batch technique by stirring an excess of the CrO_4H^- resin with the alcohols in a suitable refluxing solvent. The reaction product was then isolated by filtering off the resin and removing the solvent by distillation.

The nature of the solvent does not appear to be particularly critical. Hydrocarbons, chlorinated hydrocarbons, benzene, and ethers are equally effective, the practical choice being oriented by the solubility of the products and the desired reaction temperature. Toluene is less recommendable, owing to small amounts of benzaldehyde formed as by-product. The reaction seems to be quite general, allylic, benzylic, and saturated primary and secondary alcohols being cleanly converted to the corresponding carbonyl compounds in high yields.

No traces of carboxylic acids or other by-products were detected in all the cases studied. The only products isolated were the expected carbonyl compounds and, in the cases where the reaction had not gone to completion, the starting material was recovered.

The products were identified either by comparison with authentic samples or by spectroscopic, mass spectral, and elemental analysis.

The reaction rate depends both on the structure of the alcohol and on the substrate to resin ratio; it is faster for allylic and benzylic alcohols and for higher substrate to resin ratios. Regeneration of the resin in the chloride form is readily accomplished by washing successively with 2 N sodium hydroxide and 1 N hydrochloric acid solution.

The fact that the chromium ions in this reagent remain firmly bound to the resin before and after the reaction may be valuable in preventing environmental pollution.

Acknowledgment. This work was supported by a grant from CNR, Rome.

References and Notes

(1) (a) H. O. House, "Modern Synthetic Reactions", 2d ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 270; (b) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962); (c) R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Commun.*, 744 (1966); (d) W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967); (e) R. Ratcliffe and R. Robertson, *J. Org. Chem.*, **35**, 4000 (1970); (f) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975); (g) K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, **98**, 1986 (1976); (h) K. B. Sharpless, K. Akashi, and K. O. Oshima, *Tetrahedron Lett.*, 2503 (1976).

(2) (a) C. G. Overberger and K. N. Sannes, *Angew. Chem., Int. Ed. Engl.*, **13**, 99 (1974); (b) C. C. Leznoff, *Chem. Soc. Rev.*, **3**, 68 (1974).

(3) (a) M. Collins, D. R. Laws, *J. Chem. Soc., Perkin Trans. 1*, 2013 (1973); (b) G. Cainelli and F. Manescalchi, *Synthesis*, 723 (1975); (c) G. Cainelli, F. Manescalchi, and M. Panunzio, *Synthesis*, 472 (1976).

(4) G. A. Crosby, N. M. Weinshenker, and H.-S. Uh, *J. Am. Chem. Soc.*, **97**, 2232 (1975).

(5) (a) E. J. Corey and C. U. Kim, *J. Am. Chem. Soc.*, **94**, 7586 (1972); (b) *ibid., J. Org. Chem.*, **38**, 1233 (1973).

(6) Also Amberlyst A-29, Amberlite IRA 400, and Amberlite 904 were successfully employed.

(7) Also column technique has been employed.

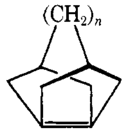
G. Cainelli,* G. Cardillo, M. Orena, S. Sandri
Istituto Chimico "G. Ciamician"
Università degli Studi, Via Selmi 2
40126 Bologna, Italy

Received April 8, 1976

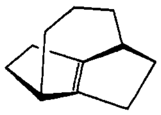
Synthesis of Tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene. A Novel Bridgehead Olefin

Sir:

Several years ago we reported the development of reductive transannular ring closure as an important step in the synthesis of olefins of type **1** from bicyclo[3.3.*n*]alkane-3,7-diones.[1] More recently, we have successfully used this scheme to prepare a derivative of the *n* = 2 member of this series.[2] In this communication we report the synthesis by a similar route of tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (**2**), a molecule belonging to another class of strained olefins.



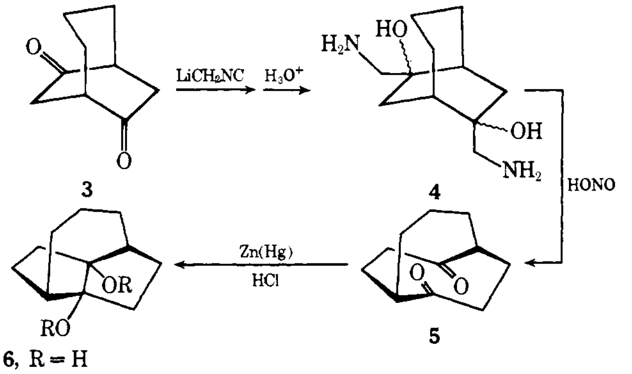
1



2

The "strain" in the double bond in **2** is quite different from that in the π bonds in molecules of type **1**, where overlap between atomic orbitals is diminished by pyramidalization of the carbons forming the double bonds.[3] Tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (**2**), in the Wiseman analysis[4] of bridgehead olefins,[5] may be viewed as a bisethano derivative of *trans*-cycloheptene. Although the olefinic carbons in such molecules may be somewhat pyramidalized,[6] overlap between the atomic orbitals forming the π part of the double bond is principally diminished by torsion. The two ethano bridges in **2** serve, of course, to prevent the trans → cis isomerization that occurs in *trans*-cycloheptene.[7] Indeed, Wiseman and Chong have synthesized a mixture of two *trans*-cycloheptene derivatives in which a single ethano bridge prevents isomerization, and they find that these molecules are stable at −70 °C but dimerize on warming to room temperature.[8] The second ethano bridge in **2** might tend to inhibit dimerization, not only by providing additional steric hindrance to cyclobutane ring formation but also by rendering impossible the ${}_{\pi}2_s + {}_{\pi}2_a$ pathway that has been proposed for the dimerization of some *trans*-cycloalkenes.[9,10]

The required diketone precursor of **2**, bicyclo[3.3.3]undeca-2,6-dione (**5**), was prepared by Tiffeneau-Demjanov ring expansion of bicyclo[3.2.2]nona-6,8-dione (**3**).[11] Of the many reactions investigated for the transformation of **3** to **4**, the most satisfactory proved to be treatment of **3** with excess isocyanomethyllithium (THF, −60 °C, 65% yield), followed by hydrolysis in refluxing methanolic HCl of the diadduct.[12] Although some monoadduct was invariably isolated from the first reaction, it could be separated from the diadduct and recycled. Rearrangement of **4** was effected by addition of sodium nitrite to the crude hydrochloride salt in a two-phase mixture of benzene and buffered acetic acid. This reaction might have led to the diketone precursor of **1**, *n* = 3, by migration of the more substituted carbon atoms. That this was not, in fact, the major reaction path[13] was indicated by the ^1H NMR spectrum ($CDCl_3$) of the crude product, which showed two methine (δ 2.9) and four methylene (δ 2.5) protons on carbons α to the carbonyls. The crude diketone (**5**) was reduced with a zinc amalgam in aqueous HCl[1] to the crystalline diol (**6**),[14] mp 141–144 °C dec, obtained in 58% overall yield from the isocyanomethyllithium diadduct of **3**. The proton decoupled ^{13}C NMR spectrum of the diol showed six singlets (δ 91.11, 44.67, 31.38, 29.29, 27.24, 18.14), corresponding to the six types of

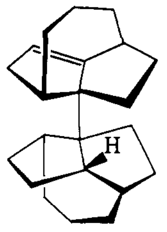


3 **4** **5**

6, R = H
7, R—R = C=S

carbons present in **6**, thus confirming this structure for the diol and that (**5**) assigned to the diketone.

Of the methods investigated for transformation of the diol (**6**) into the olefin (**2**), the Corey–Winter reaction[15] proved most efficacious. Although **6** did not react with thiocarbonyldiimidazole, when the diol was first converted to the lithium salt and then heated at reflux in THF with this reagent, the thionocarbonate (**7**)[14] was obtained in 82% yield. Decomposition of **7** in refluxing triethyl phosphite, containing diphenylisobenzofuran as trapping agent, gave the Diels–Alder adduct of **2**[14] in 85% isolated yield. When diphenylisobenzofuran was omitted from the reaction, a hydrocarbon[14] was isolated in 85% yield. Its mass spectrum showed it to be a dimer of **2**. However, its ^{1}H NMR spectrum ($CDCl_3$) clearly indicated that it was not the formal product of a $_{\pi}2_s + {}_{\pi}2_s$ reaction, for a single olefinic proton appeared as a broad doublet at δ 5.48, $J = 5$ Hz. Among the 22 resonances in its ^{13}C NMR spectrum ($CDCl_3$) the two corresponding to the olefinic carbons appeared at δ 127.19 (d) and 162.02 (s). The structure of the hydrocarbon is, therefore, formulated as that (**8**)[16,17] expected from an ene reaction[19] between two molecules of **2**. Support for this structural assignment comes from the fragmentation of the hydrocarbon on electron impact; substantial peaks at the mass of olefin (**2**) ± 1 appear in the mass spectrum. Further evidence for structure **8** was obtained by hydrogenation (Pd/C, ethanol) of the hydrocarbon. The proton decoupled ^{13}C NMR spectrum of the crystalline hydrogenation product,[14] mp 131–132.5 °C, showed only 11 resonances, indicating that it possesses either a plane or twofold axis of symmetry.[16]



8

Although this is, to the best of our knowledge, the first example of a bridgehead olefin giving an ene type dimer, the formation of such a product finds precedent in the chemistry of a torsionally strained olefin with a sterically shielded double bond.[20] Further studies of the chemistry and trapping of **2** are in progress.

Acknowledgment. We thank Dr. William Kingsley for carrying out some preliminary experiments on the isocyanomethyllithium method of ring expansion and the National Science Foundation and the Eli Lilly Company for partial support of this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the portion of this work that was carried out by T.R. and W.T.B. at Harvard.

References and Notes

(1) W. T. Borden and T. Ravindranathan, *J. Org. Chem.*, **36**, 4125 (1971).
(2) R. Greenhouse and W. T. Borden, to be submitted for publication.
(3) For a recent example of the synthesis and structure of a related olefin see R. L. Viavattene, F. D. Greene, L. D. Cheung, R. Majeste, and L. M. Trefonas, *J. Am. Chem. Soc.*, **96**, 4342 (1974).
(4) J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92**, 956 (1970).
(5) Three excellent reviews have recently appeared: G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973); R. Keese, *ibid.*, **14**, 528 (1975); G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974).
(6) W. L. Mock, *Tetrahedron Lett.*, 475 (1972); L. Radom, J. A. Pople, and W. L. Mock, *ibid.*, 479 (1972).
(7) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965); E. J. Corey and J. I. Schulman, *Tetrahedron Lett.*, 3655 (1968).
(8) J. R. Wiseman and J. A. Chong, *J. Am. Chem. Soc.*, **91**, 7775 (1969).
(9) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(10) See, however, J. Leitlich, *Angew. Chem., Int. Ed. Engl.*, **8**, 909 (1969); C. L. Osborn, D. J. Trecker, A. Padwa, W. Koehn, and J. Masaracchia, *Tetrahedron Lett.*, 4653 (1970).
(11) G. Wood and E. P. Woo, *Can. J. Chem.*, **46**, 3173 (1968).
(12) U. Scholkopf and P. Bohme, *Angew. Chem., Int. Ed. Engl.*, **10**, 491 (1971).
(13) Preferential migration of the less substituted carbon in Tiffeneau-Demjanov ring expansions is often observed. See, for instance, M. A. McKinney and P. P. Patel, *J. Org. Chem.*, **38**, 4059 (1973), and references therein.
(14) This compound gave satisfactory analytical data—elemental analysis and/or exact mass.
(15) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).
(16) Since **2** is chiral, it can in fact dimerize to give two different ene type products, only one of which is represented in structural formula **8**. From the ^{13}C NMR spectrum of the dimer and its hydrogenation product, it appears that only one is formed. We are trying to determine whether the dimer does, in fact, correspond to the one represented in **8**.
(17) It should be noted that **8** is itself a strained olefin, since it contains a bicyclo[3.3.0]oct-1(2)-ene moiety.[5,18] Indeed on prolonged refluxing (36 h) in triethyl phosphite, an isomer[14] of **8** becomes the major product isolated. The ^{1}H NMR spectrum of the isomer shows a two-proton multiplet centered at δ 5.68, and two olefinic carbons appear in the ^{13}C NMR spectrum at δ 132.38 (d) and 137.26 (d). The spectroscopic data and the fact that the isomer gives the same crystalline hydrocarbon as **8** on hydrogenation indicate that the isomer is the formal product of a 1,3 hydrogen shift, which releases the strain present in **8**.
(18) W. C. Agosta and S. Wolff, *J. Org. Chem.*, **40**, 1699 (1975).
(19) Review: H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
(20) K. Kraft and G. Koltzenberg, *Tetrahedron Lett.*, 4723 (1967).

Robert Greenhouse, T. Ravindranathan
Weston Thatcher Borden*
Department of Chemistry, University of Washington
Seattle, Washington 98195

Received May 19, 1976

The Relationship between ^{15}N^{13}C Coupling Constants and Hybridization

Sir:

In a previous paper[1] we described semiempirical calculations of ^{13}C^{15}N spin-spin coupling constants which included the three contributing terms—Fermi contact (J^{Fc}), orbital (J^{o}) and spin dipolar (J^{sd}). The importance of such calculations is that they allow the evaluation of the latter "noncontact" terms, which are often invoked ad hoc when the observed one-bond coupling constant, $^1J_{\mathrm{CN}}$, appears anomalous with respect to hybridization. It is now possible to explore a long-standing question in carbon-nitrogen coupling—why the relationship proposed by Binsch et al.[2]

$$|{}^1J_{^{13}\mathrm{C}^{15}\mathrm{N}}| = (80)^{-1}(\%S_{\mathrm{C}})(\%S_{\mathrm{N}}) \qquad (1)$$

holds for some CN constants while failing badly for others? This issue is important because reference to eq 1 has appeared in most studies to date reporting CN coupling constants and because it represents an important conceptual framework for interpreting $^1J_{\mathrm{CN}}$. An alternate approach, relating $^1J_{\mathrm{CN}}$ linearly to the square of the density matrix element $P_{S_{\mathrm{C}}S_{\mathrm{N}}}$ of molecular orbital theory has met with similar difficulties.[3,4] Only when the nature of these deficiencies are clarified will it be possible to extract hybridizations with assurance from the observed $^1J_{\mathrm{CN}}$.

To analyze this problem we have chosen to compute $(\%S_{\mathrm{C}})$ $(\%S_{\mathrm{N}})$ from INDO localized orbitals (rather than use nominal hybridizations, e.g., sp, sp^2, sp^3), utilizing the formula

$$(\%S_{\mathrm{C}})(\%S_{\mathrm{N}}) \approx (100P_{S_{\mathrm{C}}S_{\mathrm{N}}})^2 \qquad (2)$$

where the $P_{S_{\mathrm{C}}S_{\mathrm{N}}}$ is defined as $2\Sigma_j\, C_{jS_{\mathrm{C}}}C_{jS_{\mathrm{N}}}$, the sum running over products of 2S coefficients in the localized orbital(s) of the CN bond(s). Thus, for single bonds $P_{S_{\mathrm{C}}S_{\mathrm{N}}}$ is slightly larger than its delocalized counterpart,[5] since only orbitals contributing to the CN bond are included[6] and slightly smaller than the product percent s character, which is obtained by truncation to two centers. For the bent localized orbitals of multiple