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CYCLOPENTANONES—XVIII[a]

THE LITHIUM–LIQUID AMMONIA REDUCTION OF SOME 2,3-DIALKYL-(4-HYDROXY)-2-CYCLOPENTENONES. THE IMPORTANCE OF THE PROTONATION OF INTERMEDIATE ENOLATE ANIONS ON THE STEREOCHEMICAL OUTCOME

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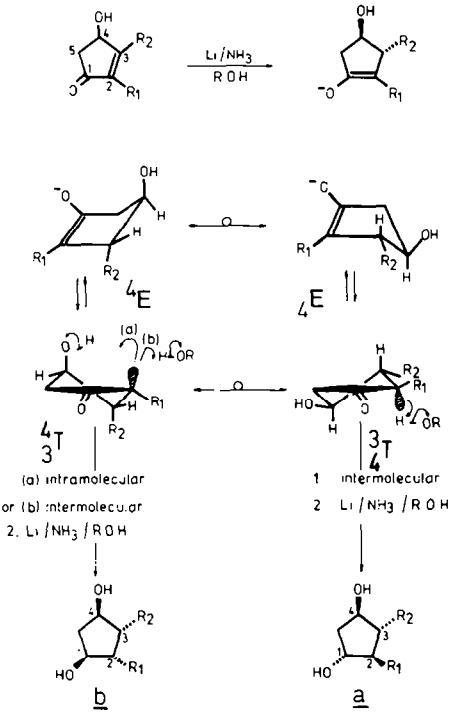
Abstract—The stereochemical outcome of the lithium–liquid ammonia reduction of 2,3-dialkyl-4-hydroxy-2-cyclopentenones and 2,3-dialkyl-2-cyclopentenones possessing bulky substituents (i-propyl and t-butyl) is investigated, using different proton donors. The relative configuration of both alkyl groups in the reduction products is interpreted on the basis of the geometry of the transition state for protonation of the intermediate enolate anions formed during the reduction.

In a previous paper[1] we discussed the proton donor dependent stereoselectivity of the lithium–liquid ammonia reduction of 2,3 - dimethyl - 4 - hydroxy - 2 - cyclopentenone **1** (Scheme 1; $R_1 = R = CH_3$). The results clearly demonstrate that the two consecutive reduction steps lead predominantly to a trans relationship between the hydroxyl groups and the vicinal alkyl substituents, thus yielding nearly exclusively (>90%) the two cyclopentanediols **2a** and **2b** ($R_1 = R_2 = CH_3$).[2] The relative configuration of the two alkyl side chains is determined solely by the protonation of the intermediate enolate anion; whereas intermolecular protonation leads to a 2,3-cis-dialkylcyclopentanediol **2b** or to a 2,3 - trans - dialkylcyclopentanediol **2a**, the competing intramolecular protonation yields exclusively the former product. Indeed, the further reduction of the saturated ketone was found to occur much faster than epimerisation at the α-position of the carbonyl group. We could furthermore prove that the acidity of the proton donor is of crucial importance in determining the degree of competition between the two modes of protonation and thus the overall stereochemical outcome of the reduction (namely the ratio of **2b**:**2a**).



Scheme 1. Stereochemical course of the lithium–liquid ammonia reduction of (4-hydroxy)-2,3-dialkyl-2-cyclopentenones.

Dissolving metal reductions are generally expected to yield the more stable products[3-10] (e.g. with all substituents equatorial). Consequently, the favoured transition state for protonation, which must lead to the typical hydroxy-ketone should resemble the twist conformations $^4_3$T (leading to the cis-products **2b**) and/or $^3_4$T (leading to the trans-products **2a**) in accordance with "product development control".[7] The results obtained for the dimethyl derivatives **1**† and **3** can be interpreted in favor of this, since the trans-dialkyl compounds are formed predominantly.‡

In order to determine the role of steric effects on the stereochemical outcome of the reduction, the present study was undertaken, involving 2,3 - dialkyl - 2 - cyclopentenones, **9** and **14**, and 2,3 - dialkyl - 4 - hydroxy - 2 - cyclopentenones, **6**, **12**, **17**, and **20**, possessing large alkyl side chains (i-propyl and t-butyl). The same set of proton donors was used as in the previous study. The different reductions were all carried out under the same experimental conditions.§

Our results now clearly support the view that the transition state, involved during the protonation of the intermediate enolate anion, resembles the reactants in geometry and that the resulting stereochemistry is

[a] Previous paper in this series: P. De Clercq, M. De Smet, K. Legein, F. Van Hulle and M. Vandewalle, *Bull. Soc. Chim. Belges*, **85**, 503 (1976).

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†Except for the reductions carried out with less acidic proton donors, where competing intramolecular protonation occurs.

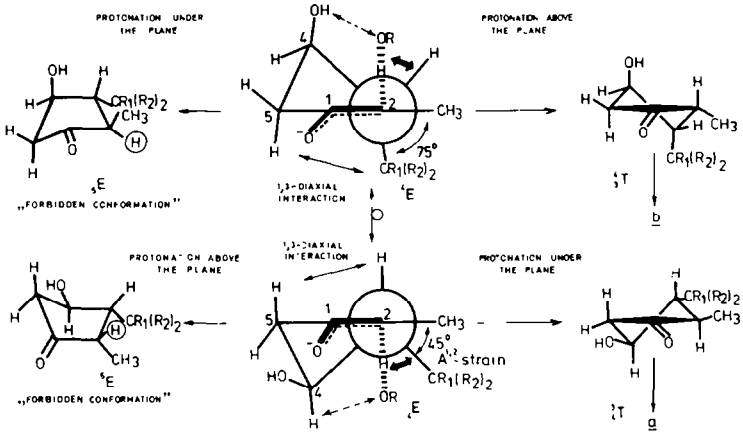
‡In agreement with the preferred twist conformation $^4_3$T.

§The configurational assignment of the resulting diols is given in the following paper.[19]

determined only by a combination of steric interference, torsional strain, and electrostatic effects in the transition state. A similar situation has been suggested for halogenation and alkylation of carbonyl compounds.[11]

Some important conclusions can be drawn from a superficial study of our results. The nearly exclusive presence of reduction products possessing either configuration **a** or **b** indicates that the reduction again leads to a trans configuration between the hydroxyl group and the vicinal alkyl group. The presence of smaller amounts partially reduced products in the reduction of compound **14** compared to **3** can partly be explained on the basis of decreased acidity of the ketone (or increased basicity of the corresponding enolate anion) compared to the alcohols used as proton donors (especially ethanol, i-propanol, and t-butanol) in liquid ammonia[13] (inductive effect of the t-butyl group versus the methyl group). At this point it should be noted that, in our opinion, the occurrence of partially reduced enones (e.g. **8** and **19**) is due to slow protonation of the enolate anion and consecutive elimination of the β-hydroxyl group in the resulting hydroxy-ketone during acid work-up, rather than to elimination of this hydroxyl function after the first reduction step.[13,14] It is also clear that in our case "product development control" does not give a true description of the transition state for protonation; indeed, in all cases the percentage of "less stable" cis-dialkyl products **b** formed is high, and in some cases nearly exclusive, e.g. **12** and **17**. Comparison of the amount saturated ketone recovered upon reduction of the cyclopentenones **3** and **9** also clearly indicates that other (e.g. steric) effects have to be considered. The analysis of the transition state for the protonation of the enolate anions formed during the reduction of 2,3 - dialkyl - 4 - hydroxy - 2 - cyclopentenones is rendered uneasy due to possible competitive intramolecular protonation. One can however expect that the use of "very acidic" (relative to the enolate anion; e.g. phenol, water or ammoniumchloride) proton donors will prohibit this mode of protonation to a large extent. This assumption is supported by the fact, that when phenol is used as proton donor the relative proportions of cis-dialkyl products versus trans-dialkyl products for the cyclopentenones, compared to the corresponding 4-hydroxy-products are nearly equal; we will therefore assume that in the reductions where phenol is used as proton donor, no intramolecular protonation occurs.

The proposed transition state for the intermolecular protonation of the enolate anions formed during the lithium liquid ammonia reduction of (4-hydroxy) - 3 - alkyl - 2 - methyl - 2 - cyclopentenones **1**, **3**, **6**, **9**, and **17** is depicted in Scheme 2. Two structures which resemble the reactants in geometry are considered, namely the two envelop conformations ^4E and $_4E$. The kinetic protonation[15] of the enolate anion at carbon must for stereoelectronic reasons[16] occur from a direction perpendicular



R_1=R_2=H ; **3** ; R_1=R_2=H , OH=H ; **6** ; R_1=R_2=CH_3 ; **9** ; R_1=R_2=CH_3 , OH=H ; **17** ; R_1=H , R_2=CH_3, Ph, CH_3, C_2H_5, i-C_3H_7 or t-C_4H_9.

Scheme 2. Transition states for the intermolecular protonation of the enolate anions formed during the lithium–liquid ammonia reduction of (4-hydroxy)-3-alkyl-2-methyl-2-cyclopentenones.

†It is known that the more stable conformation for cyclopentanone is a C_2-form, the carbonyl placed at the bisectional position; the other generally considered conformations are definitely much higher in energy.

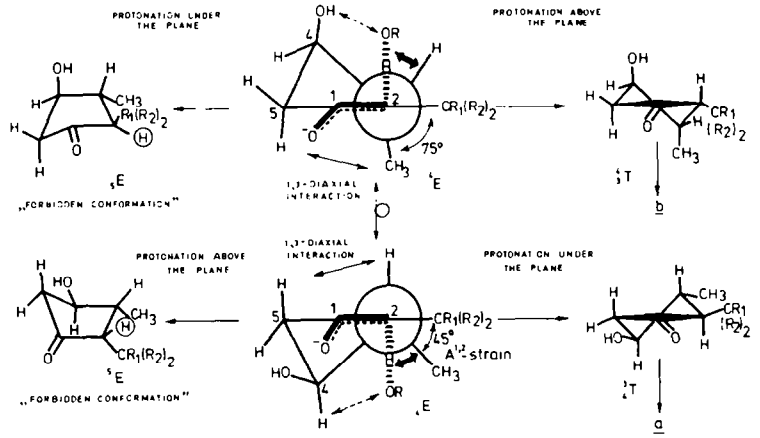
‡When competing intramolecular protonation can occur, clearly the envelop form with axial hydroxylgroup (^4E) will be involved in the transition state.

§In spite of the fact that the avenue for approach of the proton donor above the plane of the $_4E$ conformation is sterically less hindered (which is not true for the corresponding ^4E form) than from underneath the resulting ^5E form is clearly destabilised for two reasons: the above mentioned unstable envelope conformation for the cyclopentanone and the induced strain due to the bisectional eclipsed substituents.

to the plane of the enolate anion and must give rise to a "classical" conformation for the resulting ketone (in our case a twist conformation).† Thus protonation of the ^4E form will occur from above the plane of the five-membered ring since only in this case a classical ^5_3T form can be obtained and will yield a cis-dialkyl reduction product **b** after the fast reduction of the ketone; analogously, the $_4E$ form will yield the trans-dialkyl products.‡§ Whereas conformation ^4E is destablised by a large 1,3-diaxial interaction, the alternative $_4E$ form suffers from a serious non bonded repulsion; the dihedral angle between the two alkyl groups is small (45°, compared to 75° in the ^4E form) and will result in a

considerable $A^{1,2}$-strain.[17,18] Although the transition state involving the ^4E form avoids substantial torsional strain compared to the $_4E$ form (heavy arrow), more pronounced steric interference (hydroxyl vs hydrogen; dotted arrow) with axial substituents is present. Consideration of the results of the reduction of cyclopentenone **9** using phenol as proton donor, indicates that the protonation is slow (24% ketone is recovered after long reaction times)† and yields approximately equal amounts of products **a** and **b**. This can be understood in terms of equal potential energy of both transition states, involving the preferred $_4E$ conformation (no large 1,3-diaxial interaction) but faster protonation of the ^4E form (due to the absence of substantial torsional strain). The use of larger (and less acidic) proton donors leads naturally to the recovery of larger (and in the case of i-propanol and t-butanol nearly quantitative) amounts of partially reduced ketone **11**. The reduction of the corresponding 4-hydroxy-cyclopentenone **6** yields, as expected, comparable percentages cis- and trans-dialkyl products **7a** and **7b** using phenol as proton donor. Naturally, the use of less acidic proton donors favors the intramolecular protonation and thus yields relatively more cyclopentanediol **7b** (between 85% and 90%). With t-butanol as proton donor 43% ketone **8** is recovered whereas the reduction of the corresponding dimethyl derivative **1** yields only the cyclopentanediols **2**; this can easily be understood on the base of the much higher potential energy of the transition state for protonation in the case of the t-butyl compound and thus slower protonation (even in the case of intramolecular protonation of the ^4E form). Interestingly, reduction of the corresponding i-propyl compound **17** yields a larger fraction cis-dialkyl product **18b** (compared to **7b**) when phenol is used as proton donor. Whereas the destabilising factor for the $_4E$ form (namely the $A^{1,2}$-strain) is still present, the 1,3-diaxial interaction present in the ^4E conformation can be partly avoided when comparing an i-propyl group with a t-butyl group;‡ thus the resulting relative stabilisation of the ^4E or leads to a larger amount cis-product **18b**. This phenomenon will be even more accentuated when intramolecular protonation occurs; indeed, the other proton donors yield a still more important fraction cis-product **18b** (between 90 and 96%).

A similar transition state is proposed for the intermolecular protonation of the enolate anions formed during the reduction of the isomeric cyclopentenone **14** and the 4-hydroxycyclopentenones **12** and **20** (Scheme 3). The reduction of the cyclopentenone **14** leads nearly quantitatively to the cyclopentanols **15a** and **15b**, using phenol as proton donor. The less acidic proton donors also yields less ketonic material than was found with the dimethyl derivative **3**. Clearly, the presence of the t-butyl group is responsible for the higher basicity of the corresponding enolate anions (inductive effect). Since the transition state involving the $_4E$ conformation is badly destabilised by a large $A^{1,2}$-strain (and higher torsional strain than the alternative ^4E form), the stereochemical outcome of the reduction is strongly in favor of the



Scheme 3. Transition states for the intermolecular protonation of the enolate anions formed during the lithium–liquid ammonia reduction of (4-hydroxy)-2-alkyl-3-methyl-2-cyclopentenones.

†Using normal reaction times 65% ketone **11** is recovered compared to 17% of the corresponding dimethyl ketone **5**, indicating a slower reaction and thus a higher activation energy for protonation.

‡The $-\Delta G°$ value for interconversion of substituted cyclohexane derivatives equals 1.69, 2.15 and >4.5 (!) for respectively a methyl, i-propyl and t-butyl group; J. A. Hirsch, In *Topics in Stereochemistry* (Eds. N. L. Allinger and E. L. Eliel), Vol. 1, p. 199. Wiley, New York (1967).

§The smaller proportion of the latter product formed in the reductions with the less acidic proton donors is not expected, but could be due to partial epimerisation at the α-carbon atom in the presence of "stronger" bases (methoxide and t-butoxide versus phenol).

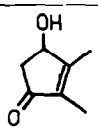
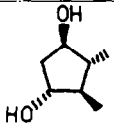
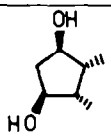
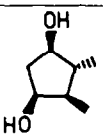
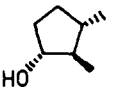
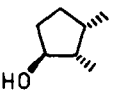
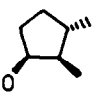
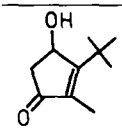
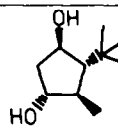
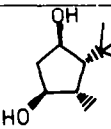
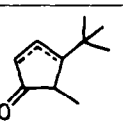
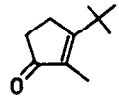
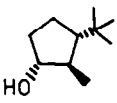
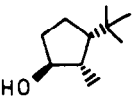
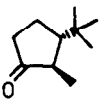
cis-dialkyl product **15b** (namely 81.5% yield with phenol).§

The corresponding 4-hydroxy-derivative **12** yields the same proportion of cis-dialkyl and trans-dialkyl products as in the case of **14**, when phenol is used as proton donor. However, the occurrence of competing intramolecular protonation using the less acidic proton donors leads to higher yields of cyclopentanediol **12b**. Comparison of the alternative envelop conformation (^4E and $_4E$) which are involved in the transition state for the protonation of the enolate anions formed upon reduction of the two isomeric cyclopentenolones **17** and **20**, enables one to understand the somewhat unexpected results obtained for the

reduction of product **20**. The $_4E$ conformation for both isomers can be considered equal in energy (the same $A^{1,2}$-strain is present in both structures); the different ^4E conformation should also possess nearly the same potential energy since in the case of **17** the i-propyl group can largely avoid 1,3-diaxial interaction. When comparing the results of both reductions the determining factor will be the torsional strain involved in the transition state when considering the $_4E$ forms. Since this strain is consistently larger in the case of the reduction of **17** (Scheme 2), one expects a larger proportion of trans-dialkyl product **21a** to be formed when the cyclopentenolone **20** (Scheme 3) is reduced (e.g. in the case of phenol **a** : **b** is 49 : 55 for **20** and 21 : 79 for **17**). Again the use of less acidic proton donors favors the occurrence of intramolecular protonation and thus the occurrence of products **b** (73–82%).

As a conclusion it may be pointed out that the stereochemical outcome of the lithium–liquid ammonia reduction of 2,3 - dialkyl - 2 - cyclopentenones and 2,3 - dialkyl - 4 - hydroxy - 2 - cyclopentenones is largely dependent on the stereochemistry of protonation of the enolate anions which are formed as intermediates during the reaction. Investigation of the transition states for protonation of an enolate anion is a difficult task, especially because under "normal" (i.e. non-reductive)

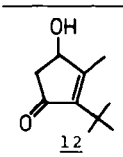
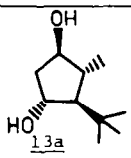
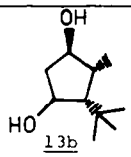
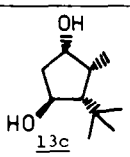
Table 1.

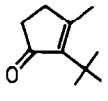
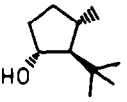
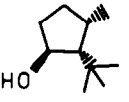
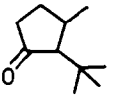
 1	 2a	 2b	 2c		Σ % diol trans alkyl	Σ % diol cis alkyl
phenol	67 %	26 %	7 %		74	26
methanol	62 %	28 %	10 %		72	28
ethanol	52 %	43 %	5 %		57	43
i.propanol	33 %	60 %	7 %		40	60
t.butanol	21 %	74 %	5 %		26	74
 3	 4a	 4b	 4c	 5	Σ % alcohol trans alkyl	Σ % alcohol cis alkyl
phenol	60 %	19 %	4 %	17 %	77	23
methanol	72 %	20 %	2 %	6 %	78	22
ethanol	72 %	23 %	-	5 %	76	24
i.propanol	48 %	19 %	3 %	30 %	72	28
t.butanol	17 %	7 %	7 %	69 %	77	23
 6	 7a	 7b		 8	Σ % diol trans alkyl	Σ % diol cis alkyl
phenol	41 %	48 %		9 %	46	54
methanol	12 %	76 %		12 %	14	86
ethanol	8 %	65 %		27 %	11	89
i.propanol	8 %	47 %		45 %	14.5	85.5
t.butanol	8 %	49 %		43 %	14	86
 9	 10a	 10b		 11	Σ % alcohol trans alkyl	Σ % alcohol cis alkyl
phenol	44 %	32 %		24 %	58	42
methanol	24 %	1 %		75 %		
ethanol	5 %	<< 1 %		95 %		
i.propanol	2 %	-		98 %		
t.butanol	2 %	-		98 %		

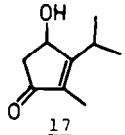
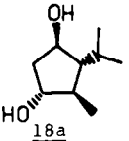
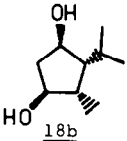
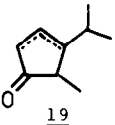
Total yield : > 95 %

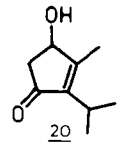
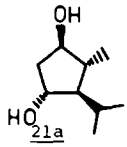
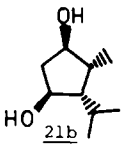
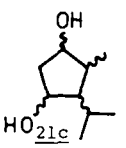
Concentration on substrate : $\pm$ 10^{-1} mol/liter

Table 1 (*contd.*)

 12	 13a	 13b	 13c	Σ % diol trans alkyl	Σ % diol cis alkyl
phenol	16 %	80 %	4 %	16	84
methanol	3 %	90 %	5 %	3	95
ethanol	7 %	86 %	7 %	7	93
i.propanol	3 %	89 %	8 %	3	97
t.butanol	4 %	89 %	7 %	4	96

 14	 15a	 15b	 16	Σ % alcohol trans alkyl	Σ % alcohol cis alkyl
phenol	16 %	81.5 %	2.5 %	16.5	83.5
methanol	30 %	68 %	2 %	30.5	69.5
ethanol	23 %	62 %	15 %	27	73
i.propanol	19 %	69 %	12 %	21.5	78.5
t.butanol	20 %	65 %	15 %	23.5	76.5

 17	 18a	 18b	 19	Σ % diol trans alkyl	Σ % diol cis alkyl
phenol	17 %	63 %	20 %	21	79
methanol	7 %	70 %	23 %	9	91
ethanol	5 %	74 %	21 %	6.5	93.5
i.propanol	3 %	72 %	25 %	4	96
t.butanol	3 %	67 %	30 %	4.25	95.75

 20	 21a	 21b	 21c	Σ % diol trans alkyl	Σ % diol cis alkyl
phenol	45 %	49 %	6 %	45	55
methanol	24 %	73 %	3 %	24	76
ethanol	17 %	80 %	3 %	17	83
i.propanol	15 %	82 %	3 %	15	85
t.butanol	16 %	80 %	4 %	16	84

Total yield : > 95 %

Concentration on substrate : $\pm$ 10^{-1} mol/liter

conditions epimerisation in α-position of the carbonyl group can easily occur.[20] The trapping of the ketone (by means of a fast reduction to the alcohol) does not allow this phenomenon to occur. Thus our model systems are ideally suited to study the mechanism of such a protonation.

We feel that the transition state we have proposed for the special case of protonation of an enolate anion, derived from a 5-membered ring ketone, in liquid ammonia, could be in fact quite more general.

EXPERIMENTAL

2-t-Butyl-3-methyl-1,4-cyclopentanediols **7a (13a), 7b (13b), 13c**

Compound **6** or **12**[19] (1 g, 6 mmol) dissolved in anhydrous alcohol (1·5 mmol) and dry tetrahydrofurane (10 ml) was added to liquid ammonia (60 ml, distilled from sodium). Lithium (0·34 g, 48 mmol) was added in small pieces over a period of 10 min. After 1 h the excess lithium was destroyed with ammonium chloride, the ammonia was evaporated off, ether was added and the inorganic salts filtered off. After acidifying with dil HCl, the water layer was extracted six times with ether. The combined ether extracts were dried (Na_2SO_4) and evaporated. Yield 96%. TLC: $R_f = 0{\cdot}36$ (silicagel, ethylacetate). All experiments were carried out in duplicate.

1,4-Diacetoxy-2-t-butyl-3-methylcyclopentanes

A solution of the diols **7a**, **7b** in acetic anhydride (10 ml) and dry pyridine (10 ml) were stirred at room temp. for 2 h. The reaction mixture was poured on to ice and extracted (after 30 min) with

n-pentane. The extract was washed with 2% aq HCl, dried (Na_2SO_4) and evaporated. Yield 97%. TLC: $R_f = 0{\cdot}75$ (silicagel, ethylacetate). The crude diacetates were analysed by GC, using a Varian 1400, on OV17 (5% on Chromosorb W, 3 m, linear temperature 150°C, 4°C min^{-1}). Configurational assignment of the isomers follows from ^1H NMR spectroscopy (see following paper[19]).

2-5-butyl-3-methylcyclopentanols **15a**, **15b** *and 3-t-butyl-2-methylcyclopentanols* **11a**, **11b**

Reduction of **9** and **14** was carried out under the same experimental conditions as described for **6**. Preparative GC of the alcohols was carried out on Carbowax 20 M (10% on Chromosorb G) at 180°C.

4-Hydroxy-2-methyl-3-i-propyl-2-cyclopentenones **17** *and* **20**

The two isomeric cyclopentenolones **17** and **20** were prepared in the same way as described for **6** and **12**.[19] For product **17**, TLC: $R_f = 0.35$ (silicagel, ether-isooctane 7/3). UV: λ_{max}(methanol) = 230 nm. IR: strong absorptions at 3400 (broad), 2980, 1690, 1620, 1480, 1390, 1370, 1230, 1030, and 950 cm^{-1}. ^1H-NMR (100 MHz, CCl_4); 2-CH_3: $\delta = 1{\cdot}67$ (m = 2, $^5J = 1{\cdot}3$ Hz); 3-CH: $\delta = 2{\cdot}96$ (m = 7, $^3J = 7{\cdot}0$ Hz); 3'-$C\underline{H}_3$: $\delta = 1{\cdot}27$ (m = 2); 3'-$C\underline{H}_3$: $\delta = 1{\cdot}23$ (m = 2); 4-C$\underline{H}$: $\delta = 4{\cdot}82$; 5-$CH_A\underline{H}_B/\delta = 2.59$ (m = 4) and 5-$C\underline{H}_AH_B/\delta = 2{\cdot}14$ (m = 4); ABX-system ($J_{AB} = -18{\cdot}4$ Hz; J_{AX}(trans) = 2·0 Hz; J_{BX}(cis) = 6·2 Hz). Found: C, 70·4; H, 9·25%. $C_9H_{14}O_2$ requires C, 70·099; H, 9·15%. For product 20. TLC: $R_f = 0{\cdot}35$ (silicagel, ether-isooctane 7/3). UV: λ_{max}(methanol) = 230 nm. IR: strong absorption at 3390 (broad), 2980, 1690, 1620, 1480, 1390, 1370, 1230, 1030, and 980 cm^{-1}. ^1H-NMR: (100 MHz, CCl_4); 3-$C\underline{H}_3$: $\delta = 2{\cdot}07$ (m = 2, $^4J = 0{\cdot}4$ Hz); 2-C$\underline{H}$: $\delta = 2{\cdot}71$ (m = 7, $^3J = 7{\cdot}1$ Hz); 2'-$C\underline{H}_3$: $\delta = 1{\cdot}13$ (m = 2); 2'-$C\underline{H}_3$: $\delta = 1{\cdot}12$ (m = 2); 4-C$\underline{H}$: $\delta = 4{\cdot}54$; 5-$CH_A\underline{H}_B/\delta = 2{\cdot}71$ (m = 4) and 5-$C\underline{H}_AH_B/\delta = 2{\cdot}13$ (m = 4); ABX-system ($J_{AB} = -18{\cdot}2$ Hz; J_{AX}(trans) = 2·1 Hz; J_{BX}(cis) = 6·5 Hz). found: C, 71·2; H, 9·28. $C_9H_{14}O_2$ requires: C, 70·099; H, 9·15%.

2-Methyl-3-i-propyl-1,4-cyclopentanediols **18a** (**21a**), **18b** (**21b**)

Reduction of **17** and **20** and conversion to the diacetates were carried out under the same conditions as described for **6**. The isomeric distribution was measured via analytical GC on 5% OV17 (Chromosorb W, 3 m, linear temp. 120°C, 4°C min^{-1}). Preparative GC on Carbowax 20M (10% Chromosorb G) at 190°C.

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