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INTRAMOLECULAR CYCLOADDITION OF CARBONYL YLIDES GENERATED FROM α-DIAZO KETONES

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Abstract—Two cases of intramolecular cycloaddition of carbonyl ylides, formed from the α-diazo-ketones **1** and **8**, to a C=C bond within the molecule are described. The structures of the products **4a** and **10** have been established from chemical and spectroscopic evidence and by single crystal X-ray crystallographic analysis of **6a** and **10**.

Recently, there has been a growing interest in the potential use of carbonyl ylides as 1,3-dipoles. Their cycloaddition to external olefinic, acetylenic and hetero multiple-bond dipolarophiles has been well demonstrated.[1] In various cycloaddition reactions intramolecular applications greatly extended the synthetic utility of the reaction. The intramolecular trapping of carbonyl ylides by multiple bonds has been reported, to our knowledge, in one case only (in which substituted oxiranes served as ylide precursors).[2] We now wish to describe our investigation and show that cyclic 5-membered carbonyl ylides, produced from diazo-ketones as described previously,[3] are capable of undergoing intramolecular cycloaddition with a C=C bond suitably located within the molecule.

Scheme 1 shows the transition-metal catalyzed decomposition of diazo-ketone **1**. The $Pd_2Cl_2(C_3H_5)_2$ complex induced preferential formation of the steroisomeric bicycloheptanones **2a** and **2b** together with minor amounts of a ketonic byproduct (route a). However, this ketone turned out to be the major product when the Pd-complex was replaced by rhodium acetate as catalyst. Its structure, **4a**, was determined as follows.

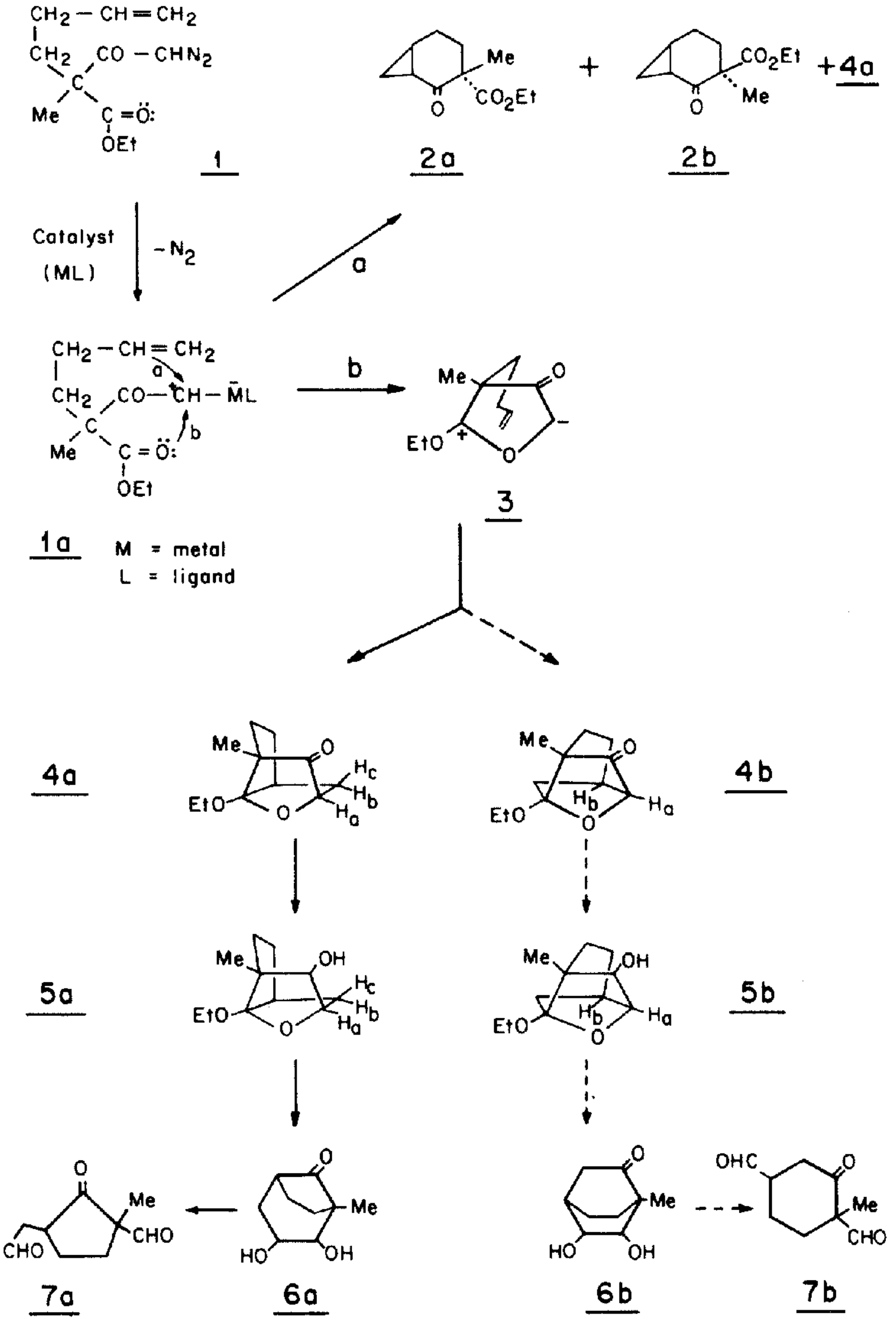
The IR spectrum of the compound showed no ester CO absorption, although the presence of an Et group in the molecule was obvious from the ^{1}H NMR spectrum. Furthermore, there was no spectral evidence for the presence of a cyclopropyl or a butenyl group in the molecule. This together with the observed molecular weight (from high resolution MS) suggests that the reaction course involved an intramolecular cyclization step between the ketocarbenoid and the O atom of the ester carbonyl to give a resonance stabilized 5-membered carbonyl ylide intermediate **3** (route b).[4] The ylide dipole could then be trapped internally by the olefinic double bond to give one of the two isomers **4a** or **4b**, depending upon the conformation of the butenyl chain. The single ketonic CO absorption observed at 1760 cm^{-1} in the spectrum of the compound and characteristic for the tetrahydrofuran-3-one ring system[5] would support this reaction pathway.

The compound was reduced with $NaBH_4$ to the corresponding **5a** or **5b**, followed by opening of the ketal bond with mild acid treatment to give the keto-diol **6a** or **6b**. A small sample of this diol was then oxidized with $Pb(OAc)_4$ to the keto dialdehyde **7a** or **7b**. Unfortunately, the ^{1}H NMR data of the parent tricyclic ketone **4** and its transformation products were insufficient for unambiguous differentiation between the alternative structures of the two series, a and **b**. In ketone **4**, for example, H_a appeared as a doublet (δ 4.28; J 6 Hz) as would be expected from structure **4b**. On the other hand, examination of Dreiding models of **4a** showed the dihedral angle H_a–H_c to be 80° and thus predicted that no coupling between these protons would be observed. Taking this consideration into account, structure **4a** could also justify the doublet for H_a. More decisive data were furnished by IR spectroscopy. The carbonyl absorption at 1745 and 1750 cm^{-1} found in the spectra of compounds **6** and **7** are suggestive of a 5-membered ring ketone, present only in the a series.

Finally, X-ray analysis confirmed the structure **6a** for the crystalline keto-diol and thus verified the other structures in the a series. **4a**, therefore, represents a product, formed by intramolecular cycloaddition of a carbonyl ylide with a C=C bond, the product again depending on the catalyst used in the decomposition of the α-diazo ketones.[3,6]

Next, the catalytic decomposition of the *bis* diazoketone **8** was investigated. $Pd_2Cl_2(C_2H_5)_2$ catalyst led only to an extremely complex mixture of products, mostly polymers. On the other hand, decomposition in the presence of $(Et)_3P$. CuCl or $Rh_2(OAc)_4$ gave a much cleaner reaction. The isolated product, a mono-ketone, showed a single CO absorption at 1765 cm^{-1}, characteristic of a tetrahydro-furan-3-one system, present also in the tricylic system **4a**. Further similarity between the two compounds was found in their ^{1}H NMR spectra. The characteristic low-field, one-proton resonance, analogous to the H_a-resonance in **4a**, appeared in the spectrum of the new monoketone at δ 4.17 as an ill-resolved A part of an ABC system. NMR spectroscopy also showed the presence of a cyclopropyl ring in the molecule but no vinylic protons were detected. Based upon these spectral properties, structural similarity was expected between **4a** and the new monoketone. Indeed, by X-ray structural determination the monoketone was found to have the pentacyclic structure **10** which consists of the tricyclic skeleton of **4a** and also includes an oxa[4.3.3]propellane moiety.

The formation of **10** (Scheme 2) represents a unique case where two diazo-ketone moieties in the same molecule under the influence of the same catalyst react in different ways: one by addition to the double bond to give intermediate **9a** (route a) and the other by carbonyl ylide formation to give the second intermediate **9b** (route b). Intramolecular trapping of this ylide affords the product **10**.



Scheme 1.

The X-ray structure of **6a**

Atom labelling diagram of **6a** is depicted in Fig. 1.† ORTEP[10] stereoscopic view of the molecular packing is shown in Fig. 2. A list of bond lengths and angles is presented in Table 1.

The 6-membered ring of the bicyclic skeleton has a distorted chair confomation with unusual folding along the C(1)–C(5) vector and flattening along the C(2)–C(4) vector. However the ring still maintains a point group symmetry C_s where the mirror plane bisects atoms C(3) and C(8). A list of torsion angles of the six membered ring is shown in Table 2.

Both folding and flattening effects are ascribed to the constraints imposed by the bridging carbons on the 6-membered ring. The formation of a 5-membered ring as a part of the bicycloheptane system, introduces unusual folding along the C(1)–C(5) vector together with a remarkable closure of the angle C(1)–C(8)–C(5), 104.2°. This angle closure results in a corresponding symmetrical opening of the angles O(1)–C(8)–C(1), 127.0 and O(1)–

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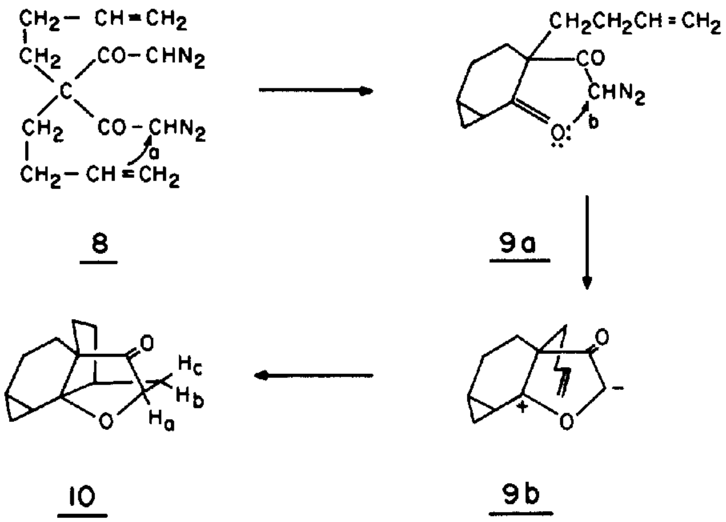
† Hydrogens are omitted for clarity. However, their assignment follows the labeling scheme of carbons to which they are attached.



Scheme 2.

C(8)–C(5), 128.8 in order to maintain the group of atoms C(1), C(8), C(5) and O(1) planar. The flattening of the second half of the molecule can be described in terms of repulsions between the hydrogens HC(62) and HC(72) attached to the bridging carbons and the axial hydrogen attached to C(3). The two OH groups are both equatorial. The 5-membered ring defined by atoms C(1), C(7), C(6), C(5) and C(8) has an envelope conformation with folding along the line joining C(1) and C(5).

The crystal structure as shown in Fig. 2, contains one water molecule of crystallization per molecule of **6a**. Both organic and water molecules are held together mainly by H-bonds of two types: the first type of bonds is formed between a pair of **6a** molecules through their

Table 1. Bondlengths in Å and angles in deg. for **6a** with e.s.d's in parentheses

C(1)	---C(2)		1.548(8)	C(2)	---HC(2)		0.99(4)
C(1)	---C(7)		1.545(7)	C(3)	---HC(3)		0.98(5)
C(1)	---C(8)		1.524(8)	C(4)	---HC(41)		0.89(4)
C(1)	---C(9)		1.523(9)	C(4)	---HC(42)		1.11(7)
C(2)	---C(3)		1.505(8)	C(5)	---HC(5)		0.89(4)
C(2)	---O(2)		1.420(7)	C(6)	---HC(61)		0.99(6)
C(3)	---C(4)		1.533(8)	C(6)	---HC(62)		0.92(8)
C(3)	---O(3)		1.436(7)	C(7)	---HC(71)		0.94(5)
C(4)	---C(5)		1.534(9)	C(7)	---HC(72)		1.02(5)
C(5)	---C(6)		1.52(1)	C(9)	---HC(91)		1.03(5)
C(5)	---C(8)		1.505(8)	C(9)	---HC(92)		1.0(1)
C(6)	---C(7)		1.55(1)	C(9)	---HC(93)		1.0(1)
C(8)	---O(1)		1.197(8)	C(3)	---HC(3)		0.87(8)
C(2)	-C(1)	-C(7)	111.1(4)	C(4)	-C(5)	-C(8)	106.6(5)
C(2)	-C(1)	-C(8)	103.7(4)	C(6)	-C(5)	-C(8)	103.7(5)
C(2)	-C(1)	-C(9)	112.2(5)	C(5)	-C(6)	-C(7)	104.1(6)
C(7)	-C(1)	-C(8)	100.4(4)	C(1)	-C(7)	-C(6)	107.7(5)
C(7)	-C(1)	-C(9)	114.5(5)	C(1)	-C(8)	-C(5)	104.2(4)
C(8)	-C(1)	-C(9)	113.8(4)	C(1)	-C(8)	-O(1)	127.0(5)
C(1)	-C(2)	-C(3)	112.8(5)	C(5)	-C(8)	-O(1)	128.8(6)
C(1)	-C(2)	-O(2)	109.8(4)	HC(41)	-C(4)	-HC(42)	104(4)
C(3)	-C(2)	-O(2)	108.7(4)	HC(61)	-C(6)	-HC(62)	103(5)
C(2)	-C(3)	-C(4)	111.9(4)	HC(71)	-C(7)	-HC(72)	107(4)
C(2)	-C(3)	-O(3)	109.6(5)	HC(91)	-C(9)	-HC(92)	105(7)
C(4)	-C(3)	-O(3)	109.2(4)	HC(91)	-C(9)	-HC(93)	115(6)
C(3)	-C(4)	-C(5)	110.3(5)	HC(92)	-C(9)	-HC(93)	104(8)
C(4)	-C(5)	-C(6)	112.6(5)				

Table 2. Torsion angles for the six membered ring of **6a** in deg.

C(8) - C(1) - C(2) - C(3) = 61.2

C(1) - C(2) - C(3) - C(4) = -49.1

C(2) - C(3) - C(4) - C(5) = 47.6

C(3) - C(4) - C(5) - C(8) = -60.8

C(4) - C(5) - C(8) - C(1) = 74.8

C(5) - C(8) - C(1) - C(2) = -72.9

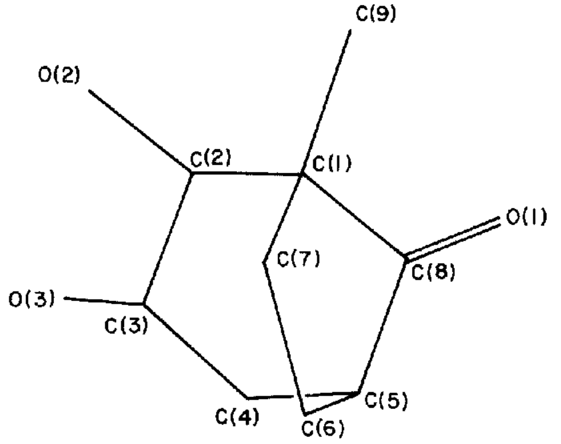


Fig. 1. Atom labelling diagram of **6a**.

OH groups. These pairs can be described as hydrogen bonded "dimers" formed around inversion centers at (1/2, 0, 0) and (1/2, 1/2, 1/2). Their O-H--- O distances are 2.751 Å. The second type of bonds is formed between bridging water molecules and the hydroxyl groups of different **6a** "dimers".

The X-ray structure of 10

Atom labelling diagram and ORTEP[1] stereopair of **10** are shown in Figs. 3 and 4 respectively. A list of bondlengths and angles is presented in Table 3.

The molecule is a pentacyclic system which has an oxa[4.3.3] propellane and a bicyclo[4.1.0] heptane moieties. Within the propellane moiety, a third 5-membered ring is formed between the other two 5-membered rings at C(8) and C(10) via the bridging atom C(9). The bicycloheptane moiety is formed by attachment of a cyclopropane ring to the 6-membered ring at atoms C(4) and C(6).

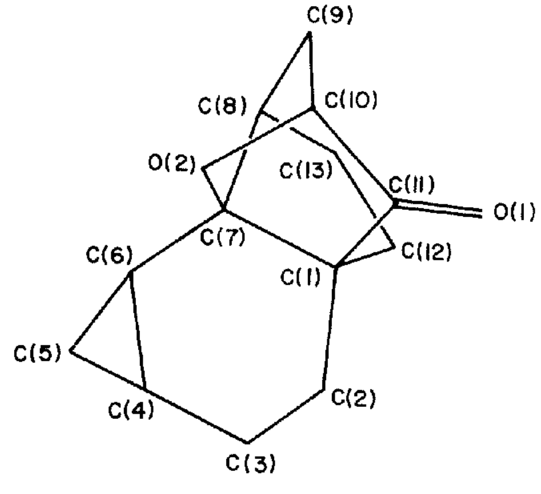


Fig. 3. Atom labelling diagram of **10**.

The 6-membered ring as a part of a bicyclo[4.1.0] heptane system, has the expected "half-chair" conformation. The torsion angle C(3)-C(4)-C(6)-C(7), −2.3° and the bond angles C(3)-C(4)-C(6), 121.1°, C(4)-C(6)-C(7), 119.4°, provide a geometry comparable with that of a group where a double bond replaces the cyclopropane ring at C(4)-C(6).[11] The apex atom C(5) of the cyclopropane ring is disposed on the same side of the 6-membered ring with respect to the heterocyclic oxygen O(2). This arrangement brings HC(52) to a close contact with O(2) (HC(52) ---- O(2) = 2.49 Å). The heterocyclic 5-membered rings defined by atoms C(1), C(7), O(2), C(10), C(11) and C(7), C(8), C(9), C(10), O(2) both have an envelope conformation with folding along the line joining C(7) and C(10). However, the third ring defined by atoms C(1), C(7), C(8), C(13), C(12) has a twist envelope conformation with a torsion angle of 6.4° at the C(12)-C(13) bond. The twisting is due to some strain imposed on this ring.

EXPERIMENTAL

IR spectra were determined for solns in CHCl$_3$ unless otherwise stated, with a Perkin-Elmer 237 or 257 spectrophotometer. NMR spectra were recorded on a Varian A-60 or T-60 spectrometer for solns in CDCl$_3$ unless otherwise stated, with Me$_4$Si as internal reference. Glc was carried out on a Varian Aerograph 90-P gas chromatograph (0.25 in × 2 m column packed with 3% Se-30 on 100-120 mesh GasChrom Q: column A) and on a Packard 7300 gas chromatograph (3/8 in. × 3 m column packed with 15% DEGS on 60-80 mesh Chromosorb W: column B or 1/8 in. × 1.8 m column packed with 15% DEGS on 60-80 mesh Chromosorb W: column C). M.ps and b.ps are uncorrected.

Ethyl 2-(but-3-enyl)-4-diazo-2-methylacetoacetate 1

Diethyl but-3-enylmalonate[7] (42.8 g, 0.199 mol) was added dropwise, with stirring, to a suspension of NaH(4.8 g, 0.2 mol) in

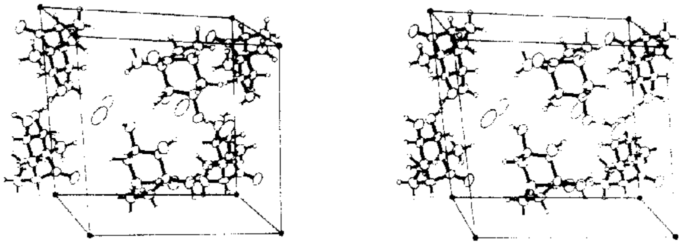


Fig. 2. ORTEP stereodrawing of the structure of **6a**, as viewed approximately along b; c and a are set as the horizontal and vertical directions, and the origin is placed at the rear bottom left corner of the unit cell.

Table 3. Bondlengths in Å and angles in deg. for 10 with e.s.d's in parentheses

C(1) ---C(2)	1.548(8)	C(12) ---C(13)	1.51(1)
C(1) ---C(7)	1.539(8)	C(2) ---H(21)	0.98(4)
C(1) ---C(11)	1.535(7)	C(2) ---H(22)	0.94(6)
C(1) ---C(12)	1.549(8)	C(3) ---H(31)	1.04(8)
C(2) ---C(3)	1.517(8)	C(3) ---H(32)	1.10(7)
C(3) ---C(4)	1.484(9)	C(4) ---H(4)	0.91(6)
C(4) ---C(5)	1.485(9)	C(5) ---H(51)	0.93(6)
C(4) ---C(6)	1.505(8)	C(5) ---H(52)	1.11(5)
C(5) ---C(6)	1.499(8)	C(6) ---H(6)	1.04(7)
C(6) ---C(7)	1.507(7)	C(8) ---H(8)	1.01(8)
C(7) ---C(8)	1.539(8)	C(9) ---H(91)	0.81(9)
C(7) ---C(2)	1.447(6)	C(9) ---H(92)	1.07(8)
C(8) ---C(9)	1.54(1)	C(10) ---H(10)	0.86(8)
C(8) ---C(13)	1.51(1)	C(12) ---H1(12)	1.07(5)
C(9) ---C(10)	1.56(1)	C(12) ---H2(12)	1.02(6)
C(10) ---C(11)	1.53(1)	C(13) ---H1(13)	0.97(8)
C(10) ---C(2)	1.426(7)	C(13) ---H2(13)	1.0(1)
C(11) ---C(1)	1.190(7)		

C(2) -C(1) -C(7)	112.7(4)	C(8) -C(7) -O(2)	105.2(4)
C(2) -C(1) -C(11)	112.2(4)	C(7) -C(8) -C(9)	102.0(5)
C(2) -C(1) -C(12)	115.3(4)	C(7) -C(8) -C(13)	104.7(5)
C(7) -C(1) -C(11)	100.3(4)	C(9) -C(8) -C(13)	115.1(5)
C(7) -C(1) -C(12)	106.4(4)	C(8) -C(9) -C(10)	101.1(5)
C(11) -C(1) -C(12)	108.8(4)	C(9) -C(10) -C(11)	105.5(5)
C(1) -C(2) -C(3)	111.3(4)	C(9) -C(10) -C(2)	103.2(5)
C(2) -C(3) -C(4)	114.2(5)	C(11) -C(10) -C(2)	101.9(5)
C(3) -C(4) -C(5)	121.4(5)	C(1) -C(11) -C(10)	103.3(5)
C(3) -C(4) -C(6)	121.1(5)	C(1) -C(11) -O(1)	128.1(5)
C(5) -C(4) -C(6)	60.2(4)	C(10) -C(11) -C(1)	128.5(5)
C(4) -C(5) -C(6)	60.6(4)	C(1) -C(12) -C(13)	104.5(5)
C(4) -C(6) -C(5)	59.3(4)	C(8) -C(13) -C(12)	107.8(6)
C(4) -C(6) -C(7)	119.4(5)	C(7) -O(2) -C(10)	97.7(4)
C(5) -C(6) -C(7)	119.3(5)	H(21) -C(2) -H(22)	103(4)
C(1) -C(7) -C(6)	116.4(4)	H(31) -C(3) -H(32)	96(5)
C(1) -C(7) -C(8)	100.5(4)	H(51) -C(5) -H(52)	116(4)
C(1) -C(7) -C(2)	103.5(3)	H(91) -C(9) -H(92)	103(7)
C(6) -C(7) -C(8)	117.1(4)	H1(12)-C(12) -H2(12)	99(4)
C(6) -C(7) -O(2)	112.5(4)	H1(13)-C(13) -H2(13)	114(7)

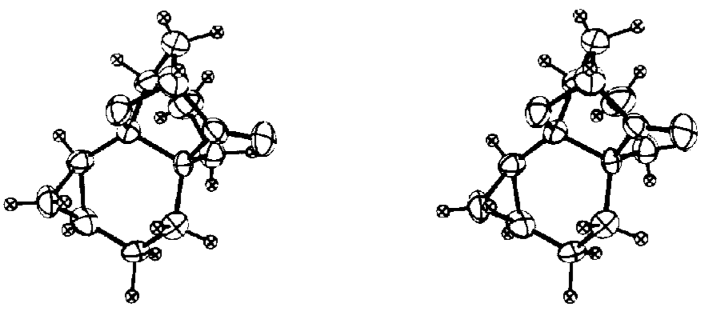


Fig. 4. ORTEP stereopair of 10. Atoms are shown with 50% probability ellipsoids.

dry DMF (100 ml). Stirring was continued until all the hydride had reacted and to the mixture MeI(30 g, 0.21 mol) was added dropwise. The reaction is exothermic. After addition was complete, stirring was continued for 0.5 hr at room temp., then for 2 hr at 70–80°. The end of the reaction was indicated by reaching to pH 7. The mixture was then poured into cold water and extracted with ether. The extract was washed with water (3 × 100 ml), dried (Na_2SO_4) and evaporated. Distillation of the oily residue gave pure *diethyl* (*but*-3-*enyl*) *methylmalonate* (34 g, 75%), b.p. 120/11 mmHg (lit.[8] 123–127°/17 mmHg); IR: 1725 (C=0) and 1640 cm^{-1} ($CH_2{=}CH$); ^1H NMR: δ 1.27 (t, 6H, $CO_2CH_2C\underline{H}_3$), 1.44 (s, 3H, $CH_3{-}C$), 1.95–2.10 (m, 4H, $C\underline{H}_2{-}C\underline{H}_2$), 4.23 (q, 4H, $CO_2C\underline{H}_2CH_3$), 4.83–5.27 (m, 2H, $C\underline{H}_2{=}CH$), and 5.40–6.18 ppm (m, 1H, $CH_2{=}\underline{C}H$).

A cooled soln of KOH (2.8 g, 50 mmol) in anhyd EtOH (40 ml) was added to the foregoing ester (11.4 g, 50 mmol) in anhyd EtOH (30 ml) and the mixture was kept at room temp. overnight. The EtOH was then removed (water pump), water was added, and the cooled soln was washed twice with ether in order to recover starting material. The aqueous layer was then acidified to pH 1 with cold 10% HCl and extracted several times with ether. The combined ether extracts were washed with water, dried (Na_2SO_4) and evaporated to give the crude *monoethyl* (*but*-3-*enyl*)*methylmalonic acid* (8.7 g, 87%); IR: 3000–3600 (0H) and 1724 cm^{-1} (C=O); ^1H NMR: δ 1.21 (t, 3H, $CO_2CH_2C\underline{H}_3$), 1.40 (s, 3H, $CH_3{-}C$), 1.88–2.06 (m, 4H, $C\underline{H}_2{-}C\underline{H}_2$), 4.17 (q, 2H, $CO_2C\underline{H}_2CH_3$), 4.80–5.20 (m, 2H, $C\underline{H}_2{=}CH$), 5.45–6.13 (m, 1H, $CH_2{=}C\underline{H}$), and 9.4 ppm (s, 1H, COOH).

To a stirred and ice-cooled mixture of the foregoing monoacid (8.6 g, 43 mmol), dry benzene (40 ml) and anhydrous pyridine (0.4 ml) a soln of freshly distilled oxalyl chloride (10 ml, 116 mmol) in dry benzene (20 ml) was added dropwise. The icebath was then removed, the mixture was slowly heated to 60° and kept at this temp. for 2 hr. The excess of oxalyl chloride and benzene were removed under reduced pressure and the residue was washed several times with dry ether. From the combined ethereal extracts *ethyl* (*but*-3-*enyl*)*methylmalonyl chloride* was isolated by distillation at 40–44°/0.05 mmHg (8.5 g, 90%). IR(CCl_4): 1748 (ester C=O), 1800 (COCl) and 1645 cm^{-1} ($CH_2{=}CH$); ^1H NMR (CCl_4): δ 1.33 (t, 3H, $CO_2CH_2C\underline{H}_3$), 1.53 (s, 3H, $CH_3{-}C$), 2.04 (m, 4H, $C\underline{H}_2{-}C\underline{H}_2$), 4.27 (q, 2H, $CO_2C\underline{H}_2CH_3$), 4.88–5.10 (m, 2H, $C\underline{H}_2{=}CH$), and 5.48–6.21 ppm (m, 1H, $CH_2{=}C\underline{H}$).

A soln of the acid chloride (8.3 g, 38 mmol) in dry ether (200 ml) was added dropwise with swirling to ice-cold ethereal diazomethane [from nitrosomethylurea (23 g)[9]]. After 2 hr the soln was filtered and the solvent was removed under reduced pressure. To the residue dry ether was added and insoluble material was filtered off. Evaporation of the ether gave crude, oily *diazo-ketone* **1** (8.5 g). IR: 1645, 1728 and 2110 cm^{-1}. ^1H NMR: δ 1.28 (t, 3H, $CO_2CH_2C\underline{H}_3$), 1.40 (s, 3H, $CH_3{-}C$), 1.89–2.14 (m, 4H, $C\underline{H}_2{-}C\underline{H}_2$), 4.21 (q, 2H, $CO_2C\underline{H}_2CH_3$), 4.86–5.26 (m, 2H, $C\underline{H}_2{=}CH$), 5.50 (s, 1H, $COCHN_2$), and 5.44–6.27 ppm (m, 1H, $CH_2{=}C\underline{H}$).

The oily diazo-ketone was characterized by conversion into the hydrazinotriphenylphosphine derivative. To a soln of $(C_6H_5)_3P$ (3.28 g, 12.5 mmol) in dry ether (10 ml) the diazo-ketone **1** (2.8 g, 12.5 mmol) in dry ether (25 ml) was added, followed by light petroleum (b.p. 40–60°, 5 ml). The mixture was kept in the refrigerator and the crystalline precipitate was filtered off (4.75 g, 78%). Recrystallization from acetonitrile gave pure *hydrazinotriphenylphosphine derivative*, m.p. 120–123° (dec.) IR(KBr): 1640, 1725 cm^{-1}; ^1H NMR: δ 0.92 (t, 3H, $CO_2CH_2C\underline{H}_3$), 1.29 (s, 3H, $CH_3{-}C$), 1.79–2.00 (m, 4H, $C\underline{H}_2{-}C\underline{H}_2$), 3.44 (q, 2H, $CO_2C\underline{H}_2CH_3$), 4.70–5.12 (m, 2H, $C\underline{H}_2{=}CH$), 5.37–6.05 (m, 1H, $CH_2{=}C\underline{H}$), and 7.25–7.97 ppm (m, 16H, Ph, $COCHN_2$) (Found: C, 71.42; H, 6.44; N, 5.71. $C_{29}H_{31}N_2O_3P$ requires: C, 71.59; H, 6.42; N, 5.76%).

Decomposition of the diazo-ketone 1 *with bis*(*chloro-π-allylpalladium*)

A cold soln of crude **1** (2.0 g, 8.93 mmol) in dry benzene (120 ml) was added dropwise during *ca.* 5 hr to a stirred soln of the π-allylic Pd-complex (0.04 g, 0.11 mmol) in benzene (120 ml) at 5–10°. Stirring was then continued, if necessary, until complete decomposition was indicated by disappearance of the IR band at 2110 cm^{-1}. The soln was then filtered and concentrated. Bulk-to-bulk distillation of the residue (1.8 g) at 85° (bath temp.)/0.03 mmHg gave a mixture (0.95 g) of the stereoisomeric *ethyl* 3-*methyl*-2-*oxobicyclo*[4.1.0]*heptane*-3-*carboxylates* **2a** and **2b** and the tricyclic ketone **4a**. Their relative yields, 26, 17 and 3.5%, respectively, were determined by glc. Compounds **2a** and **2b** were separated by preparative glc on column B at 175°. (**2a** had the shorter retention time). The analytical samples, prepared by further purification on column C, had the following data:

Compound **2a** IR: 1685 and 1725 cm^{-1}; ^1H NMR: δ 0.88–1.17 (m, 2H, cyclopropyl-CH_2), 1.27 (t, 3H, $CO_2CH_2C\underline{H}_3$), 1.30 (s, 3H, $CH_3{-}C$), 1.48–2.25 (m, 6H, $CH_2{-}CH_2$), and cyclopropyl protons), and 4.19 ppm (q, 2H, $CO_2C\underline{H}_2CH_3$) (Found: C, 67.07; H, 8.04; M^+ 196. $C_{11}H_{16}0_3$ requires: C, 67.32, H, 8.22%, M 196.2).

Compound **2b** IR: 1690 and 1742 cm^{-1}; ^1H NMR: δ 0.88–1.58 (m, 3H, cyclopropyl protons), 1.23 (t, 3H, $CO_2CH_2C\underline{H}_3$), 1.33 (s, 3H, $CH_3{-}C$), 1.61–2.47 (m, 5H, $CH_2{-}CH_2$ and cyclopropyl CHCO), and 4.18 ppm (q, 2H, $CO_2C\underline{H}_2CH_3$). (Found C, 66.99; H, 8.02; M^+ 196. $C_{11}H_{16}O_3$ requires: C, 67.32, H, 8.22%, M 196.2).

Decomposition of the diazo-ketone 1 *with rhodium acetate*

Preparation of 8 - *ethoxy* - 1 - *methyl* - 9 - *oxatricyclo*[3.2.1.1^{3,8}] *nonan*-2-*one* **4a**. Freshly prepared **1** (5.6 g, 25 mmol) in dry ether (300 ml) was added dropwise during *ca.* 3 hr to a stirred suspension of $Rh_2(OAc)_4$ (0.08 g, 0.181 mmol) in dry ether (600 ml) at room temp. Stirring was then continued at room temp. until complete decomposition of the diazo-ketone was shown by the disappearance of the IR band at 2110 cm^{-1} (24–40 hr). The soln was filtered, concentrated and the oily residue (5.0 g) was distilled. Two fractions, boiling at 60–65°/0.2 mm Hg and at 75–85°/0.2 mmHg were collected. The low-boiling fraction (1.72 g, 35%) was identified by glc as pure **4a** and the second fraction was found to be a mixture of **2a** and **2b** (together 1.29 g, 26%) and of **4a** (0.41 g, 8%). An analytical sample of **4a** was prepared by glc on column A at 157° (helium flow rate 40 ml min^{-1}, t_R 233 sec). IR: 1760 cm^{-1}, ^1H NMR: δ 1.08 (s, 3H, $CH_3{-}C$), 1.29 (t, 3H, $OCH_2C\underline{H}_3$), 1.6–2.84 (m, 7H, ring), 3.84 (m, 2H, $OC\underline{H}_2CH_3$), and 4.28 ppm (d, 1H, OCHCO). (Found: C, 66.95; H, 8.45; M^+ 196. $C_{11}H_{16}O_3$ requires: C, 67.32; H, 8.22%, M 196.2).

Reduction of 4a

Preparation of 8-*ethoxy*-1-*methyl*-9-*oxatricyclo*[3.2.1.1^{3,8}]-*nonan*-2-*ol* **5a**. To a magnetically stirred cold soln of **4a** (1.37 g, 7 mmol) in MeOH (60 ml), $NaBH_4$ (0.76 g, 20 mmol) was added in small portions. The mixture was left overnight at room temp., the solvent was removed, water was added and again concentrated. Extraction with ether and the usual workup gave **5a** as an oil (1.30 g, 94%) and this was used in the next step without further purification. The analytical sample was obtained by glc on column A at 157° (helium flow rate of 40 ml min^{-1}, t_R 380 sec); IR: 3440 and 3595 cm^{-1}. ^1H NMR: δ 1.01 (s, 3H, $CH_3{-}C$), 1.24 (t, 3H, $OCH_2C\underline{H}_3$), 1.45–2.60 (m, 8H, OH and ring), 3.75 (m, 3H, $OC\underline{H}_2CH_3$ and $C\underline{H}OH$), and 4.10 ppm (t, 1H, $OC\underline{H}CHOH$). (Found: M^+, 198.1258. $C_{11}H_{18}O_3$ requires: M, 198.1256).

2,3-*Dihydroxy*-1-*methylbicyclo*[3.2.1]*octan*-8-*one* 6a

To a soln of **5a** (1.20 g, 6 mmol) in ether (70 ml) 10% HCl aq (0.5 ml) was added and the mixture was magnetically stirred for 1 hr. The ether was then removed, acetone was added and after stirring for a few min the solvent was evaporated under reduced pressure. The oily residue solidified on repeated trituration with light petroleum (b.p. 40–60°) in the cold (1.0 g, 98%) and was purified by crystallization from wet cyclohexane to give **6a**, m.p. 69°; IR: 1745, 3425, 3575 and 3665 cm^{-1}; ^1H NMR: δ 1.07 (s, 3H, CH_3-), 1.24–2.55 (m, 7H, ring), 3.28 (d, J = 9 Hz, 1H, $CH_3{-}C{-}C\underline{H}OH$), 3.45 (s, 2H, OH) and 3.96 ppm (m, 1H, $CH_2{-}C\underline{H}(OH){-}CHOH$). (Found: M^+, 170.0947. $C_9H_{14}O_3$, requires: M, 170.0943).

A small sample of **6a** (0.17 g) in dry benzene (20 ml) was oxidized with $Pb(OAc)_4$ (0.5 g) by stirring for 2 hr. After decomposition with water and the usual workup, the spectral properties of the oily *dialdehyde* **7a** (0.15 g, 90%) were investigated; IR: 1725 (aldehyde C=O), 1750 (ketone C=O) and 2730 cm^{-1}; ^1H

NMR: δ 1.33 (s, 3H, CH_3), 9.44 (s, 1H, CHO) and 9.75 ppm (s, 1H, CHO); M^+, 168. $C_9H_{12}O_3$ requires M, 168.19.

Diethyl bis-(but-3-enylmalonate

Diethyl molonate (60 g, 0.37 mol) was added dropwise, with stirring to a suspension of NaH (9.0 g, 0.375 mmol) in dry DMF (200 ml). Stirring was continued until all the hydride had reacted and to the mixture 4-bromo-1-butene (51 g, 0.378 mol) was added dropwise. The reaction is exothermic. After addition was complete, the soln was stirred for 0.5 hr at room temp., then NaH (9.0 g, 0.375 mol) was added in portions, followed by 4-bromo-1-butene (51 g, 0.378 mol).† After being stirred at 80° for 2 hr, the mixture was poured into cold water and extracted with ether. The extract was washed with water (3 × 100 ml), dried (Na_2SO_4) and evaporated. Distillation of the oily residue gave pure ester (80 g, 80%), b.p. 140/11 mm Hg. IR: 1730 (ester C=O) and 1645 cm^{-1} (CH_2=CH); ^1H NMR: δ 1.25 (t, 6H, $CO_2CH_2C\underline{H}_3$), 1.95 (d, 8H, $C\underline{H}_2$-$C\underline{H}_2$), 4.13 (q, 4H, $CO_2C\underline{H}_2CH_3$), 4.80–5.17 (m, 4H, $C\underline{H}_2$=CH), and 5.45–6.18 ppm (m, 2H, CH_2=C$\underline{H}$) (Found: C, 67.46; H, 9.08; O, 23.67. $C_{15}H_{24}O_4$ requires C, 67.13; H, 9.02; 0.23.85%).

Bis-(but-3-enyl)malonic acid

To a mixture of aqueous KOH (36 g in 54 ml) and the foregoing ester (43 g, 0.16 mol), EtOH was added until a homogeneous soln was obtained. The mixture was refluxed for 4 hr, EtOH was removed under reduced pressure, and the cooled soln was washed with ether. The alkaline layer was acidified with 10% HCl to pH 1, saturated with NaCl, and extracted several times with ether. The combined extracts were dried (Na_2SO_4) and evaporated to give the crude product (27 g, 76%), m.p. 120–125°. Recrystallization from cyclohexane afforded the pure *acid*, m.p. 126°. ^1H NMR: δ 2.07 (d, 8H, $C\underline{H}_2$-$C\underline{H}_2$), 4.92–5.27 (m, 4H, $C\underline{H}_2$=CH), 5.50–6.17 (m, 2H, CH_2=C$\underline{H}$) and 11.8 ppm (s, 2H, COOH). (Found: C, 62.26; H, 7.55. $C_{11}H_{16}O_4$ requires C, 62.25; H, 7.60%).

3,3-Bis-(but-3-enyl)-1,5-bisdiazopentane-2,4-dione **8**

This was obtained from *bis*-(but-3-enyl)malonic acid (6.3 g, 29 mmol) as described for **1**. The intermediate *bis*-(but-3-enyl) malonyl chloride (IR in CCl_4: 1790 cm^{-1}) was characterized as the *dianilide*, m.p. 196° (from benzene). (Found: C, 76.03; H, 7.01; N, 8.06; O, 8.99. $C_{23}H_{26}N_2O_2$ requires C, 76.21; H, 7.23; N, 7.73; O, 8.83%).

The *bisdiazo-ketone* was obtained as a solid (5.8 g; 75%), m.p. 90° (from ether). IR: 2110 and 1620 cm^{-1}; ^1H NMR: δ 1.95 (d, 8H, $C\underline{H}_2$-$C\underline{H}_2$), 4.87–5.32 (m, 4H, $C\underline{H}_2$=CH), 5.53 (s, 2H, CHN_2) and 5.50–6.18 ppm (m, 2H, CH_2=C$\underline{H}$). (Found: C, 59.68; H, 6.04. $C_{13}H_{16}N_4O_2$ requires C, 59.98; H, 6.20%).

Catalytic decomposition of the bis-diazo-ketone **8**

A cold soln of the crude **8** (10 g, 38 mmol) in dry benzene (500 ml) was added dropwise during *ca.* 5 hr to a stirred soln of $(EtO)_3PCuCl$ complex (0.5 g, 1.88 mmol) in benzene (500 ml) under N_2. Complete decomposition was indicated by the disappearance of the IR band at 2110 cm^{-1}. The soln was then filtered and concentrated, and the residue was purified by column chromatography on Florisil (60–100 mesh). Column was prepared in light petroleum (b.p. 40–60°) and elution was started with the same solvent. The polarity of the eluent was gradually raised by addition of benzene.‡ Light petroleum-benzene (8 : 2) eluted **10** (2.82 g, 36%). IR: 1765 cm^{-1}; UV: λ_{max} (MeOH)222(ε 84), and 309 (ε 24); ^1H NMR: δ 0.53–2.48 (m, 15H, ring protons) and 4.17 ppm (m, 1H, OCHCO) (Found: C, 76.26; H, 7.97. $C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%).

X-ray crystallographic data and structure analyses of **6a** *and* **10**

Transparent prismatic crystals of both compounds were grown from cyclohexane. Accurate cell parameters were obtained from 25 carefully centered reflections. No measured density for **6a** is available since the crystals are unstable in various suspension liquids. Crystal density of **10** was measured in Nessler's solution. Crystallographic data of **6a** and **10** are presented as follows:

	6a	**10**
Formula	$C_9H_{14}O_3 \cdot H_2O$	$C_{13}H_{16}O_2$
F.W.	188.2	204.3
F(000)	408	440
Lattice	monoclinic	orthorhombic
a	12.040(6)	15.897(6)
b	6.727(5)	10.104(6)
c	12.522(6) Å	6.429(5) Å
β	100.99(5)°	—
V	995.6 Å^3	1032.7 Å^3
Space group	$p2_1/c$ (No. 14)	$p2_12_12_1$(No. 19)
D_m	—	1.313 g cm^{-3}
D_c	1.256 g cm^{-3}	1.314 g cm^{-3}
Number of unique reflections	1334	801
Number of Fo > 3 $\sigma(F_o)$	965	—
R	0.077	0.063
R_w	0.072	0.076
Weighting scheme	$1.18/(\sigma^2(F_o) + 0.002\, F_o^2)$	$0.22/(\sigma^2(F_o) + 0.03\, F_o^2)$

A **6a** crystal of dimensions 0.12 × 0.12 × 0.15 mm and a **10** crystal of dimensions 0.15 × 0.25 × 0.3 mm were mounted on the Philips PW 1100/20 four circle diffractometer. Intensities were collected with graphite monochromated Mokα radiation using the ω/2θ mode. The scanning speed and width were 1.5° min^{-1} and 1.2°, respectively. Background was measured for 10s at each side of the peak. Intensities were corrected for Lorentz and polarization and reduced to unique sets of structure factors.

The structure of **6a** was solved by SHELX 76[12] direct methods. The E maps revealed the molecular positions of the nonhydrogen atoms. An additional peak of the water oxygen was identified later on from difference Fourier maps. The structure of **10** was solved by MULTAN.[13] The E maps gave the correct positions of all nonhydrogen atoms. Both structures were refined by SHELX 76[12] least squares method. Scattering factor tables for C and O were taken from Crommer and Mann[14] and for H from Stewart, Davidson and Simpson.[15] The nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Statistical weights were introduced at the final stages of the refinement.

Lists of final atomic coordinates and thermal parameters of **6a** and **10** were deposited with the Cambridge Crystallographic Data Centre. Structure factor tables were deposited with the British Lending Division.

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†The NaH was allowed to react completely before addition of the bromide.

‡From some batches, a chlorine containing by-product was isolated in *ca.* 5% yield.

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