# Synthesis of a Bicyclobutane Derivative

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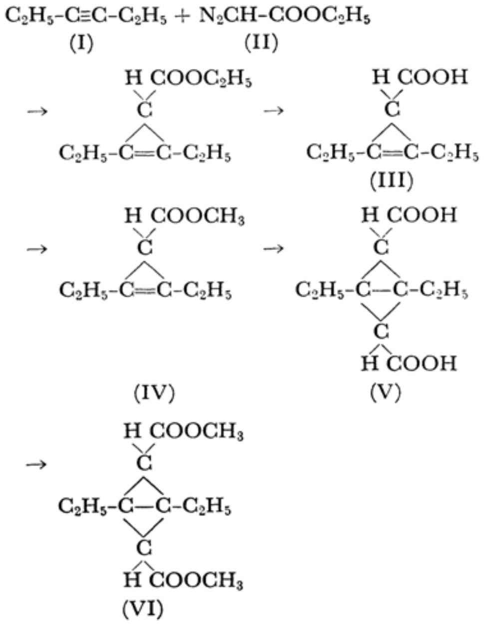
Bicyclobutane and its derivatives¹⁾ have been prepared recently and some of them by double sequences.²⁾

We wish to report the formation of 1, 3-diethylbicyclobutane-2, 4-dicarboxylic acid (V) by adding carbethoxycarbene twice to 3-hexyne (I).

1, 2-Diethylcyclopropenecarboxylic acid (III) was prepared in the following procedure.³⁾ Ethyl diazoacetate (II) was added in a mixture of I and catalytic copper dust in di-*n*-butyl ether under nitrogen atmosphere of 140°C, and distilled (bp 95—105°C/30 mmHg fraction). After treating with a solution of potassium hydroxide in *n*-propanol, III was isolated as white crystals (mp 44°C; 25% yield; IR; cyclopropene absorption at 1820 and 995 cm$^{-1}$. Found: C, 68.52; H, 8.72%. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.62%. Titration with 0.1 N NaOH (phenolphthalene), 99.3%). The acid (III) gives a positive Halphen test.⁴⁾



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[2] W. Mahler, *J. Am. Chem. Soc.*, **84**, 4600 (1962).

[3] I. A. D'yakonov, *Zhur. Obshchei Khim.*, **29**, 3848 (1959); R. Breslow, H. Hoever and Hai won Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

[4] A. J. Deutschman and I. S. Klaus, *Anal. Chem.*, **32**, 1809 (1960).

III was esterified with the 7% boron trifluoride in methanol reagent and distilled (bp 88°C/35 mmHg). The methyl ester of III was treated with II again and saponified, as described above, to yield a white crystalline product (V) (mp 217°C (decomp.); 5% yield on the base of III. Found: C, 60.34; H, 7.37%. Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12%. Titration with 0.1 N NaOH (phenolphthalene), 99.5%).

V was esterified with the boron trifluoride in methanol reagent. The dimethyl ester (VI) was prepared as white crystals (mp 69—71°C. Found: C, 63.54; H, 8.04%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%. NMR ($CCl_4$) 8.99(T), 8.81(S), 7.94(Q), 6.33(S)$\tau$, relative areas 3 : 1 : 2 : 3).

V. p. c. analysis of VI shows just one peak under each of several condition.

No band characteristic of olefinic unsaturation appears in the infrared spectrum of V and VI. Bromine in carbon tetrachloride is not discharged with them.

The dimethyl ester (VI) in ethanol consumed one mole of hydrogen over 5% palladium on charcoal at room temperature and atmospheric pressure.

The bicyclobutanes, V and VI, decolorize immediatly a solution of potassium permanganate in ethanol and give a positive Tollens test.

The bicyclobutane V or VI has stereochemically a *trans*- and two *cis*-isomers, and it is expected that one of the two *cis*-free acids is transformed with ease into a cyclic anhydride.[5] But attempts for our sample V to get an anhydride were without definite result.

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[5] R. M. Beesley and J. F. Thorpe, *J. Chem. Soc.*, **1920**, 591.