187. *Cis, anti, cis*-Tricyclo[5.3.0.0^{2,6}]deca-4,9-dione

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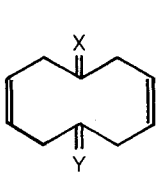
(24. II. 77)

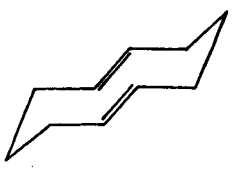
Summary

The chemical behavior and some physical properties (dipole moment, IR. *vs. Raman* spectra) of the titled compound are not fully consistent with a strictly centrosymmetric structure which might be expected for the *anti* configuration. The carbonyl groups are less reactive toward nucleophilic reagents and $sp^2 \rightarrow sp^3$ transformations as compared to cyclopentanone systems.

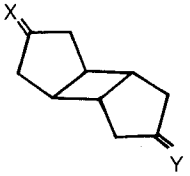
It has been shown that upon irradiation, *cis, cis*-cyclodeca-1,6-diene system (I) and *trans, trans*-cyclodeca-1,6-diene (II) yielded the tricyclo[5.3.0.0^{2,6}]decane skeleton [1]. By chemical means the product was proved to be the *anti* isomer (III) [2] rather than the *syn* (IV) or crossbonded (V) isomers.



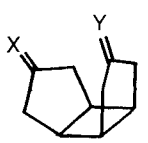
I a X=Y=H$_2$
b X=Y=O
c X=O, Y=(OCH$_3$)$_2$
d X=Y=(OCH$_3$)$_2$
e X=O, Y=CH$_2$
f X=O, Y=H,OH



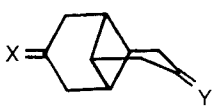
II



III a X=Y=H$_2$
b X=Y=O
c X=O, Y=(OCH$_3$)$_2$
d X=Y=(OCH$_3$)$_2$
e X=O, Y=CH$_2$
f X=O, Y=H,OH



IV



V a X=Y=H$_2$
b X=Y=O

However, the chemical behavior and some of the physical properties of IIIb are not fully consistent with a strictly centrosymmetric structure which might be expected with the *anti* configuration. It seems that IIIb either suffers from some steric hindrance at the carbonyl region or conformational strain or distortion in the five-membered rings of the molecule. The three dimensional X-ray structure analysis [3] gives the full structure of IIIb and explains some of the unexpected results. The main features are as follows: (a) The cyclobutane ring is folded about an axis through the transannular atoms with a dihedral angle of 163.1°; (b) Although the cyclopentanone rings are

[1]) Taken in part from M. Sc. Thesis, School of Pharmacy, The Hebrew University, Jerusalem.

anti to each other, the folding of the cyclobutane ring precludes a molecular inversion center; (c) The folding of the cyclopentanone rings is such that both oxygen atoms are *endo* to the cyclobutane ring [3] (see *Fig. 1*). (This fact is also illustrated in the reduced compounds and explained later.)

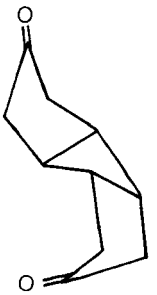


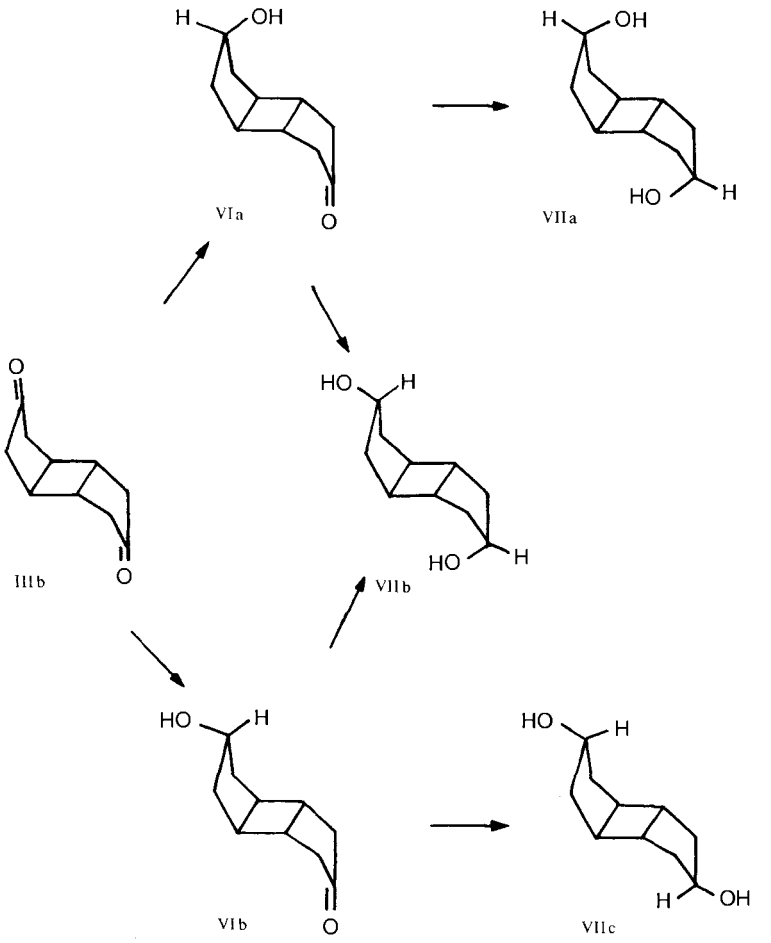
Fig. 1. *Molecular structure of* cis,anti,cis-*tricyclo*[*5.3.0.0*^{2,6}]*deca-4,9-dione* (IIIb)

It is known that the reactivity of the carbonyl group in cyclopentanone is diminished in $sp^2 \rightarrow sp^3$ type reactions (as compared to cyclohexanone), but it is still sufficiently reactive to participate in nucleophilic reactions and reductions [4]. Therefore, it was surprising to find that IIIb was somewhat stable to *Grignard* reaction, cyanohydrin formation and other $sp^2 \rightarrow sp^3$ reactions. Vigorous and occasionally drastic conditions were needed to obtain products, and even then, considerable amounts of starting material could be recovered.

Catalytic reduction of IIIb with PtO_2 in C_2H_5OH gave two isomers of monohydroxy ketone VI, the major one being less polar on a TLC. plate. On further reduction of the major isomer, two isomer of the dihydroxy system VII were also obtained, again the major one being less polar on a TLC. plate. It is interesting to note that while the first equivalent of H_2 was absorbed within a few minutes, it took much longer for the second one to react. This difference in behavior of the two carbonyl groups might be explained by the assumption that after reduction of one carbonyl function some change in conformation occurs, which causes steric hindrance at the other carbonyl function. Alternatively, it could be that the *endo* conformation of the carbonyl groups is such that one carbonyl is less hindered than the other while attached to the surface of the catalyst. This behavior might be a reflection of the non-symmetry of the molecule.

Two isomeric structures of the hydroxyketone are conceivable, namely VIa and VIb (see *Scheme 1*). Hydrogenation of the carbonyl group in IIIb is expected to be predominantly from its less hindered side. Inspection of *Dreiding* stereomodels shows, that the more stable conformation of the cyclopentanone rings is such that the rings are bent 'inwards', toward the center of the molecule. The reason for this is illustrated in *Fig. 2*, which shows severe 1,3-nonbonded interactions and eclipsing of H^1 and H^3, H^2 and $H^{3'}$, H^5 and H^7 and $H^{5'}$ and H^6 (the same situation applies to the second ring) when the ring is bent outwards. By bending inwards, these interactions are eliminated through formation of the 4 *pseudogauche* conformations of the above pairs of hydrogens. This implies that the major product would be VIa and the minor one VIb. The difference in polarity (see *Table 1*) of the isomers is in line with that expected

Scheme 1



from related cyclopentanols [5], namely, the *endo*-alcohol VIa will be less polar than the *exo*-alcohol VIb. The ratio of VIa to VIb is *ca.* 9:1.

Another clue to the structure is found in the NMR. spectrum. Chemical shift data for C*H*(OH) show the difference between the two isomers (see *Table 1*). The coupling constants fit the calculated values taken from the *Karplus* plot [6] for the different dihedral angles of the *endo*- and *exo*- with the vicinal hydrogen atoms [90° and 45° for the *endo*-alcohol (*exo* H), X = H, Y = OH, and 30° and 160° for the *exo*-alcohol (*endo* H), X = OH, Y = H, in *Fig. 2*].

In principle, reduction of the two mono-hydroxyketones VIa and VIb might be expected to yield four isomeric diols. In fact, the identity of two of these products leads to a total of only 3 observed isomers.

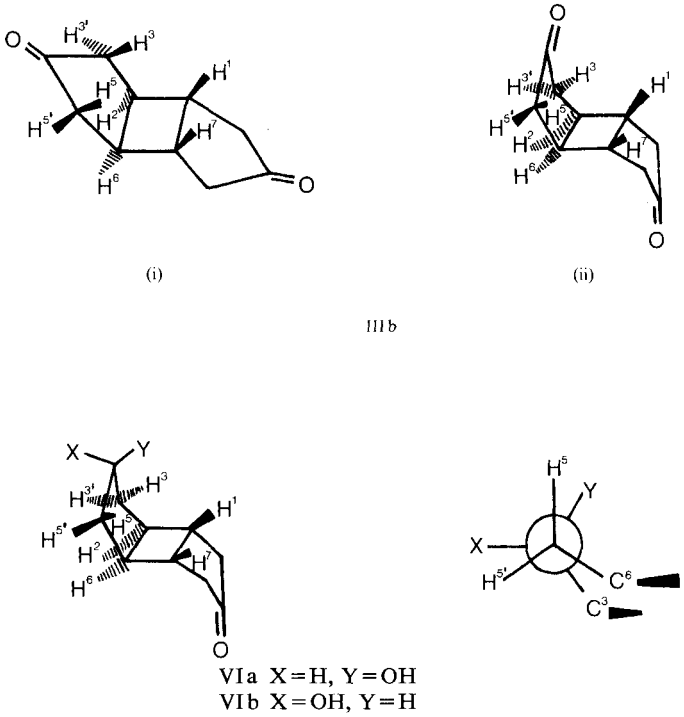


Fig. 2. *Two possible conformations of the cyclopentanone ring in III b and the cyclopentanol ring in VI.* The non-bonded interactions and eclipsing appear to a much lower extent in (*ii*) as compared to (*i*)

The reduction of VIa would be expected to give 2 isomers which, in fact, occurred. Based on the above arguments of polarity and steric effects of the reaction we expect *trans-endo, endo*-diol (VIIa) to be a less polar and the major isomer. The second isomer, *cis-endo, exo*-diol (VIIb), would be more polar, but present as the minor component (see *Scheme 1* and *Table 1*).

Table 1. *Properties of isomeric monohydroxy ketones VI and diols VII*

Isomer	M.p.	Polarity (TLC.)	Rf[a])	H^4 NMR. (δ, $CDCl_3$)	
Monohydroxy monoketone (VI)					
major, VIa	85–86°	less polar	0.50	4.50 (*t*), J=3–4	
minor, VIb	82–83°	more polar	0.37	4.65 (*tt*), J=9, 6	
Diols (VII)				H^4, H^9	O–H (DMSO)
major, VIIa	195–196°	less polar	0.53	4.25	4.19
minor, VIIb	174–176°	more polar	0.37	4.23–4.27	4.19, 4.40
traces, VIIc		most polar	0.29		

[a]) After 3 successive runs in 70% ether in light petroleum on analytical TLC. plate. The fact that the Rf's are identical made it difficult, at first, to differentiate between the different products after reduction. For comparison, Rf of the diketone III b under these conditions is 0.53 and that of XIII is 0.58.

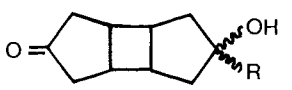
Reduction of VIb might give 2 isomers, the above mentioned *cis-endo*, *exo*-diol (VIIb) and the most polar of the 3 isomers *trans-exo,exo*-diol (VIIc). This compound was hardly detected after reduction of IIIb by $NaBH_4$ in EtOH and careful column chromatography. It was found only as a mixture with VIIb and could be detected on TLC. plate and by GC. as the disylyl ether of the diol. The ratio of VIIa to VIIb and VIIc is *ca* 30:7:1.

NMR. spectra of the diols (VIIa and VIIb) in DMSO show the difference in the O–H ··· solvent interaction, as demonstrated earlier [5]. *Exo*-alcohol, in which the OH group is pointing outwards would interact more strongly with molecules of solvent, *via* hydrogen bonds, than the *endo*-alcohol. One might conclude that a hydrogen-bonded *exo*-hydroxyl proton should resonate at lower field than its *endo* counterpart [5]. The results of NMR. measurements in DMSO are summarized in *Table 1* and confirm this. Retention time of the disylyl ethers on 3% carbowax 20 M column also follows the polarity of the diols on the plate.

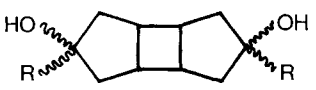
This observation of the inwards conformation in solution might explain the structure of IIIb in the solid state, in which the cyclopentanone rings adopt the *endo* conformation and cause folding of the cyclobutane ring (see above).

The reluctance of the carbonyl group to undergo a hybridization change of the type $sp^2 \rightarrow sp^3$ with nucleophilic reagents, is demonstrated in Grignard, enamine and cyanohydrin reactions.

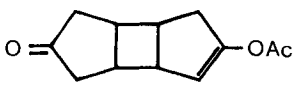
IIIb did not react with CH_3MgI or C_6H_5MgBr in ether or THF; in boiling toluene about 15% of VIII was collected, in addition to 40% of recovered IIIb. This low reactivity of the carbonyl may be illustrated by the preponderant formation of the enol (by the RMgX, acting as base) thereby conserving sp^2 hybridization in the ring, which subsequently reverts to the starting carbonyl[2]). In support of this hypothesis is the relatively facile reaction leading to the monoenol acetate IX in 20–30% and dienol acetate X in 45–50% yield and also the easy exchange of the α-hydrogens with D_2O



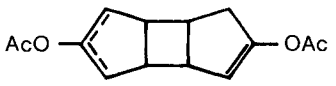
VI R = H
XI R = CN



VII R = H
VIII R = CH_3
XII R = CN

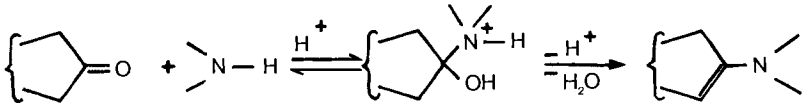


IX



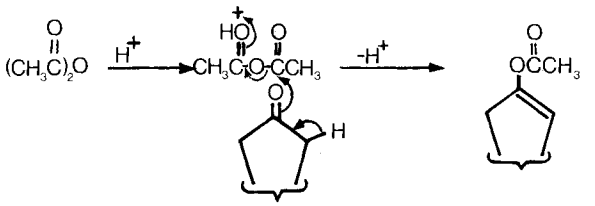
X

[1a]. The fact that pyrrolidine or morpholine failed to give enamines of IIIb might be explained by the mechanism of reaction which includes a change in hybridization:



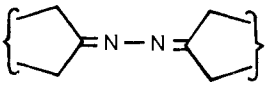
[2]) When other basic reagents (such as $Na[CH_2NO_2]$, Mg(Hg), Na in xylene, BuLi) were used no definite product could be isolated, except considerable starting material.

Such change of hybridization does not occur with the formation on enol acetate. Direct attack of the oxygen atom eliminates any change in sp^2 hybridization of the carbon atom in the carbonyl group:



Alternatively, it might be that the reason for this unreactivity of the secondary amines with IIIb arises from the fact that in such a reaction, the equilibrium constant is not favorable to product formation (amino alcohol). Dehydration of this intermediate would form some steric hindrance because of the inward bending and also nonbonded interactions of H^3 and/or H^5 (see *Fig. 2*) with the hydrogen atoms of the saturated heterocyclic moiety.

It is interesting to note the difference between IIIb and XIII under *Wolff-Kishner* reduction. While XIII is readily reduced, IIIb is not reduced at all, but instantaneously forms an azine derivative [1a,2b].



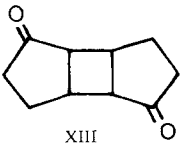
The high reactivity of hydrazine as compared to pyrrolidine or morpholine might be explained by the fact that steric hindrance in hydrazine molecule is small and it immediately released by reaction of the second amino group thus enabling the system to revert to its sp^2 hybridization.

When reacted with KCN and H_2SO_4 in CH_3OH a 40–50% yield of XI and a 10–30% yield of XII were obtained as labile products which readily released HCN to give IIIb. Preliminary experiments showed that the equilibrium constant for XI $\rightleftharpoons$ IIIb is much higher than the value of 0.02 for decomposition of cyclopentanone cyanohydrin to its components. We have also noticed the fast decomposition (on standing, without solvent) of IIIc and IIId to IIIb [1a,c]. This is in contrast to the ready reaction of XIII to form a stable diacetal [7].

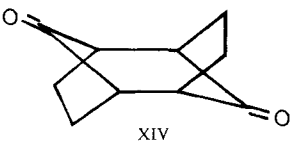
In addition to the unusual chemical behavior of IIIb, the dipole moment of the compound, which is expected to be small, due to a nearly centrosymmetric molecular configuration, is found to be considerable high. The value of 1.34 D (in dioxane, 30°)[3]) might be attributed, in part, to the solvent[4]) and in part to the fact that the mole-

[3]) We would like to thank Dr. *H. Weiller-Feilchenfeld*, The Hebrew University, Jerusalem, for this measurement. Dipole moment was determined according to *I. F. Halverstadt & W.O. Kumler*, J. Amer. chem. Soc. *64*, 2988 (1942), in dioxane at 30°. The molar refraction was calculated according to *LeFiore & Steel* (Chemistry & Ind. *1961*, 670).

[4]) Known as 'dioxane effect' which gives higher values compared to benzene as solvent. *cf.*, *L. Skulski & W. Waclawek*, Bull. Acad. Poland *19*, 277 (1971).

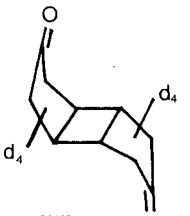


XIII



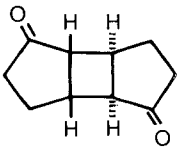
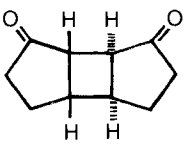
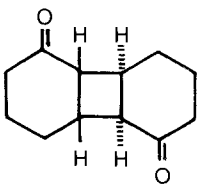
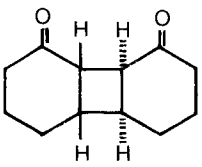
XIV

XV



XVI

Table 2. *Comparison of the* Raman *and Infrared Frequency coincidences*

	IR.	R.	Coinc.		IR.	R.	Coinc.
	24	24	6		36	31	26
	46	24	10		42	33	24

[a]) IR., R., and Coinc. denote infrared peaks, *Raman* lines, and coincidences, respectively.

In our case we had only one isomer[5]), namely IIIb, but the results show a molecule which lacks an inversion center: IR. 30; R. 27; Coinc. 20[6]).

cule is not strictly centrosymmetric (the calculated value is 0.71 D), since the cyclobutane ring is not planar and chemically equivalent torsion angles in the two cyclopentanone rings differ by small, but significant amounts [3] [8]. For comparison, the centrosymmetric compound XIV, a small and somewhat rigid molecule shows a zero dipole moment (0.1 ± 0.3 D) [9]. Other examples are known [10].

[5]) We could isolate a very small amount of a crystalline material which was saturated and which proved to be isomeric with IIIb. Its structure is tentatively assigned to be the cross-bonded diketone Vb, based on its IR., NMR. and Mass spectrum. (See discussion concerning Mass spectra and experimental part.)

[6]) We would like to thank Prof. *I. Zelig*, The Hebrew University, Jerusalem, for these measurements.

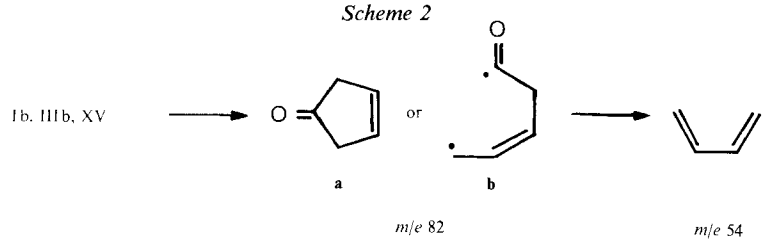
The identification of a molecular center of symmetry by IR. and *Raman* spectroscopy is based on the difference in vibrational selection rules. In a centrosymmetric molecule, a vibrationally active IR. transition cannot be active in *Raman* and *vice versa*; in molecules lacking the inversion center, vibrations of the same frequency, which are termed coincidences, appear in both the IR. and *Raman* spectra. For illustration some results [11] are given in *Table 2*.

The mass spectra of the ketonic compounds are summerized in *Table 3*, which contains the main peaks of these spectra with their relative intensities. The main features are as follows:

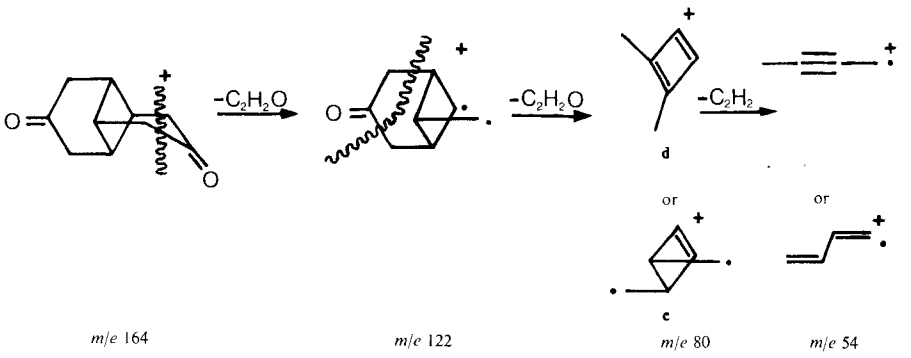
i) The tricyclic diketone IIIb and the new isomer, to which we tentatively assign the cross-bonded structure Vb, seem to be more stable than the monocyclic diketone Ib and XV, although Vb is less stable than IIIb. If this isomer were to possess a *syn* structure as in IV, we would then expect it to show similar stability to that of IIIb;

ii) The amount of ketene elimination (C_2H_2O, *m/e* 42, 164 → 122 → 80) is different for the ketonic compounds. While Ib, IIIb and XV show essentially the same mode of fragmentation (*e.g.* formation of half molecule (**a**) or the corresponding diradical **b** (C_5H_6O, *m/e* 82) and then butadiene (*m/e* 54) as illustrated in *Scheme 2* (or 58 for $C_4D_4H_2$ in the octadeuterated IIIb, XVI), the new isomer forms also cyclobutene derivative (**c**, C_6H_8, *m/e* 80) or cyclobutadiene (**d**) as illustrated in *Scheme 3*.

Scheme 2



Scheme 3

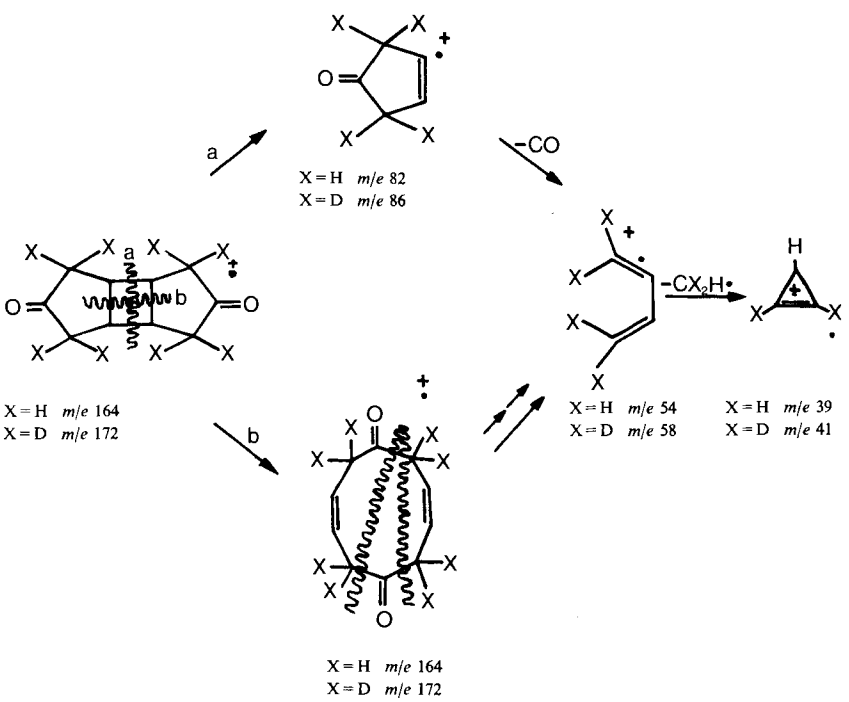


This mode of fragmentation suggests that the butadiene formation from Vb may arise from a different route as compared to that of Ib, IIIb or XVI (see *Scheme 4* as compared to *Scheme 3*). If the new isomer were *syn* IV we, again, would expect it to behave as the above mentioned ketones.

Table 3. *Main peaks and relative intensities* (in percent) *of fragment ions of the ketonic compounds*

Peak	Ib		XV		IIIb		Vb		Peak	XVI	
	% of sum	% of highest	% of sum	% of highest	% of sum	% of highest	% of sum	% of highest		% of sum	% of highest
164	6.1	20.8	6.6	19.3	14.1	35.9	11.9	97.7	172	8.3	22.0
136	0.7	2.5	0.8	2.4	1.2	3.1	1.0	8.5	144	0.8	2.0
122	0.5	1.8	1.0	2.8	2.9	7.4	7.8	63.8	128	2.0	5.3
94	0.5	1.8	0.7	2.0	2.3	5.9	4.3	35.4			
82	7.1	24.2	4.9	14.1	6.3	16.2	7.8	63.8	86	4.8	12.7
81	4.8	16.5	3.4	10.0	2.5	6.4	3.4	27.7			
80	0.8	2.7	1.0	3.0	2.4	6.2	12.0	98.5	84	3.8	10.0
79	4.2	14.2	3.5	10.2	3.8	9.7	11.5	94.6	83	2.3	6.0
68	4.7	16.2	2.5	7.2			0.7	5.4			
54	29.4	100.0	34.3	100.0	39.2	100.0	12.1	100.0	58	37.8	100.0
53	6.2	21.0	6.9	20.2	3.2	8.2	7.7	63.1			
39	9.8	33.3	12.3	35.9	5.7	14.6			41	5.5	14.7

Scheme 4

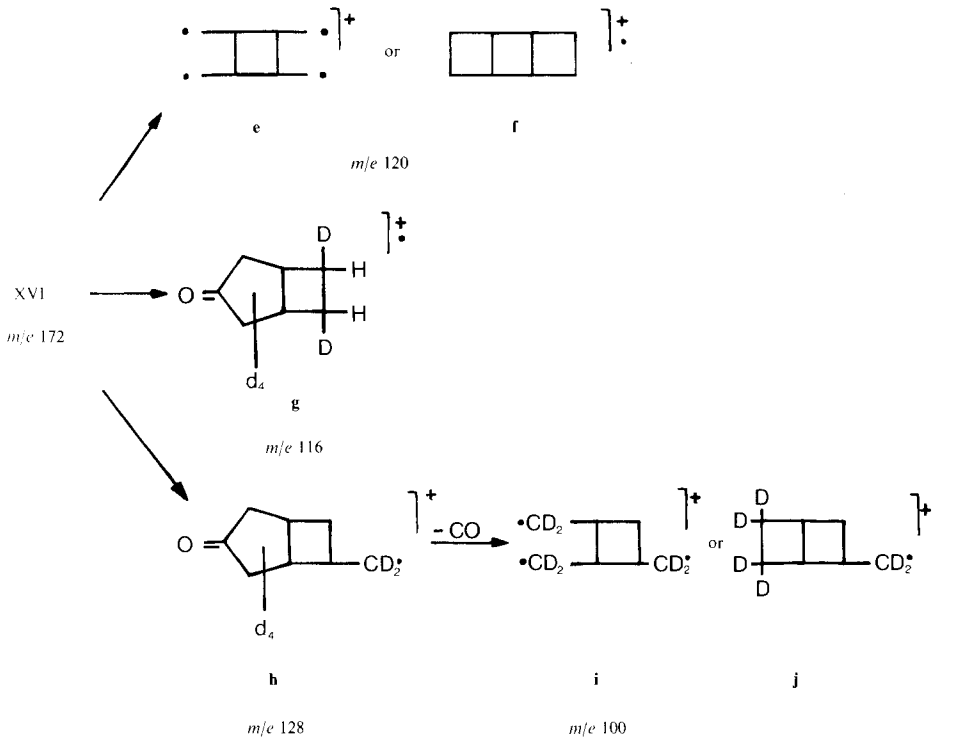


iii) The fragment *m/e* 54 might also be C_3H_2O (Cyclopropenon) but this possibility is eliminated because of the existence of a metastable peak at 28.2, which corresponds to the fragmentation 54 → 39, namely, elimination of CH_3 to form cyclopropenium ion, $C_3H_3^{\oplus}$.

iv) The spectrum of XVI shows, among others, two metastable peaks at 120 and 78.2, which might arise from the molecular peak: 172 → 144 and 172 → 116 or

128 → 100. The first one is loss of 2 CO to form **e** or **f** and the second one is cleavage of C_3D_2O (*m/e* 56) to form **g** (*m/e* 116), or another cleavage such as **h** (*m/e* 128) –CO to yield **i** or **j** (*m/e* 100) (see *Scheme 5*)

Scheme 5



Experimental Part

Instrumentation. IR.: *Perkin-Elmer* Model 137, and Models 21 and 621 for comparison with *Raman* spectrum; *Raman*: Spex 1400, *Laser Spectrophysics* Helium-Neon 125; NMR.: *Jeol* C-60H and *Varian* XL-100, recorded in $CDCl_3$ with TMS at the internal reference standard; chemical shifts, δ, are expressed in ppm measured downfield from the reference; Mass spectra: *Atlas* CH4, 70 ev; TLC.: Kieselgel G, *Merck*; spray of a 0.5% solution of $KMnO_4$ in saturated solution of cupric acetate, and then heating of conc. H_2SO_4 spray in an oven at 110°. Microanalyses were carried out by the *Hebrew University* microanalytical laboratories.

Catalytic reduction of IIIb to VI and VII. A solution of 740 mg of IIIb (4.5 mmol) in 60 ml EtOH and PtO_2 was reduced under atmospheric pressure. Within 10 min 4.5 mmol of H_2 were absorbed, while 1.5 mmol more of H_2 were absorbed slowly during 1 h. The reduction was stopped at this stage. The crude product was crystallized from $CHCl_3$ to yield 145 mg of diol, m.p. 195–196° (VIIa). – IR. (λ_{max}^{KBr}): 2.95, 7.05, 7.46, 7.72, 7.96, 8.21, 8.62, 9.78*s*, 9.97, 10.59 μ.

$C_{10}H_{16}O_2$ (168) Calc. C 71.43 H 9.52% Found C 71.70 H 9.75%

Further crystallization of the filtrate from CH_2Cl_2 light petroleum yielded 60 mg of diol, m.p. 174–176° (VIIb). – IR. (λ_{max}^{KBr}): 2.95, 7.03, 7.48, 7.72, 8.00, 8.64, 9.29*s*, 9.47, 9.89*s*, 10.00, 10.60 μ.

$C_{10}H_{16}O_2$ (168) Calc. C 71.43 H 9.52% Found C 71.58 H 9.44%

Further crystallization from light-petroleum yielded 415 mg of monohydroxy derivative (VIa), m.p. 85–86°. – IR. (λ_{max}^{KBr}): 2.84, 5.80*vs*, 7.05, 7.16, 7.47, 7.57, 7.72, 7.81, 7.99, 8.38, 8.57, 8.76, 9.18, 9.82, 10.00*s*, 10.52 μ. – NMR.: 4.50 (*t*, 1H); 2.80 (2H); 2.50–2.20 (6H); 2.00 (*s*, 1H, OH); 1.95–1.80 (4H).

$C_{10}H_{14}O_2$ (166) Calc. C 72.29 H 8.45% Found C 72.36 H 8.43%

The residue of 75 mg was separated on preparative TLC., eluted with ether, to yield 15 mg of VIa and 35 mg of the other isomer, VIb, m.p. 82–83°. – IR. (λ_{max}^{KBr}): 2.88, 5.80*vs*, 7.02, 7.18, 7.45, 7.55, 7.80, 7.95, 8.03, 8.45, 8.67, 8.90, 9.30*s*, 9.90, 10.25, 10.75 μ. – NMR.: 4.65 (*t* × *t*, 1H); 2.55–2.35 (6H); 2.10–1.60 (*m*, 6H); 1.70 (*s*, 1H, OH).

$C_{10}H_{14}O_2$ (166) Calc. C 72.29 H 8.45% Found C 72.45 H 8.63%

Catalytic reduction of monohydroxy derivative VI to diol VII. A solution of 95 mg of VIa (m.p. 86–87°, 0.57 mmol) in 5 ml EtOH and PtO_2 was reduced under atmospheric pressure. 0.55 mmol of H_2 were absorbed during 2 h. The crude residue (90 mg) was crystallized from $CHCl_3$, yielding 60 mg of VIIa, m.p. 195–196°, identical with the diol obtained by direct reduction of IIIb. The filtrate contained 16 mg of the impure isomeric diol, VIIb, m.p. 168–170°.

Reduction of IIIb with $NaBH_4$. A solution of 74 mg of IIIb (0.45 mmol) and 360 mg of $NaBH_4$ (10.6 mmol) in 20 ml abs EtOH was kept at RT. for 24 h. The crude residue after addition of H_2O and extraction with $CHCl_3$ (64 mg) was chromatographed on 10 g of basic alumina (BDH, grade 1). Two fractions were collected: (i) 50% ether in light petroleum eluted 25 mg of diol, m.p. 194–195° (recrys. from $CHCl_3$) identical in IR. and TLC. to VIIa from catalytic reduction. – NMR. (DMSO): 4.25 (br. *s*, 2H); 4.19 (br. *s*, 2H); 2.50–2.40 (*s*, 4H); 1.61 (*s*, 8H). – R_t as disylyl ether on 3% carbowax 20 M on chromosorb W at 155° is 2.08 min; (ii) 70% ether in light petroleum eluted 16 mg of mixture of 3 diols m.p. 164–169°. Rechromatography of this fraction afforded 3 fractions: (a) 7 mg of mixture of VIIa and VIIb; (b) 6 mg of pure VIIb, m.p. 168–170°, identical in IR. and TLC. to the minor isomer obtained from catalytic reduction. – NMR. (DMSO): 4.40 (*m*, 1H); 4.27–4.23 (*m*, 2H); 4.19 (*m*, 1H); 2.01 (*s*, 4H); 1.61 (*s*, 8H). – R_t as disylyl ether on the same column as above is 2.36 min; (c) 2 mg of mixture of VIIb and VIIc in ratio of ~2:1; R_t of VIIc as disylyl ether on the same column as above is 2.88 min.

Reactions of Grignard reagents with IIIb. A solution of 164 mg of IIIb (1 mmol) in 30 ml dry THF was added dropwise to a solution of 200 mg of C_6H_5MgBr (1.1 mmol) in 20 ml dry THF. Yellow color developed in the solution. The reaction mixture was stirred for 3 h and then poured into H_2O. The crude residue was washed on a short column of silica gel to yield 138 mg of starting material. When the same reaction was tried again and heated to reflux for 10 h, only 100 mg of starting material was recovered.

The same result was obtained when 2 mmol of C_6H_5MgBr were used to react with 1 mmol of IIIb in THF.

A solution of 820 mg of IIIb (5 mmol) in 20 ml dry toluene was added dropwise to 3.65 g of CH_3MgI [(22 mmol) prepared from 3.2 g CH_3I and 535 mg Mg in ether] in 30 ml dry toluene (after evaporation of the ether) and then was refluxed for 4 h. The drude residue (1 g) was chromatographed on 85 g silica gel. Elution with ether/light petroleum 1:1 yielded 110 mg of VIII, m.p. 167–168°. – IR. (λ_{max}^{KBr}): 2.9, 6.95, 7.4, 7.67, 8.0, 8.15, 8.63, 9.55, 9.72, 10.7, 11.15, 12.95 μ. – NMR. [$(CD_3)_2CO$]: 3.2 (*s*, 2H, OH, disappeared in D_2O); 2.95–2.50 (*m*, 4H); 1.9–1.6 (8H); 1.3 (*s*, 6H, $2CH_3$).

$C_{12}H_{20}O_2$ (196) Calc. C 73.47 H 20.20% Found C 73.30 H 10.22%

The same solvent eluted 330 mg of starting material.

Reaction of IIIb with HCN. To a cooled solution of 164 mg of IIIb (1 mmol) and 220 mg KCN (3 mmol) in 20 ml MeOH cold solution of 3 mmol H_2SO_4 in MeOH (1 ml) were added dropwise. The reaction mixture was left at RT. for 24 h. Two products were isolated on prep. TLC.: monocyanohydrin, XI, 85 mg as yellow oil, which decomposed spontaneously and released HCN within a few days. – IR. (λ_{max}^{neat}): 2.95, 5.88, 7.2, 7.55, 8.0, 8.7, 9.25, 9.75, 9.95, 10.05 μ. – NMR.: 3.85 (*s*, 1H, OH); 3.0–1.9 (*m*, 12H).

The more polar product, dicyanohydrin, XII, 22 mg, m.p. 176–178° (from $CHCl_3$). The material decomposed much faster than XI. – IR. (λ_{max}^{KBr}): 2.9, 4.42, 7.15, 7.65, 7.95, 8.2, 8.55, 9.1, 9.65, 10.95, 12.0, 12.85 μ. – NMR. (CD_3OD): 2.85 (br. *s*, 4H); 2.22 (br. *s*, 8H).

No analysis could be obtained because of the very high instability of the material and no parent peak could be found in mass spectrum. When large excess of HCN was used (ratio 7:1) and the reaction mixture was left for 48 h, the yield of XII raised to ~50%.

Reaction of IIIb with acetic anhydride to yield IX and X. A solution of 82 mg of IIIb (0.5 mmol) and 4–5 mg of *p*-TsOH in 0.5 ml acetic anhydride was heated to ~125° for 3.5 h. Then the dark solution was kept at RT. for 48 h. By prep. TLC. the monoenol acetate IX was separated, 15 mg, as yellow oil [IR. (λ_{max}^{neat}): 5.8, 6.15, 7.35, 8.5, 10.0, 11.09, 11.5, 11.55 μ. – NMR. (CCl_4): 5.5 (br.*s*, 1H, olefin); 3.0–2.15 (*m*, 10H); 2.1 (*s*, 3H, acetyl)]; then 10 mg of starting material and finally dienol diacetate X, 45 mg, m.p. 86–87° (from light petroleum) [IR. (λ_{max}^{KBr}): 5.7, 6.05, 7.3, 8.2, 8.45, 8.7, 9.9, 10.9, 11.5, 13.98 μ; NMR. 5.5 (br.*s*, 2H); 3.2–2.2 (*m*, 8H); 2.15 (*s*, 6H, 2 acetyl groups)].

$C_{14}H_{16}O_2$ (216.0) Calc. C 67.46 H 6.62% Found C 67.70 H 6.40%

Reaction of IIIb with pyrrolidine. A solution of 164 mg of IIIb (1 mmol), 3–4 mg of *p*-TsOH and 250 mg of pyrrolidine (3.5 mmol) in 15 ml C_6H_6 was heated under reflux in a *Dean-Stark* apparatus for 2 h and then 250 mg more of pyrrolidine was added and the heating continued. Total reflux was 5 h, and then was kept at RT. for 24 h. By prep. TLC. no product could be isolated except for starting material (110 mg). The same result was obtained when the same quantities as above were used in toluene solution and morpholine as the amine.

Isolation of the isomeric tricyclic diketone. By repeating crystallizations of IIIb a small amount of another crystalline material could be isolated from the mother liquer (on TLC. plate it is slightly more polar than IIIb and after spray gives greenish-gray color – as compared to the brown color of IIIb) by prep. TLC. (3 run in ether/light petroleum 1:1), m.p. 148–150° [IR. (λ_{max}^{KBr}): 5.84*s* (1712 cm^{-1} as a six-membered ring ketone), 7.20, 7.53*m*, 8.39, 8.69*m*, 9.92, 10.14, 11.46 μ; (For comparison is the IR. of IIIb: 5.78*s* (1730 cm^{-1}), 7.20*m*, 8.01, 8.57*m*, 8.95, 9.72, 10.50, 12.59 μ. – NMR.: 2.70 (two sharp *s* almost overlapping) and 2.12 (sharp *s* with a low shoulder at 2.19), in ratio of 1:2].

REFERENCES

[1] a) *A. Shani*, Tetrahedron Letters *1968*, 5175; b) *A. Shani*, ibid. *1970*, 569; c) *Z. Tasma & A. Shani*, unpublished results.

[2] a) *J. R. Scheffer & M. L. Lungle*, ibid. *1969*, 845; b) *J. W. Stankorb & K. Conrow*, ibid. *1969*, 2395.

[3] *J. Bernstein*, Acta crystallogr. *B30*, 1728 (1974).

[4] *Eliel* 'Stereochemistry of Carbon Compounds'. McGraw Hill, N.Y. 1962, p. 268 and references 41 and 42 therein.

[5] *R. K. Sehgal*, R. M. *Koenigsberger & T. J. Howard*, Tetrahedron Letters *1974*, 4173.

[6] *L. M. Jackman & S. Sternhell*, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', 2nd Ed., Pergamon, Oxford 1969, p. 282.

[7] *P. E. Eaton*, J. Amer. chem. Soc. *84*, 2344 (1962).

α^1	β^1	P_{2_0}	MR_{cal}	μ (D)
3.21	−0.61	77.65	41.40	1.34

[8] See also, *S. Sasson, I. Rosenthal & D. Elad*, Tetrahedron Letters *1970*, 4513, who found 1.19 D for a centrosymmetric dimer of a pyrimidine derivative.

[9] *G. Kobrich & H. Heinemann*, Chem. Commun. *1969*, 493.

[10] *T. Mukai, T. Oine & H. Sukawa*, Chem. Commun. *1970*, 271.

[11] *H. Ziffer & I. W. Levin*, J. org. Chemistry *34*, 4059 (1969).