Synthesis and *X*-Ray Crystal Structure of 1,5-Bis(acetoxymethyl)-tricyclo[2.1.0.$0^{2,5}$]pentan-3-one

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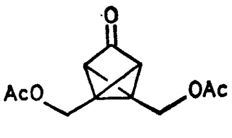
Summary 1,5-Bis(acetoxymethyl)tricyclo[2.1.0.$0^{2,5}$]pentan-3-one (**1**) has been synthesized from 1,2-bis(acetoxymethyl)-3-diazoacetylcyclopropene by dirhodium tetra-acetate-catalysed intramolecular addition of the diazoketone to the cyclopropene double bond; an *X*-ray crystal structure determination of (**1**) reveals an extremely short bridging carbon–carbon bond.

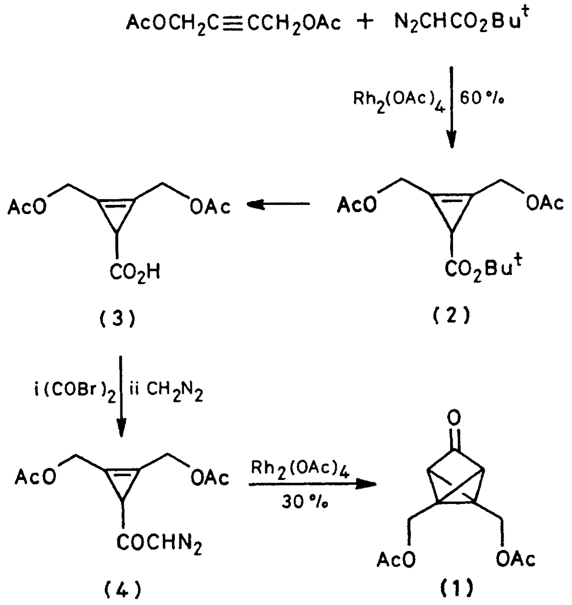
DURING our studies on the synthesis of molecules of theoretical interest, we required substantial amounts of the title compound (**1**). Although the corresponding 1,5-dimethyl-[1] and the 1,5-diphenyl-[2] derivatives were prepared some years ago, no further synthetic development of this highly strained condensed ring system has occurred in the meantime. There have been two problems. Whereas the parent but-2-yne reacts smoothly with ethyl diazoacetate,[1] the analogous reaction with 1,4-disubstituted butynes has, in our hands, proved unsuccessful with copper catalysts. In addition, early attempts[1] at the intramolecular closure of the cyclopropene diazoketone to the tricyclic ketone were hampered because the traditional copper catalysts available then gave only 1—2% yields of the desired tricyclic ketone.

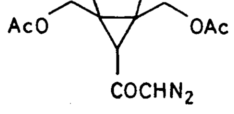


(**1**)

The advent of rhodium carboxylates and their use[3] in catalysing the addition of diazo-esters to multiple bonds ameliorates both difficulties.

Dirhodium(II) tetra-acetate-catalysed reaction of t-butyl diazoacetate with 1,4-diacetoxybut-2-yne yielded t-butyl 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylate (**2**) in 60% yield.† The t-butyl group was cleanly removed by treatment with trifluoroacetic acid and the resulting carboxylic acid (**3**) was converted into the acid bromide, treatment of which with ethereal diazomethane at − 78 °C for 65 h yielded the diazoketone (**4**).‡ The latter was then added at 55—60 °C to an ethanol-free chloroform solution of 0·006 equiv. of dirhodium tetra-acetate. Controlled nitrogen evolution was observed immediately. The tricyclic ketone diacetate (**1**) produced was isolated in 25—30% yield following chromatography on silica gel.





(**5**)

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† Approximately 2% of the crystalline *exo,exo*-di-t-butyl 1,3-bis-(acetoxymethyl)bicyclo[1.1.0]butane-2,4-dicarboxylate, m.p. 101·5—102 °C, the product of t-butyl diazoacetate addition to the double bond of (**2**), was isolated in the course of the chromatographic purification of (**2**).

‡ In contrast with the behaviour of 1,2-dimethylcyclopropene-3-carboxylic acid,[1] conventional formation of the diazoketone through the acid chloride and treatment with diazomethane at 0 °C was not successful. The product isolated under these conditions was the pyrazoline diazoketone (**5**). Apparently, the electron-withdrawing acetate groups tip the balance of reactivity sufficiently to cause addition of diazomethane to the double bond to be competitive with formation of the diazoketone. This is the reason for our use of the somewhat unorthodox procedure described above.

This is the first application of rhodium carboxylate catalysts to the preparation of the rare tricyclo[2.1.0.0^{2,5}]-pentanone system and to the intramolecular cycloaddition of a diazoketone to an olefin.[4] Formation of the tricyclic ketone (**1**) was observed using copper and copper(II) sulphate, but the rhodium catalyst was found to be superior.

The structure of the tricyclo[2.1.0.0^{2,5}]pentanone (**1**) has been established by X-ray diffraction (Figure).

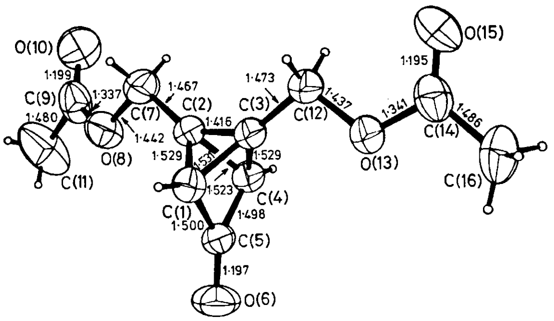

FIGURE. ORTEP drawing with bond lengths in Å of compound (**1**).

Crystal data: monoclinic, space group $P2_1/c$, $M = 224{\cdot}22$; $a = 6{\cdot}5497(5)$, $b = 12{\cdot}654(1)$, $c = 13{\cdot}887(2)$ Å; $\beta = 101{\cdot}902(8)°$; $U = 1126{\cdot}2$ Å^3; $Z = 4$; $D_c = 1{\cdot}32$ g cm^{-3}. The cell dimensions were determined by least squares from 63 high-order reflections ($2\theta > 42°$). 2711 Independent reflections were recorded on a Siemens AED, computer-controlled diffractometer for $\sin\theta/\lambda < 0{\cdot}664$ Å^{-1} with graphite-monochromated Mo-K_α radiation. 1086 reflections were treated as unobserved $\{F_o^4/[\sigma(F_o^2)]^2 < 7\}$.

The crystal structure was solved by direct methods with the program MULTAN.[5] After several least-squares refinement cycles in the full-matrix procedure with isotropic temperature parameters for the hydrogen atoms and anisotropic temperature parameters for the carbon and oxygen atoms we obtained a final R-value of 0·05 (excluding unobserved reflections) and 0·06 (unobserved reflections included) ($R = \Sigma|kF_o - |F_c||/\Sigma kF_o$). In the last refinement cycle 297 unobserved reflections were included ($|F_c| > kF_o$).§

The bridge bond in bicyclo[1.1.0]butane derivatives is a bent bond with substantial π-character.[6] At 1·416(2) Å the C(2)–C(3) bond is very short (Figure) in comparison with normal C(sp^3)–C(sp^3) bonds (1·54 Å) or with the bridge bond in bicyclo[1.1.0]butane itself (1·497 Å).[7] It has been shown[7] that the length of this bond in bicyclo[1.1.0]butane derivatives is dependent on the dihedral angle between the planes of the two cyclopropane rings, which has the small value of 95·7° in (**1**).

This research was generously supported by the National Science Foundation, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie.

(*Received, 22nd December* 1980; *Com.* 1354.)

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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