycloaddition reactions of ethyl propynoate with the enamines of cyclic ketones lead ultimately to bishomologated ketones.[10,11] Thus, we sought to prepare the enamine derivative of **2**. Enamine preparation was at first problematical owing, presumably, to the strain associated with introduction of a double bond into the bicycloheptyl system.[12] The classical method[13] (pyrrolidine and *p*-toluenesulfonic acid) was not at all fruitful. We chose dimethylamine as the base and investigated the various catalysts previously employed. Anhydrous calcium chloride[14] gave only trace amounts of the desired product **3**. Stannic chloride,[15] on the other hand, proved to be most

satisfactory. We originally ascribed this to more efficient water scavenging by stannic chloride. Recently[16] **3** has been prepared using tris(dimethylamino)borane. This result, when considered along with the apparent reaction between dimethylamine and stannic chloride, suggests that for 2-norbornanone the crucial factor for enamine formation is simultaneous incorporation of the amine and a carbonyl-polarizing function within the same complex, i.e.

$$M = B; n = 3; L = (CH_3)_2N-$$
$$M = Sn; n = 4; L = (CH_3)_2N-$$

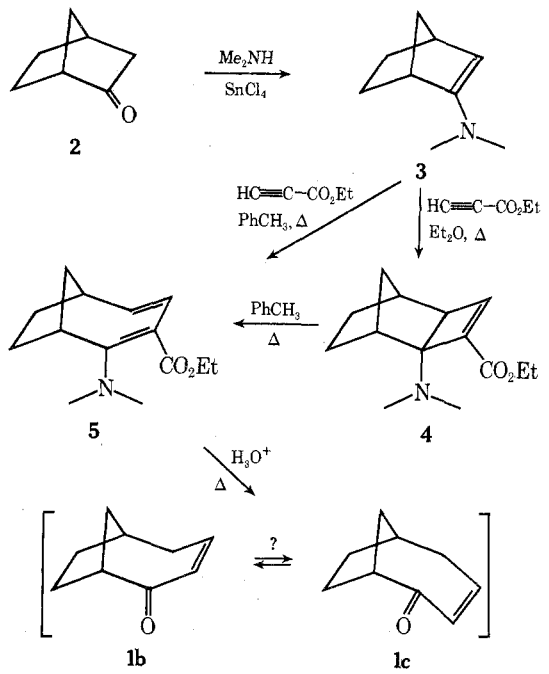


Cycloaddition[10,11] of the enamine **3** and ethyl propynoate leads smoothly and exothermally to the cyclobutene adduct **4** in ether. Actually under the reaction conditions (refluxing for 20 hr) it was anticipated that **5** would be the direct product. **4** was identified by the olefinic portion of the NMR spectrum. A singlet corresponding to one vinyl proton appears at δ 6.54. Such a signal is to be expected, since the dihedral angle between the vinyl proton and the bridgehead proton is approximately 90°.[10,17] Refluxing of **4** in toluene yields **5**. The cyclobutene adduct **4** exhibits unusual thermal stability, since most of the adducts[10] formed from other enamines are only stable below room temperature and undergo ring opening when refluxed in ether. Refluxing in ether for 20 hr leaves **4** unchanged. If the cycloaddition is carried out in refluxing toluene, the intermediate **4** is not isolated, since it is converted directly to **5**. One can, therefore, isolate **5** in a straightforward manner. Finally, acid-catalyzed hydrolysis of **5** produces the desired bicyclic unsaturated ketone **1** in 71% yield from the enamine **3**. This final step accomplishes four separate reactions in situ—hydrolysis of the enamine, hydrolysis of the ester, decarboxylation, and isomerization of the carbon–carbon double bond to the α,β position. These reactions are summarized in Scheme I.

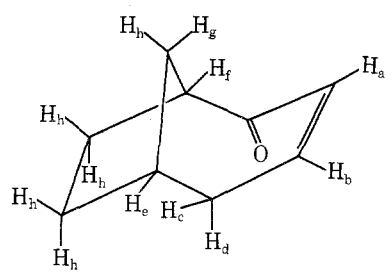
The preparation is accomplished in three steps with an overall yield of 41%. No intermediate product in the sequence need be purified. In fact, one obtains a better overall yield if intermediate purification is neglected owing to the sensitivity of the amino derivatives, **3**, **4**, and **5**. In addition, the final step can be affected essentially by a change of solvent. The product at the end of the synthetic route, bicyclo[4.2.1]non-3-en-2-one (**1**), has the added advantage of sufficient functionality for further adaptations on the four-carbon bridge.

We have indicated in Scheme I the possibility of a chair–boat equilibrium for **1**, using the seven-membered ring as the reference ring. Most, if not all, representations of the bicyclo[4.2.1] system presume a chair conformation.[3-9] Molecular mechanics calculations for the saturated hydrocarbon indicate a preference for the chair form by 1.8 or 0.3 kcal/mol, depending upon the details of the force field employed.[18] Indeed, this preference may be predicted from Dreiding models, based on torsional effects. No such preference, on the other hand, may be deduced for **1** from models. The ^{1}H NMR spectra of **1**, conversely, contain features that suggest a predominance of the boat form. A discussion of the ^{1}H NMR results is appropriate, as it highlights the particular strengths and weaknesses of current 100- and 300-MHz spectrometers in routine conformational analysis.

Scheme I

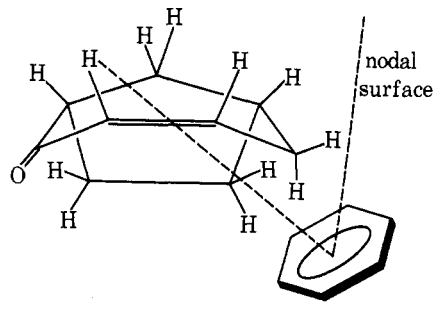


We have employed the proton labeling scheme for the boat indicated below, noting that protons c and d should be reversed in stereochemistry for the chair conformation, i.e., c = endo, d = exo.

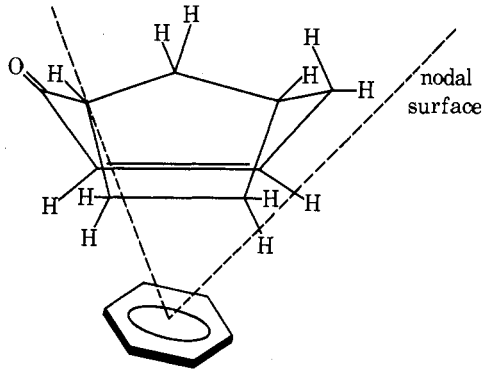


When the ^{1}H NMR spectrum of **1** is taken in deuteriochloroform at 100 MHz, the signals for four protons are sufficiently separated for identification. The apparent doublet of quartets at δ 5.82 (1 H) is assigned to H_a, while H_b appears as an apparent doublet of quartets of doublets at δ 6.21 (1 H). The multiplet at δ 2.98 (1 H) was assigned to H_f. The only other unique feature was a multiplet at δ 1.62 (1 H) clearly distinct from the complex signal arising from the remaining aliphatic protons. This last signal could only be understood in terms of a boat conformation for which H_g is directly above, and shielded by, the carbon–carbon double bond. We sought further evidence for the boat form of **1** by considering the aromatic solvent-induced shift (ASIS) for its protons, defined as $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$.[19] Unfortunately, in perdeuteriobenzene the signal for H_g could not be unequivocally identified at 100 MHz; hence we obtained 300 MHz spectra in both chloroform-d_1 and benzene-d_6.

It is generally held[20] that ketones tend to form collision complexes with benzene, though the precise geometry of such complexes is currently unsettled. It *is* clear, nonetheless, that the π system of the benzene ring interacts with the positive end of the carbonyl dipole. Examination of models suggests that in either the chair or boat form of **1** this association may best take place on the endo face of the molecule. This is due primarily to adverse interactions with the 9-syn hydrogen (H_g). Our "best guess" regarding the approximate geometries of the two complexes is shown below.



1b



1c

The pertinent ^{1}H NMR data for 1 are collected in Table I. Let us focus first on the solvent shift data. If the collision complex for **1c** is even approximately as shown, we would anticipate rather different ASIS values for H_b vs. H_c and H_d. Models do not permit prediction of an ASIS value for H_g since the 9-syn proton appears to be too far from the benzene ring for significant shielding to occur. The collision complex for **1b**, on the other hand, can permit near-equal shielding of H_b, H_c, and H_d. In addition, close approach of the benzene molecule to these protons will bring the 9-syn proton within a region of finite shielding. For these reasons, we consider **1b** to be the preferred conformation.

Table I
Selected NMR Data for Bicyclo[4.2.1]non-3-en-2-one

Proton	δ (CDCl3)	δ (C_6D_6)	Δ = [δ ($CDCl_3$) − δ (C_6D_6)]
H_a	5.82[a,b]	5.86[a,b]	−0.04[a,b]
H_b	6.21[a,b]	5.59[a,b]	+0.62[a,b]
H_c	2.62[b]	2.02[b]	+0.60[b]
H_d	2.56[b]	1.92[b]	+0.64[b]
H_f	2.98[a,b]	2.93[a,b]	+0.05[a,b]
H_g	1.62[a,b]	1.25[b]	+0.37[b]

Coupling constants, hertz:[a] J_{ab} = 12.9; J_{bc} = 4.7; J_{bd} = 3.4; J_{be} = 1.3; $J_{ac} \approx J_{ad} \approx J_{af} \approx$ 2.0.

[a] Observed at 100 MHz. [b] Observed at 300 MHz.

Since the shielding of the 9-syn proton was the original basis for considering the boat conformation, it is important to consider the predicted shielding by the double bond for the boat form and the carbonyl group for the chair form. The observed shielding is ~0.3 ppm. This value is within the range predicted from the long-range shielding contour maps[21] for the double bond based on either the Tillieu[22] or Pople[23] values for the principal susceptibilities. Tillieu's values lead to a predicted shielding of ~0.2 ppm while those of Pople predict shielding to the extent of ~0.4 ppm. In the chair conformation only the carbonyl group is close enough to affect the chemical shift of the 9-syn proton. Using shielding plots for the carbonyl group,[24] derived from Pople's values,[23] we find that the predicted value is only ~0.08 ppm, indicating that the carbonyl group is too far removed from the 9-syn proton to shield it significantly.

First order analysis of the olefinic multiplets observed at 100 MHz permitted the evaluation of some of the relevant coupling constants (Table I). These multiplets were only partially resolved at 300 MHz. The vinylic coupling constants J_{bc} and J_{bd} merit some comment. Dreiding models predict the following dihedral angles: $\omega(H_b–C_4–C_5–H_c)$ 0°; $\omega(H_b–C_4–C_5–H_d) \approx 110°$. Using the equations for vinylic coupling constants of Garbisch[25a] and Sayed,[25b] we find that J_{bc} (4.7 Hz) is smaller than expected. The value for J_{bd} (3.4 Hz), while corresponding approximately to the predicted value from the Garbisch equation, is significantly larger than the Sayed prediction. These findings suggest either a chair–boat equilibrium (predominantly boat) or a somewhat flattened boat. We cannot at this time distinguish between these two possibilities, but the ultraviolet spectrum is consistent with a flattened boat. The observed uv maximum [λ_{max} (EtOH) 229.5 nm (ϵ 10060)] is close to that predicted by Woodward rules[26] (227 nm), suggesting that conjugation between the carbonyl and vinylic groups is not significantly different from that in cyclohexenone derivatives.

Experimental Section

The ir data were taken on a Perkin-Elmer Model 257 grating spectrometer. The spectrometers used for ^{1}H NMR spectra are as follows: 60 MHz, Varian T-60; 100 MHz, Varian XL-100; 300 MHz, Varian HR300. The 300-MHz spectra were obtained through the NMR Center, Institute of Polymer Science, University of Akron, Akron, Ohio.

***N,N*-Dimethylbicyclo[2.2.1]hept-2-en-2-amine (3).** $SnCl_4$ (89.1 g, 0.342 mol) in 40 ml of dry pentane was added dropwise to a mechanically stirred solution of 58.20 g (0.528 mol) of 2-bicyclo-[2.2.1]heptanone (**2**) and 141.5 g (3.14 mol) of dimethylamine in 1.05 l. of dry pentane under nitrogen at 0°C. The reaction mixture was stoppered and stirred under nitrogen at room temperature for 72 hr. The solids were removed by filtration of the reaction mixture on a medium porosity glass funnel. The solid was rinsed with hot, dry pentane, and the combined pentane solutions were fractionally distilled to remove all of the pentane. Crude enamine (49.45 g, ~86% pure by NMR) remained (58% yield). Because of its sensitivity to moisture and air the enamine was used directly in the preparation of the cyclobutene adduct **4**: ir (neat) 3070, 2950, 2860, 2780, 1605, 1446, 1363, 1104 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.5 (m, C-5, C-6, C-7 H), 2.9 (m, C-1, C-4 H), 2.62 (s, 2 CH_3), 4.42 (d of d, J = 2.2, ~1 Hz, C-3 H) [lit.[16] ir (neat) 3080, 2950, 2860, 2800, 1610, 1450, 1370, 1100 cm^{-1}].

Ethyl 2-(*N,N*-Dimethylamino)tricyclo[4.2.1.0^{2,5}]non-3-ene-3-carboxylate (4). Crude enamine **3** (0.1 mol) in 45 ml of anhydrous ether was stirred while 9.81 g (0.1 mol) of ethyl propynoate in 15 ml of ether was added dropwise over a 1-hr period. When addition was complete and when the exothermic reaction had subsided, the solution was refluxed for 20 hr. Removal of ether in vacuo left an oil corresponding to the cyclobutene **4**: NMR ($CDCl_3$, 60 MHz) δ 1.6 (m, C-7, C-8, C-9 H), 1.27 (t superimposed on m, J = 6.5 Hz, $-OCH_2CH_3$), 2.32 [s, $N(CH_3)_2$], 3.0 (m, C-1, C-6 H), 3.28 (s, C-5 H), 4.17 (q, J = 6.5 Hz, OCH_2CH_3), 6.54 (s, C-4 H).

The oil **4** was dissolved in 30 ml of toluene and refluxed for 15 hr. The toluene was removed in vacuo leaving **5**, which solidified as a glass.

Ethyl 2-(*N,N*-Dimethylamino)bicyclo[4.2.1]nona-2,4-diene-3-carboxylate (5). To 49.32 g of the crude enamine **3** (86% pure) (~0.31 mol) in 93 ml of anhydrous toluene (distilled from CaH_2) was added 33.4 g (0.34 mol) of ethyl propynoate with stirring. After addition was complete the solution was stirred for 1 hr under nitrogen at room temperature and then at reflux for 15 hr. The toluene was removed in vacuo, leaving a viscous oil **5** which was used directly in the preparation of bicyclo[4.2.1]non-3-en-2-one (**1**): NMR ($CDCl_3$, 60 MHz) δ 1.27 (t, 3, J = 6.5 Hz, $-OCH_2CH_3$), 1.9 (m, 6, C-7, C-8, C-9 H), 2.9 (m, 2, C-1, C-6 H), 2.90 [s superimposed on m, 6, $N(CH_3)_2$], 4.15 (q, 2, J = 6.5 Hz, OCH_2CH_3), 5.38 (d of d of d, 1, J = 12.5, 7, 1.5 Hz, C-5 H), 6.31 (d, 1, J = 12.5 Hz, C-4 H).

Bicyclo[4.2.1]non-3-en-2-one (1). The crude ethyl 2-(*N,N*-dimethylamino)bicyclo[4.2.1]nona-2,4-diene-3-carboxylate (**5**) in

121 ml of glacial acetic acid was refluxed for 12 hr with 39.7 ml of concentrated HCl and 33 ml of water. The reaction mixture was poured into 300 ml of water and extracted with three 200-ml portions of ether. The ether solution was divided into two portions. Each portion was washed with 100-ml portions of 10% NaOH until basic, with another 50 ml of 10% NaOH, and with 50 ml of saturated NaCl solution. The ether was dried over $MgSO_4$ and removed in vacuo leaving a dark oil, which was fractionally distilled yielding 29.62 g of **5** (71% yield from the enamine **2**). Analytical samples were prepared by preparative VPC on a 6-ft 15% Apiezon L–Chromosorb P column (column temperature 134°, carrier flow rate 182 ml/min, retention time 21.0 min): bp 89.5–90° (6 mm); $n^{23}D$ 1.5244; uv λ_{max} (95% EtOH) 229.5 nm (ϵ 10060); NMR ($CDCl_3$, 100 MHz) δ 1.62 (m, 1, H_g), 1.95 (m, 5, H_h), 2.6 (m, 3, $H_c + H_d + H_e$), 2.98 (m, 1, H_f), 5.82 (d of d of d of d of d, 1, $J_{ab} = 12.9$, $J_{ad} = J_{ac} = J_{ae} = J_{af} = 2.0$ Hz, H_a), 6.21 (d of d of d of d of d, 1, $J_{ab} = 12.9$, $J_{bc} = 4.7$, $J_{bd} = 3.4$, $J_{be} = 1.3$ Hz, H_b); ir (neat) 3017, 2940, 2871, 1661, 1450, 1418, 1402, 1340, 1283, 1223, 1129, 898, 819 cm^{-1}.

Anal. Calcd mass for $C_9H_{12}O$: 136.0887. Measured mass: 136.0894.

Registry No.—**1**, 56533-25-6; **2**, 497-38-1; **3**, 41455-23-6; **4**, 56533-26-7; **5**, 56533-27-8; dimethylamine, 124-40-3.

References and Notes

(1) Taken from the Ph.D. Thesis of D. W. Boerth, University of Minnesota, 1975.
(2) This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.
(3) G. Opitz and H. Mildenberger, *Justus Liebigs Ann. Chem.*, **650**, 115 (1961).
(4) H. Onoue, I. Moritani, and S. I. Murahashi, *Tetrahedron Lett.*, **No. 2**, 121 (1973).
(5) N. A. Belikova, M. Ordubadi, A. F. Plate, T. I. Pekhk, and E. T. Lippmaa, *Zh. Org. Khim.*, **9**, 1855 (1973).
(6) M. Hartmann, *Justus Liebigs Ann. Chem.*, **729**, 8 (1969).
(7) L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966).
(8) C. W. Jefford, J. Burger, and F. Daley, *Helv. Chim. Acta*, **56**, 1083 (1973).
(9) W. Kraus, W. Rothenwöhrer, H. Sadlo, and G. Klein, *Angew. Chem., Int. Ed. Engl.*, **11**, 641 (1972).
(10) K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **29**, 818 (1964).
(11) C. J. Huebner, L. Dorfmann, M. M. Robison, E. Donoghue, W. G. Pierson, and P. Strachan, *J. Org. Chem.*, **28**, 3134 (1963).
(12) R. B. Turner, W. R. Meadov, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).
(13) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).
(14) E. P. Blanchard, Jr., *J. Org. Chem.*, **28**, 1397 (1963).
(15) W. A. White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1967).
(16) K. G. R. Sundelin, R. A. Wiley, R. S. Givens, and D. R. Rademacher, *J. Med. Chem.*, **16**, 235 (1973).
(17) Two other examples of singlets for tricyclo[4.2.1.$0^{2,5}$]non-3-ene systems appear in the recent literature. See E. W. Turnblom and T. J. Katz, *J. Am. Chem. Soc.*, **95**, 4292 (1973); R. M. Coates and K. Yano, *ibid.*, **95**, 2203 (1973).
(18) E. M. Engler, J. D. Androse, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).
(19) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, pp 112, 246 ff.
(20) D. H. Williams and D. A. Wilson, *J. Chem. Soc. B*, 144 (1966).
(21) Reference 19, pp 83–88
(22) J. Tillieu, *Ann. Phys.*, **2**, 471, 531 (1957).
(23) J. A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).
(24) Reference 19, pp 88–92.
(25) (a) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **86**, 5561 (1964); (b) Y. Sayed, Ph.D. Thesis, University of Minnesota, 1972.
(26) L. F. Fieser and M. Fieser, "Steroids", Reinhold, New York, N.Y., 1959, pp 15–25.

Molecular Design by Cycloaddition Reactions. XXIII.[1] Synthesis of Some Highly Strained Bridged Polycyclic Hydrocarbons

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Addition of dichlorocarbene (DCC) in aqueous medium to basketene, snoutene, and bullvalene gave the homobasketene, homosnoutene, and trishomobullvalene skeletons, respectively. Similar DCC addition of bicyclo[4.2.2]deca-2,4,7,9-tetraene afforded the formal 1:2 adduct of DCC to tetracyclodecadiene. Possible mechanisms for the reactions are also discussed.

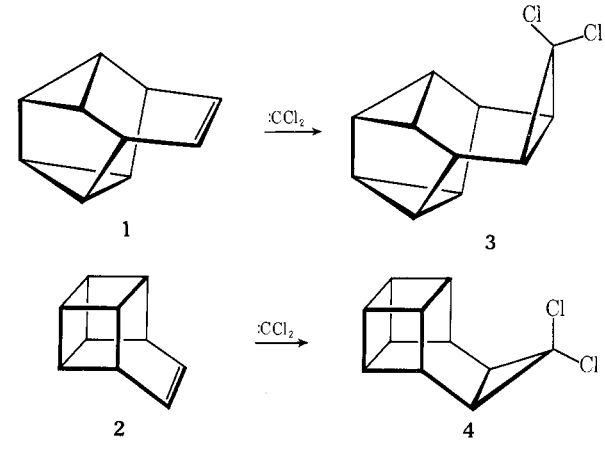
The synthesis of strained bridged polycyclic hydrocarbons is of considerable interest and continues to be a challenging objective to organic chemists.

As a continuation of our previous reports for providing a synthetic entry for new carbon-skeleton construction and further additional data for understanding the capability of a phase transfer catalyzed carbene addition[2] to some strained unsaturated compounds, we examined the carbene addition reactions of snoutene (**1**), basketene (**2**), bullvalene (**6**), and bicyclo[4.2.2]deca-2,4,7,9-tetraene (**11**), all of which are theoretically important $(CH)_{10}$ isomers connected on an energy surface with other $(CH)_{10}$ isomers.[3]

Results and Discussion

The reactions of snoutene (**1**)[4] and basketene (**2**)[5] with a 20-fold molar excess of dichlorocarbene (DCC) prepared at room temperature from chloroform in the presence of 50% aqueous sodium hydroxide–benzene with triethylbenzylammonium chloride (TEBA) as a catalyst afforded 1:1 adducts **3** and **4** in 45 and 60% yields, respectively (Scheme I). However, similar carbene addition reaction of **1** or **2** with excess phenyl(trichloromethyl)mercury gave only tarry materials and the 1:1 adduct could not be detected.

Scheme I



The NMR spectrum consisted of bridgehead protons at δ 2.87 (m, 2 H), cyclopropyl protons at δ 1.93 (m, 6 H), and characteristic dichlorocyclopropyl ring protons at δ 1.57 (s, 2 H) in compound **3**, and of two peaks of dichlorocyclopro-