Tetrahedron Letters No.12, pp. 1059-1064, 1967. Pergamon Press Ltd. Printed in Great Britain.

PENTACYCLO[7.5.0.0^{2,7}.0^{5,13}.0^{6,12}]TETRADECA-3,10-DIEN-8-ONE

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(Received 21 December 1966; in revised form 10 January 1967)

The formation of exo-tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-11-one by the thermal addition of tropone and cyclopentadiene, the first example of a 6+4 cycloaddition (1), has been described recently (2). We now wish to report the synthesis of pentacyclo [7.5.0.0^{2,7}.0^{5,13}.0^{6,12}]tetradeca-3,10-dien-8-one (I), a novel cage-molecule produced by reaction of tropone and cycloheptatriene.

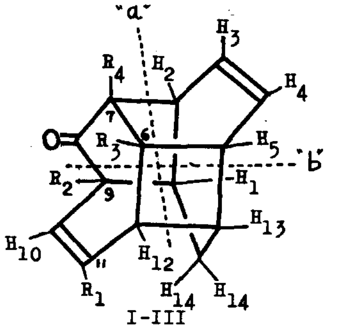
Cycloheptatriene and tropone when heated together without solvent at 200° for 5 hrs afforded, after chromatography on silica gel, a 15% yield of the adduct I, $C_{14}H_{14}O$, with physical properties given in Table 1. Its NMR spectrum (Fig. 2a) proved too complicated for a complete assignment, and accordingly the monochloroadduct (II) and the trideuteriomonochloroadduct (III) were prepared from 2-chlorotropone and 2-chlorotropone-3,5,7-d_3, respectively. The physical properties and the method of preparation of these two derivatives are given in Table 1 which also records data for the alcohols IV, V and VI, obtained by reduction of I, II and III, respectively, and for the tetrahydro derivatives VII and VIII of I and II, respectively.

TABLE 1. Properties of the Adducts and their Derivatives

Compd§ No.	Mol.† Formula	m.p. (°C)	λ_{max}^{MeOH}(ε) (mμ)	ν_{max}^{KBr} (cm^{-1})	MS peaks (m/e) [M]$^+$	major peaks
I	$C_{14}H_{14}O$	150-2.5	301.5(220)	3045, 1735, 1638, 780, 755, 690, 670	198	91, 92**
II	$C_{14}H_{13}OCl$	149-51	303(242)	3050, 1752, 1635, 775, 680	232, 234	91, 92**
III	$C_{14}H_{10}D_3OCl$	151.5-2.5	300(235)	3040, 2230, 1752, 750, 680	235, 237	91, 92, 93, 94**
IV	$C_{14}H_{16}O$	~170(d)$^{\Delta}$	end abs.	3300, 3050, 1110, 840, 740, 690, 665		
V	$C_{14}H_{15}OCl$	~180(d)$^{\Delta}$	end abs.	3480, 3050, 1115, 1050, 756, 748, 687, 678		
VI	$C_{14}H_{12}D_3OCl$	~180(d)$^{\Delta}$	end abs.	3500, 3050, 2200, 1100, 728, 650		
VII	$C_{14}H_{18}O$	~150(d)⁎	289(40)	1735, 760	2,4-DNP. $C_{20}H_{22}O_4N_4$,	
VIII	$C_{14}H_{17}OCl$	191-4⁎	294(47)	1750, 880, 780		m.p. 212-3°

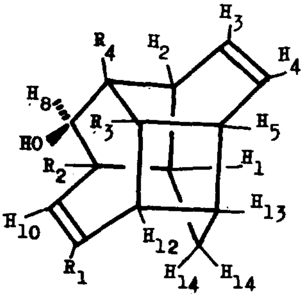
§ Methods of Preparation: II and III; reactants heated at 140° for 5 hrs in xylene. IV; $LiAlH_4$ reduction of I in ether. V and VI; $NaBH_4$ reduction of II and III, respectively, in 95% methanol. VII and VIII; catalytic (10% Pd-charcoal)hydrogenation of I and II, respectively, in methanol. ** base peak. Δ gradual decomposition. ⁎ sublimes easily. † All elementary analyses are in good agreement with the molecular formulae.

* From Varian, Palo Alto, U.S.A. Stationed at Tohoku University.



I-III

I,IV: $R_1=R_2=R_3=R_4=H$
II, V: $R_1=R_2=R_3=H$; $R_4=Cl$
III,VI: $R_1=R_2=R_3=D$; $R_4=Cl$



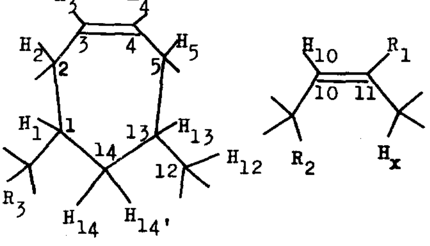
IV-VI

FIG. 1

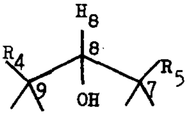
From a comparison of the NMR and mass spectra and other properties of the adducts I, II and III, it is clear that these adducts have the same basic carbon skeleton.

The 100 Mc spectrum of adduct III (Fig. 2b) was fully assigned (Table 4) with the aid of decoupling experiments (Table 2) and, in conjunction with the data provided by a partial assignment of the spectrum of II (Table 4), established the presence of part-structures Ia, IIa and IIIa for adducts I, II and III, respectively. H_{14} and $H_{14'}$, which appear as the AB of an ABXY pattern (J_{AB}=14 cps) in the spectra of I (Fig. 2a) and V (Fig. 3b) are assigned to geminal methylene protons. From a comparison of the NMR of II (H_{10} shows splittings of 9.5, 9.5 and 1 cps; H_{11} shows splittings of 9.5, 7.2 and 1 cps) and III(Fig. 2b, 2c), and from NMDR experiments (strong irradiation of the five-proton complex at 3 ppm in the spectrum of II causes protons H_{10} and H_{11} to appear as a matching pair of doublets with $J_{10,11}$=9.5 cps), it is clear that in adducts I and II H_{10} and H_{11} are strongly coupled to two hydrogens (designated H_x and H_y in part structures Ia and IIa) appearing near 3 ppm so that $J_{10,y}$=9.5 and $J_{11,x}$=7.2 cps. It is also apparent that H_1 (a doublet of doublets of triplets in II but a doublet of triplets in III) is coupled to a hydrogen (H_z in Ia and IIa) appearing near 3 ppm ($J_{1,z}$=6.5 cps) in the spectrum of II.

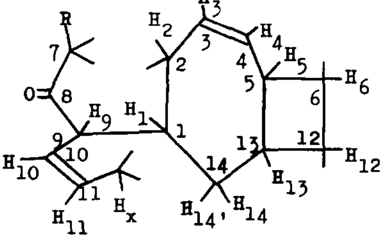
The spectra of the alcohols IV, V and VI (Figs. 3 & 4; Tables 3 & 4) provided sufficient additional information to deduce the complete structures of these three alcohols and adducts I, II and III. From the multiplicities of the H_8 signal (a quartet in IV, a doublet in V, and a broad singlet in VI) (3) it is concluded that the sequences IVa, Va and VIa exist in IV, V and VI respectively. Moreover, in the appropriate solvent, the multiplets due to H_9 and H_6 in V could be distinguished (Fig. 3). Decoupling experiments established that H_9 is strongly coupled to H_1, H_8 and H_{10}; thus $H_9=H_y=H_z$. H_6 was found



Ia,IIa: $R_1=H_{11}$; $R_2=H_y$; $R_3=H_z$
IIIa: $R_1=R_2=R_3=D$



IVa: $R_4=H_9$; $R_5=H_7$
Va: $R_4=H_9$; $R_5=Cl$
VIa: $R_4=D$; $R_5=Cl$



Ib: R=H IIb: R=Cl

to be coupled to H_2 and H_{13} but not to H_1, H_3, H_4, H_8, H_9, H_{10}, H_{11}, H_{14} or $H_{14'}$. Since the splitting pattern of the H_6 signal (Fig. 3b) indicates that it must be strongly coupled (J=7 and 8 cps) to two protons besides H_2 and H_{13}, it follows that both H_5 and H_{12} must be coupled to H_6. Thus part-structures Ia and IIa can be extended to Ib and IIb for the adducts I and II, respectively.

Because part-structure IIb accounts for all fourteen carbons (numbered 1-14) and all thirteen hydrogens (1-6,9-14,14′) in II, it is obvious that H_x must be identical with one of these hydrogens and that C_{11} must be bonded to one of the carbons C_2, C_6, C_7, or C_{12} in IIb. Since H_{11} is not coupled to H_2 and H_6 (cf. Table 3, Exp. 2) and since there is no hydrogen at C_7 in II and V, the identity of H_x and H_{12} is apparent. Having established

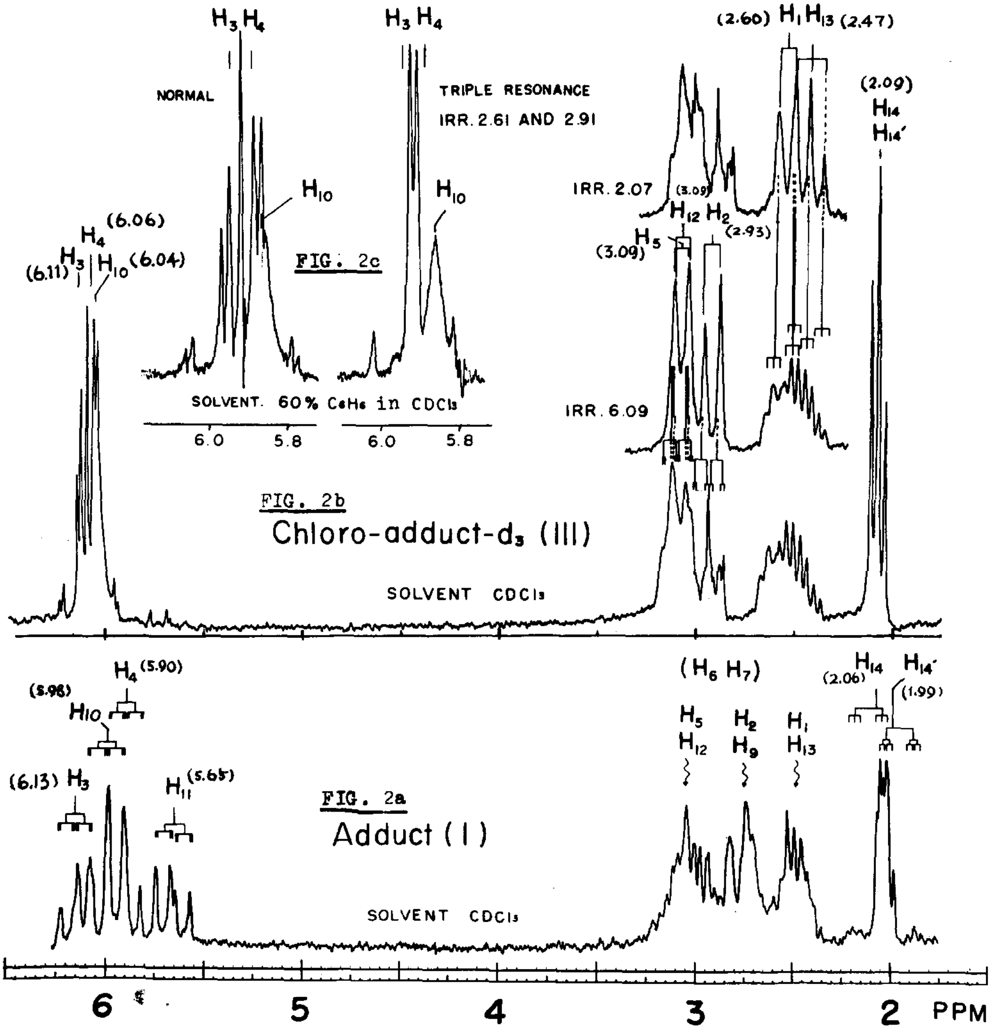


FIG. 2 100 Mc Spectra of Adducts I and III that C_{11} is bonded to C_{12}, it immediately follows that both C_2 and C_6 must be bonded to C_7, and this of course means that the adducts I, II and III have the structures depicted in Fig. 1 which are the only structures compatible with the NMR data.

The stereochemistry at C_8 in alcohol IV (Fig. 1) was deduced from the magnitudes of $J_{7,8}$(=5) and $J_{8,9}$(=9 cps) and an inspection of Dreiding models of the two possible isomers.

Structures I-III (Fig. 1) are also completely in accord with the infrared, ultraviolet and mass spectral properties (Table 1). For example, in I, absorptions at 1735 cm^{-1} and 301.5 mμ (ε=220) are those expected for a β,γ-unsaturated carbonyl group in a five-membered ring (4). In alcohol IV, both absorptions are absent and in the tetrahydro

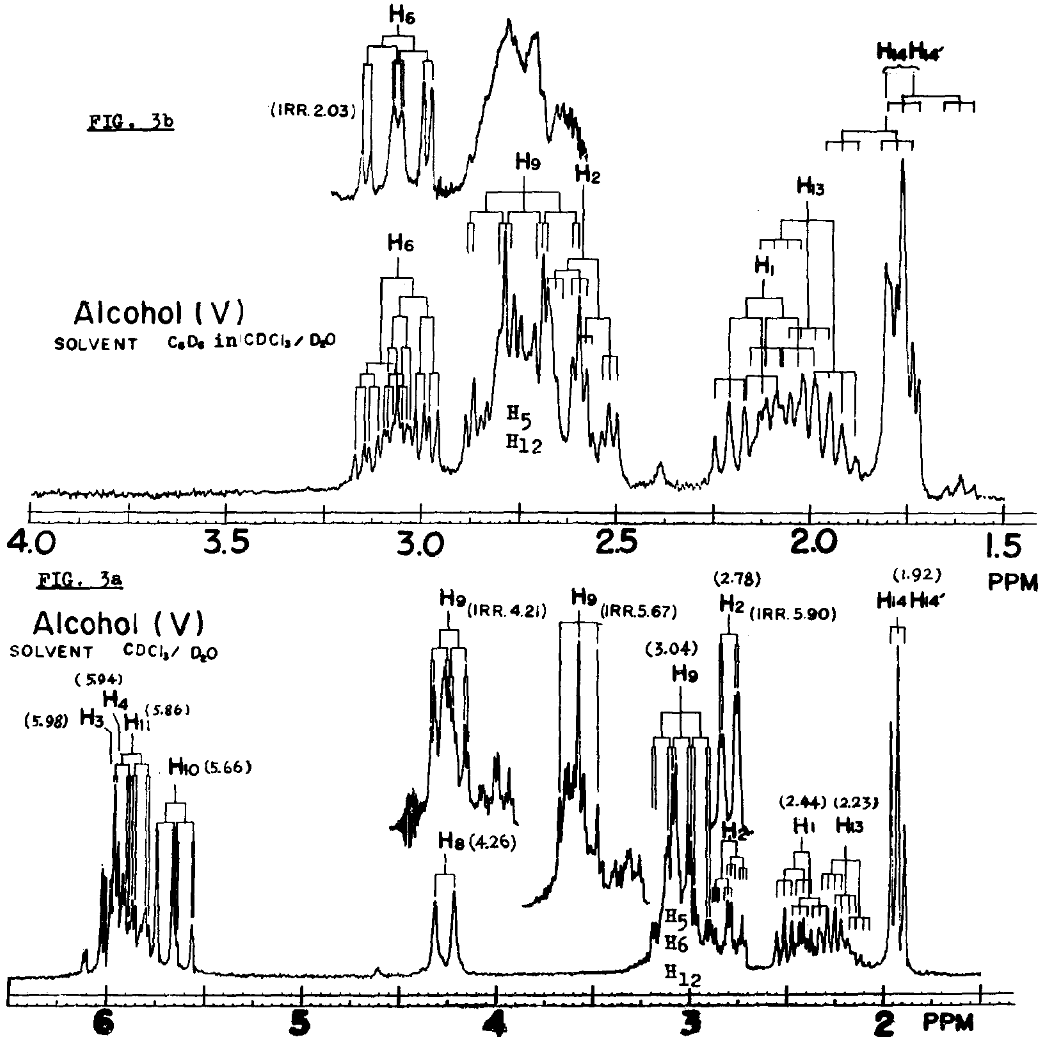


FIG. 3 100 Mc NMR Spectrum of the Alcohol V

TABLE 2. Decoupling Experiments with Adduct III ($CDCl_3$)*

Proton signal	δ_{ppm}	multi-plicity	Exp. 1	Exp. 2	Exp. 3+	Exp. 4	Exp. 5	Exp. 6
H_3	6.11	complex	←	weak ←	d(J=9.3)	n.e.	←	←
H_4	6.06	complex	←	?	d(J=9.3)	n.e.	←	←
H_{10}	6.04	br.s	?	?	n.e.	n.e.	?	?
H_2	2.93	ddd	d(J=8)	strongly perturbed	←	n.e.	d(J~8)	s
H_5	3.09	br.ddd	br.d(J=7)	small effect	←	n.e.	br.s	br.s
H_{12}	3.09	br.d	n.e.	n.e.	?	n.e.	br.s	br.s
H_1	2.60	br.dt	n.e.	n.e.	?	d(J=8)	?	←
H_{13}	2.47	dddd or tt	n.e.	n.e.	?	t(J=7)	←	←
H_{14} $H_{14'}$	2.07	t	n.e.	n.e.	?	←	?	?

+ $CDCl_3$ plus ca 60% C_6D_6 was used as solvent (Fig. 2c); H_{10} separates from H_3 and H_4; H_2, H_5 and H_{12} are at 2.71, 2.81 and 2.77 ppm, respectively.

TABLE 3. Decoupling Experiments with the Chloro-Alcohol V ($CDCl_3$-C_6D_6)*

Proton signal	δ_{ppm}	multi-plicity	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6
H_3	5.88	ddd	←	?	n.e.			
H_4	5.81	ddd	←	?	n.e.			
H_{11}	5.55	ddd	?	←	n.e.			
H_{10}	5.45	ddd	?	←	n.e.			
H_8	4.17	d	n.e.	n.e.	←			
H_6	3.05	dddd	n.e.	n.e.	n.e.	←	ddd (J=8,7,2)	ddd (J=8,7,3.5)
H_9	2.74	ddt	?	t (J=9.5)	ddd (J=9.5,8,1.5)	?	?**	?
H_2	2.59	ddt	dd (J=8,2)	n.e.	n.e.	decoupled	?	←
H_1	2.14	ddt	n.e.	n.e.	n.e.	n.e.	?	
H_{13}	2.04	dtt	n.e.	n.e.	n.e.	tt (J=7,3.5)	←	
H_{14} $H_{14'}$	~1.76 ~1.78	dt dt	n.e.	n.e.	n.e.	n.e.	?	

* In these tables each column represents one experiment; the arrows indicate the protons irradiated. n.e. means no effect; br.s=broad singlet; t=triplet; ddt=doublet of doublets of triplets, etc.

** Strong irradiation near 2.1 ppm causes H_9 to become decoupled (from H_1), as can be seen in Fig. 3b, but the resulting H_9 signal pattern cannot be distinguished.

TABLE 4. Assignment of 100 Mc Spectra* (Adducts I-VI)

J	1,2	1,9	1,14(14')	2,3	2,4	3,4	3,5	4,5	5,13	9,10	9,11	10,11	10,12	11,12	13,14(14')	12,13
I	?	?	~ 3.5	6.8	0.7	9.3	1	6.8	?	9.8	1	9.8	0.5	7.8	~ 3.5	?
II	8	6.5	~ 3.5	6.5	~1.3	9.3	~1.5	6.5	7	9.5	~ 1	9.5	~ 1	7.2	~ 3.5	7
III	8	—	~ 3.5	6.5	~1.3	9.3	~1.5	6.5	7	—	—	—	0?	—	~ 3.5	7
V	8	9.5	~ 4	6	~2	?	?		7	8	~1.5	10	~ 1	6.8	~ 3.5	7
VI	8	—	~ 3.5	5.8	~2	?	~1.5	7	7	—	—	—	0	—	~ 3.5	7

Additional Assignments. I: $J_{14,14'}$=14. II: δ_1=2.60(ddt); δ_2=2.93(m); δ_3=6.11(m); δ_4=6.06(m); δ_6 ca 3 ppm; δ_9 ca 3 ppm; δ_{10}=6.04(ddd); δ_{11}=5.70(ddd); δ_{12} ca 3.1; δ_{13}=2.46(ddt or dddt); $\delta_{14}=\delta_{14'}$=2.07(t). IV: $J_{7,8}$=5; $J_{8,9}$=9; δ_8=4.12(dd) in $CDCl_3/D_2O$. V: $J_{2,6}$=2; $J_{5,6}$=7; $J_{6,12}$=8; $J_{6,13}$=3.5; $J_{8,9}$=9.5; $J_{14,14'}$=14. VI: δ_3=5.99(m); δ_4=5.94(m); δ_{10}=5.66(br.s); δ_8=4.26(br.s) in $CDCl_3/D_2O$.

* Other assignments are given in Figs. 2 and 3; integrals are in accord with all assignments. Coupling constants have been equated with first order splittings. A Varian HA-100 was used. All Js are in cps and δs are in ppm downfield from TMS.

compound VII, ν_{max}^{KBr}=1735 cm^{-1} and ε_{max}^{MeOH}=40 at 287 mμ. The mass spectra of I and II show major peaks at m/e 91 and 92, whereas that of III exhibits strong peaks at m/e 91, 92, 93 and 94, thus indicating that cleavage at "a" or "b" (see Fig. 1) occurs easily. In the case of III, cleavage at "a" produces cycloheptatriene (m/e 92) and tropylium (m/e 91) ions, while cleavage at "b" produces cycloheptatriene-d_2 (m/e 94) and tropylium-d_2 (m/e 93) ions.

These adducts are obviously formed by two consecutive additions of the two reactants, namely, by addition of C_2, C_3, C_4 and C_7 in the tropones to C_2, C_5, C_6 and C_1, respectively, in cycloheptatriene. This reaction, which may be considered as a 6+4 cycloaddition followed by an intramolecular 4+2 cycloaddition, is one more example of a trans 6+4 cycloaddition.

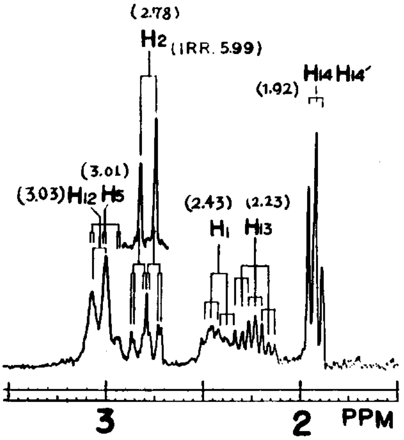


FIG. 4 100 Mc Spectrum of Alcohol VI in $CDCl_3/D_2O$

The authors express their gratitude to Mr. I. Miura for his assistance in measuring NMR spectra.

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3) In the absence of D_2O, an additional splitting (J=10 cps) was observed between H_8 and the OH signal at 2.56 ppm.

4) Cf. A. I. Scott, Interpretation of the Ultraviolet Spectra of Natural Products, p. 75, Pergamon Press, Oxford (1964).