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RING CONTRACTIONS OF trans-FUSED CYCLOPROPANES

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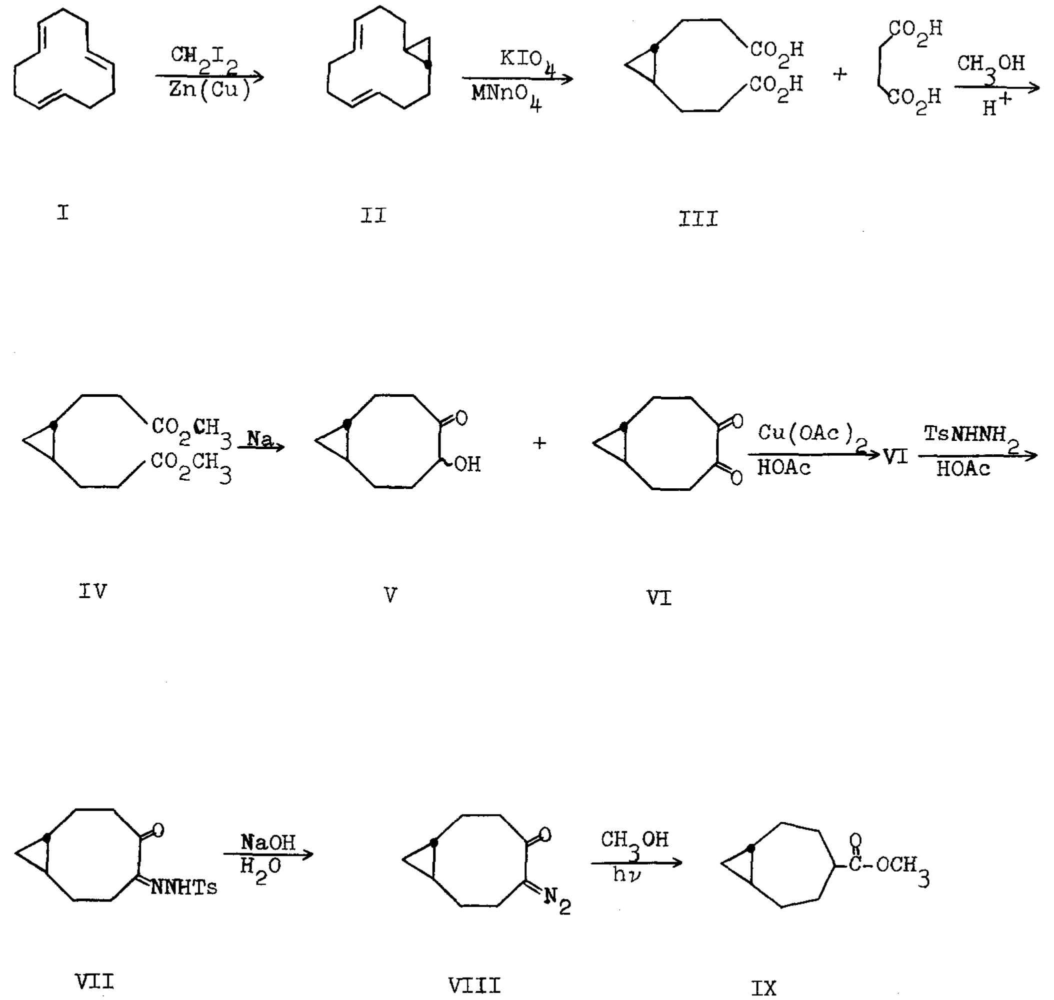
There has been much interest in the synthesis of strained bicyclic hydrocarbons involving two relatively small trans-fused rings. The 7-4 system, trans-bicyclo[5.2.0]nonane[1], the 6-4 system, trans-bicyclo[4.2.0]octane[2], and the 5-4 system, trans-bicyclo[3.2.0]heptane[2] have been synthesized. On the other hand the smallest compound with a trans-fused cyclopropane ring had been the 8-3 system, trans-bicyclo[6.1.0]octane.[3] A recent preliminary report of the synthesis of trans-bicyclo[5.1.0]octane-4-carboxylic acid[4] prompts us to report our data on the synthesis of trans-fused cyclopropanes.[5]

The readily available trimer of butadiene, trans,trans,trans-1,5,9-cyclododecatriene (I), can be stereospecifically converted to trans,trans,trans-bicyclo[10.1.0]trideca-3,7-diene (II) by the Simmons-Smith reaction. A Lemieux-Rudolph[6] oxidation of this diene gave an oily mixture of diacid III and succinic acid, which were converted without isolation to their dimethyl esters.

In our hands the Dieckmann ring closure of diester IV failed. However, the acyloin reaction gave a 40% yield of a mixture of the trans-bicyclo[6.1.0]-nonan-4-ones (V) and trans-bicyclo[6.1.0]nona-4,5-dione (VI). This mixture could be oxidized by cupric acetate to dione VI, which showed carbonyl absorption at 1710 cm^{-1} (CCl_4) in the IR. No enol could be detected in the golden yellow dione.[7]

The dione gave a monotosylhydrazone (VII), mp 170° dec. (CH_3CN), whose IR ($CHCl_3$) showed absorbtion at 1700 cm^{-1}. The rather unstable yellow diazoketone VIII, showing IR (CCl_4) absorption at 2100 cm^{-1}, was produced by treatment with aqueous base. Photolysis of this diazoketone in methanol using a hanovia lamp with a corex filter gave methyl trans-bicyclo[5.1.0]octane-4-carboxylate (IX).


CH2I2
Zn(Cu)
KIO4
MNnO4
CO2H
CO2H
+
CO2H
CO2H
CH3OH
H+
I
II
III
CO2CH3
CO2CH3
Na
O
OH
+
O
O
Cu(OAc)2
HOAc
VI
TsNHNH2
HOAc
IV
V
VI
O
NNHTs
NaOH
H2O
O
N2
CH3OH
hν
O
C-OCH3
VII
VIII
IX

This ester had an IR absorbtion in CCl_4 at 1735 cm^{-1}. The mass spectrum gave a parent peak at m/e 168, while peaks at m/e 137 ($P-OCH_3$) and m/e 109 ($P-CO_2CH_3$) were prominent. The complex NMR spectrum showed: a singlet at 6.4 τ (3H) due to the carbomethoxy group, a broad absorbtion centered at 7.35 τ (1H) due to the methine proton adjacent to the carbomethoxy group, two complex envelops of peaks 7.6-8.3 τ (6H) and 8.7-9.4 τ (4H) due respectively to six protons of the cycloheptane ring and to the two bridgehead cyclopropyl protons along with the two remaining cycloheptyl protons, and a broad absorbtion centered at 10.0 τ (2H) due to the two secondary cyclopropyl hydrogens. These data together with the mode of synthesis establish the structure as methyl trans-bicyclo[5.1.0]octane-4-carboxylate.

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References

1. N. L. Allinger, M. Nakazaki and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4079 (1959).
2. J. Meinwald, J. J. Tumariello and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964).
3. A. C. Cope and J. H. Hecht, *J. Amer. Chem. Soc.*, **85**, 1780 (1963).
4. P. G. Gassman, F. J. Williams and J. Seter, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1968, No. 098.
5. Satisfactory analyses have been obtained on all new compounds. The infrared spectra were recorded on a Perkin-Elmer 237 spectrometer using balanced 0.1 mm cells. The mass spectrum was taken on CEC-103 spectrometer while the NMR spectra were recorded using a Varian A-60 machine with tetramethylsilane as an internal standard.
6. R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).
7. Models indicate that a 3,4 double bond might add considerable extra strain.