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Dimethylenebicyclo[1.1.1]pentanone[§]

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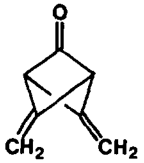
Abstract. The highly strained and reactive dimethylenebicyclo[1.1.1]pentanone (I), was prepared as follows. Treatment of 1,5-bis(chloromethyl)tricyclo-[2.1.0.0^{2,5}]pentan-3-one diethyl ketal (III) with di-t-butyl hydrazodicarboxylate (VII), followed by pyridinium p-toluenesulfonate and trifluoroacetic acid, yielded the keto hydrazine X which was oxidized to the desired ketone I. The ketone I decomposes very rapidly above -30°C.

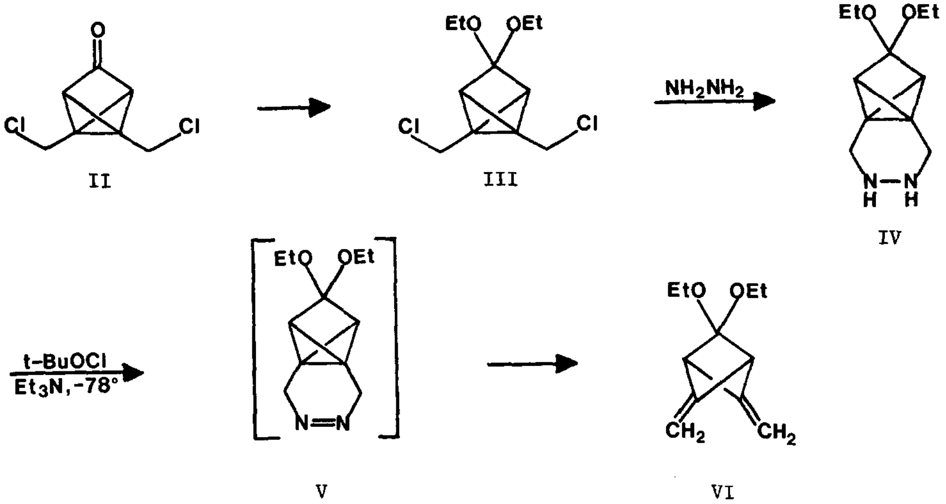
There are no known bicyclo[1.1.1]pentanes with sp^2 carbons at all the bridges. Thus, it was attractive to explore the synthesis and reactivity of the dimethylene bicyclic ketone I. The latter was expected to be particularly reactive as a consequence of the increased strain from the addition of three sp^2 centers to the already highly strained bicyclo[1.1.1]pentane skeleton.[1] Of equal importance, the ketone I provides an attractive photolytic entry to the long sought dimethylenecyclobutadiene diradical.[2]



I

[§] Dedicated with warmest best wishes to Professor Harry Wasserman on the occasion of his sixty-fifth birthday.

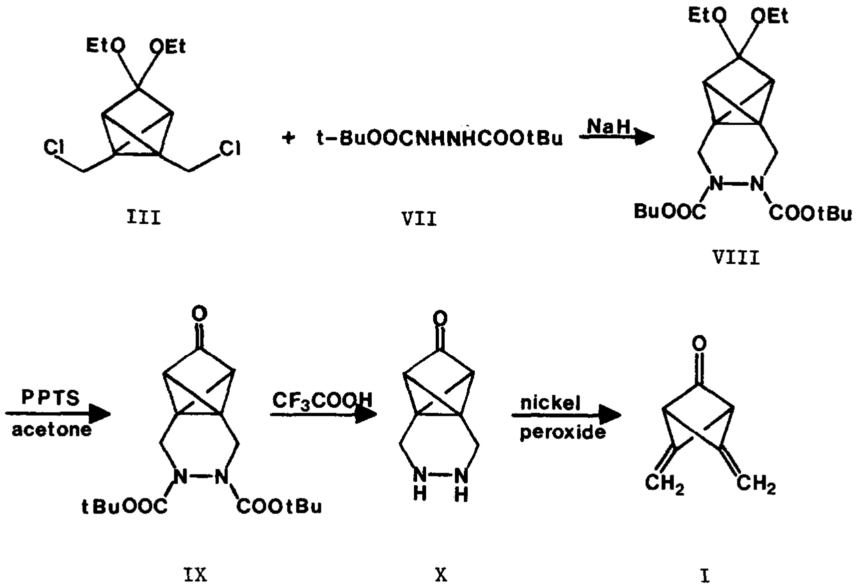
Synthesis of I was approached as follows. 1,5-Bis(chloromethyl)tricyclo[2.1.0.0^{2,5}]-pentan-3-one (II)[3] was converted to its ketal III, then treated with hydrazine to generate the hydrazino ketal IV (60%).[4] The hydrazine IV was oxidized with freshly prepared t-butyl hypochlorite and triethylamine in methylene chloride-d_2 at -78°C. The oxidation-nitrogen elimination reaction was monitored by following the appearance of the vinyl protons in the nmr spectrum of the ring-opened ketal VI.[5]



The loss of nitrogen is extremely rapid and no azo absorption between 200 and 400 nm was evident at -70° in the UV spectrum. Such exceptional reactivity is not unexpected. Although this is the first bicyclobutane fused azo intermediate to be prepared for nitrogen extrusion, loss of nitrogen from cyclopropyl fused azo compounds has been studied extensively.[6]

The low temperature of the oxidation reaction is essential because the product ketal VI is very unstable even at -30°C. All attempts to hydrolyze the ketal VI to the ketone I were unsuccessful and resulted in unchanged ketal VI, a consequence of the low temperatures required to prevent decomposition.

Accordingly, a new tack was adopted. The dichloro ketal III was treated with di-t-butyl hydrazodicarboxylate (VII) in the presence of sodium hydride, yielding the ketal VIII. The ketal group was removed by exchange with acetone in the presence of pyridinium



p-toluenesulfonate.[7] Treatment of the resulting ketone IX with trifluoroacetic acid followed by neutralization with Dowex 1-X8 at 0°C yielded the oxygen sensitive and labile hydrazino ketone X.

The hydrazino ketone X was oxidized to the desired ketone I with t-butyl hypochlorite-triethylamine in methylene chloride-d_2 at -78°C or (preferably) with freshly prepared nickel peroxide in methylene chloride-d_2 at -78°C. The proton nmr spectrum (300 MHz) of the ketone I at -60°C showed sharp singlets at δ4.78 and δ3.62 in the ratio 2:1. Although the ketone I more than rivaled the ketal VI in its instability, I can be distilled bulb-to-bulb at -60°C and 10^{-6} Torr. The proton nmr spectrum showed the product ketone I to be free of impurities except t-butanol, which was carried over in the distillation. When nickel peroxide is used the substantial losses associated with the distillation can be avoided, and, since there are no organic by-products from the reaction, the nmr spectrum shows only the peaks at δ4.78 and δ3.62;[8] the nickel peroxide is simply removed by filtration at -78°C.

With an MM2 strain energy of 101 kcal/mol the ketone I must be included among the most strained bicyclic molecules known. This is manifest in its great ease of decomposition. It has a half-life of approximately 90 min at -30°C. This is to be compared with reactivity of the parent bicyclo[1.1.1]pentane (MM2 strain 77 kcal/ mole) which decomposes at approximately 200°C and bicyclo[1.1.1]pentanone (MM2 strain 89 kcal/mole) which decomposes near 100°C.[9]

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(2) P. Dowd, Y. H. Paik, **J. Am. Chem. Soc.**, in press; G. J. Snyder, D. A. Dougherty, **J. Am. Chem. Soc.**, **1985**, 107, 1774.

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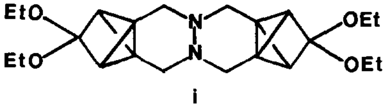
(4) *The structurally interesting dimer i was also isolated in 20% yield.* The dimeric



i

adduct i is the major product of this reaction if 20 equiv of hydrazine is added all at once to the dichloro ketal III.

(5) The proton nmr spectrum (300 MHz, CD_2Cl_2, -70°C) of the ketal VI showed two singlets at δ4.57 and δ3.83 in the integrated ratio of 2:1 corresponding to the vinyl and bridgehead methine protons, a four-proton quartet at δ3.56 and a six-proton triplet at δ1.18. The spectrum also shows trimethylamine and t-butyl alcohol resonances. The carbon-13 nmr spectrum (75.46 MHz, $CDCl_3$, -53°C) showed: a quaternary ketal carbon singlet at δ105.0, a vinyl carbon singlet at δ142.5, a methylene vinyl triplet (^1J=162 Hz) at δ84.5, a bridgehead methine doublet (J=172.6 Hz) at δ61.6, a methylene triplet (J=141 Hz) at δ6.09 and a methyl quartet (J=126.2 Hz) at δ15.2.

(6) E. L. Allred, J. C. Hinshow, A. L. Johnson, **J. Am. Chem. Soc.**, **1969**, **91**, 3382; J. A. Berson, S. S. Olin, **J. Am. Chem. Soc.**, **1969**, 91, 777; J. A. Berson, S. S. Olin, **ibid.**, **1969**, **91**, 1086; J. A. Berson, E. W. Petrillo, Jr., P. Bickert, **ibid**, **1974**, **96**, 636.

(7) N. Miyashita, A. Yoshikoshi, P. A. Grieco, **J. Org. Chem.**, **1977**, **42**, 3772.

(8) *The carbon-13 nmr spectrum of I (CD_2Cl_2, -60°C) showed a carbonyl carbon singlet at* δ172.1, a quaternary vinyl carbon singlet at δ131.0, a vinyl carbon triplet (^1J=165 Hz) at δ87.6, and a methine carbon doublet (^1J=184 Hz) at δ67.4.

(9) M. B. Sponsler, D. A. Dougherty, **J. Org. Chem.**, **1984**, 49, 4978. In this paper, an MNDO calculation was used to estimate the strain in bicyclo[1.1.1]pentane and bicyclo[1.1.1]pentanone and to arrive at the somewhat surprising conclusion that the strain energies were essentially the same for these two substances.

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