Tetrahedron Letters Vol. 22, pp 371 - 374
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0040-4039/81/0129-0371$02.00/0

A NOVEL ETHYLENE-BRIDGED SPIRO[3.2]HEXANE

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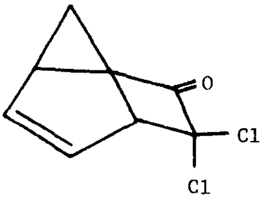
Abstract

3,3-Dichlorotricyclo[5.1.0.$0^{1,4}$]oct-5-en-2-one (1) was prepared by addition of dichloroketene to 1,3-cyclohexadiene followed by allylic bromination and dehydrobromination.

We wish to report the convenient synthesis[1] and definitive proof of structure of a surprisingly stable tricyclooctane derivative 1 incorporating an ethylenic bridge joining the α-positions of a spiro[3.2]hexane system.[2] 3,3-Dichlorotricyclo[5.1.0.$0^{1,4}$]-oct-5-en-2-one (1) was obtained inadvertently during the attempted synthesis of diene 2[4] by dehydrobromination of the allylic bromination product 4 of the adduct 3 between dichloroketene and 1,3-cyclohexadiene.[6] Generation of dichloroketene from dichloroacetyl chloride and triethylamine in the presence of a 10-fold excess of 1,3-cyclohexadiene gave 3 (63%; bp 62-67° (0.2 mm.); mp 12°). Allylic bromination of 3 by means of N-bromosuccinimide in carbon tetrachloride gave a mixture



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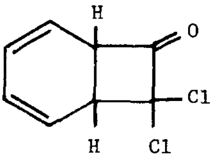

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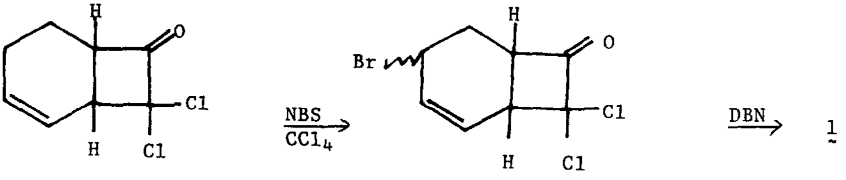


3

4

of two bromides 4 separable by column chromatography on florisil via elution with pentane into a liquid and a solid (mp 88°).[7] Treatment of the mixed bromides[8] with 1,3-Diazabicyclo[3.4.0]-nonene-5 (DBN) gave the tricyclic compound 1 in up to 70% yield. Structure 1 was assigned on the basis of a careful analysis of the ^{1}H-NMR spectrum.[9] Computer simulation of the spectrum via input of the chemical shifts and extracted coupling constants via the LAOCOON II program[10] produced a close match of the observed spectrum. No change in the spectrum was observed over a temperature range from -50 to 60°. Cyclobutanone carbonyl absorption appeared in the IR spectrum at 1790 cm^{-1}.[11] The presence of the cyclopropane ring was supported by IR[12] (3035, 1018 cm^{-1}) and near IR[13] absorptions (1.637 μ, ε 0.363). The ^{13}C nmr spectrum confirms the structure.[14]

The UV absorption [λmax (EtOH) 251 nm, ε 1300; (octane) 242.5 nm (ε 1240); 302 (ε 88)] appeared anomalous at first sight. Although transmission of electronic effects through a 3-membered ring has been observed, in general the cyclopropyl ketone chromophore absorbs below 200 nm.[15] On the other hand the observed absorption can be correlated with a unique chromophore recognized first by Cookson[16] which is due to coupling of an olefinic linkage and a carbonyl group through an appropriately positioned σ-bond. Cycloadduct 3 also exhibits this chromophore [λmax 227.5 nm (ε 783)].

Crystals of 1 (mp 45-46°) suitable for crystallographic analysis were obtained from pentane at -78°. All crystallographic data collection was done at low temperature (ca. -80°) because of the low melting point of the crystals. Preliminary X-ray experiments indicated that the space group of the crystals was $P2_1/n$ with a = 7.540 (1) Å, b = 9.245 (2) c = 11.556 (2) and β = 97.73 (1)° with Z = 4 for a calculated density of 1.57 g/cm^3. Of the 1067 unique reflections measured with CuK α radiation (λ = 1.5418 Å), 1000 (94%) were observed ($I \geq 3\sigma I$) and corrected for polarization and Lorentz effects. Initial structural parameters found using standard direct methods techniques[17] were refined using full-matrix least-squares[18] by minimizing $\Sigma w\,(|F_o|-|F_c|)^2$ with $w = 1/(\sigma\, F_o)^2$. The final unweighted residual is .048 using isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms. An ORTEP[19] view of the crystal structure of 1 is shown in Fig. 1.

Compound 1 is unusually stable considering the degree of ring strain present, with 3-, 4- and 5-membered rings meeting at a single carbon atom. The reactivity of 1 is currently under study.

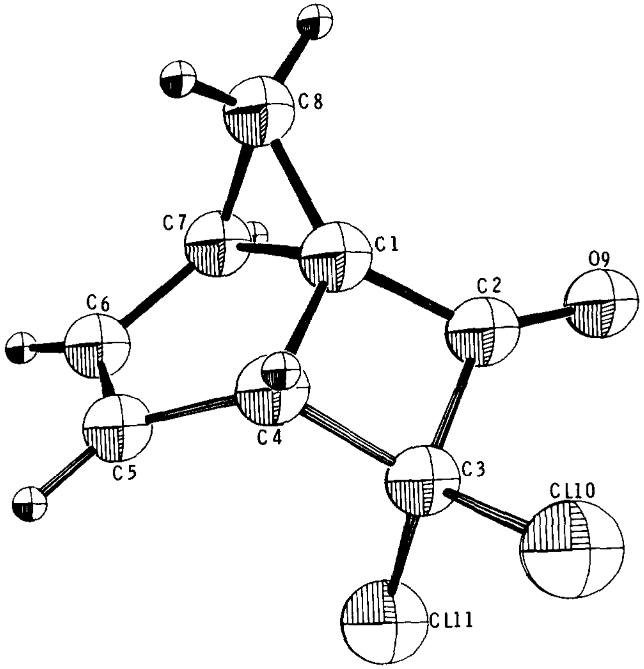


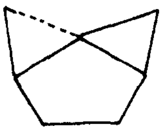
Fig. 1

Acknowledgments. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are also indebted to Profs. Bernie Miller and George W. Cannon for stimulating discussions and suggestions, and to Drs. Alan Douglas and Dorothy Denney for obtaining and interpreting the ^{13}C nmr spectrum.

Bibliography

1) A portion of this work has been presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1970; Abstracts, ORGN-23.

2) No such ethylene bridged small-ring spiroalkanes appear to have been described. The closest analog reported to date is the saturated bridged spiropentane i. For a fascinating and ex-



i

haustive discussion of highly strained hydrocarbons two recent reviews by Greenberg and Liebman[3] may be consulted.

3) (a) A. Greenberg and J. F. Liebman, "Strained Organic Molecules", Academic Press, New York, N.Y., 1978; (b) A. Greenberg and J. F. Liebman, Chem. Rev., 76, 311 (1976).

4) Diene 2 was sought as a possible precursor via hydrolysis of the corresponding theoretically interesting diketone.[5]

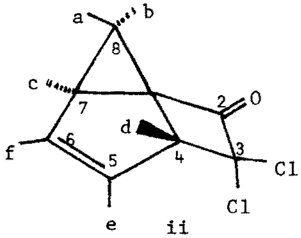
5) See also L. A. Carpino and J.-H. Tsao, J. Org. Chem., 44, 2387, 2564 (1979).

6) Compare (a) H. C. Stevens, D. A. Reich, D. R. Brandt, K. P. Fountain and E. J. Gaughan, J. Am. Chem. Soc., 87, 5257 (1965); (b) L. Ghosez, R. Montaigne and P. Mollet, Tetrahedron Lett., 135 (1966); (c) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde and P. Mollet, Tetrahedron, 27, 615 (1971).

7) Satisfactory elemental analyses and consistent spectral data were obtained for all new compounds.

8) The liquid bromide was obtained in major amount. In one run a 4% yield of the solid isomer was obtained. The latter on dehydrobromination gave only a trace of 1 suggesting that only in the liquid isomer is the bromo substituent positioned for facile back-side displacement by the 4-ring enolate.

9) Nmr spectrum at 60 MHz (CDCl$_3$, assignments shown in ii): δ 1.37 (a), 2.20 (b), 3.07 (c),



ii

3.88 (d), 5.92 (e), 6.37 (f): J_{ab} = 5.7 cps, J_{ac} = 5.7, J_{bc} = 8.7, J_{bd} = 0.5, J_{bf} = 1.6, J_{cd} = 2.8, J_{ce} = 1.5, J_{cf} = 0.3, J_{de} = 2.7, J_{df} = 1.6, J_{ef} = 5.6.

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14) C nmr spectrum at 25.2 MHz (CDCl$_3$, numbering shown in ii): 193.7 (C$_2$), 137.5 (C$_6$), 132.2 (C$_5$), 89.1 (C$_3$), 61.3 (C$_4$, $^1J_{CH}$ = 147), 47.3 (C$_7$, $^1J_{CH}$ = 173), 45.3 (C$_1$), 23.0 ppm. (C$_8$, $^1J_{CH}$ = 163).

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(Received in USA 16 October 1980)