10,11-dimethyltricyclo[4.3.2.$0^{1,6}$]undec-10-en-7-one (6) and 10% 2,3-dimethyltricyclo[5.4.0.$0^{3,7}$]undec-1-en-4-one (9). The same mixture was obtained by acid treatment of 9 for 12 hr. at room temperature (23–26°) in benzene solution. Treatment of 6 in the above manner gave the same 90:10 mixture of 6 and 9.

Reduction of 6.—Lithium aluminum hydride was added to a solution of 46 mg. (0.24 mmole) of 6 in 5 ml. of dry ether until vigorous reaction had subsided. The reaction mixture was stirred for 2 hr. Water was added slowly to decompose unreacted hydride, followed by 10% sulfuric acid to dissolve hydroxides. The ether layer was separated and the aqueous layer was extracted twice with 10-ml. portions of ether. The ethereal solutions were combined and dried. After removal of the ether at reduced pressure, the residual oil was distilled in a short-path still, bath temperature 80° (0.55 mm.). After having stood overnight in a refrigerator, the distillate solidified. The solid was sublimed, yielding 34.5 mg. (75.1%) of **16**, m.p. 34–35°.

10,11-Dimethyltricyclo[4.3.2.$0^{1,6}$]undec-10-en-7-ol (**16**), $C_{13}H_{20}O$, had mol. wt. 192.25[6]; $\nu_{\max}^{CCl_4}$ 3620, 3450 (broad), and 1690 cm.$^{-1}$; and τ = 8.52 (s) (3H), 8.41 (s) (3H), and 6.40 (m) (1H) p.p.m.

Anal. Calcd. for $C_{13}H_{20}O$ (192.25): C, 81.20; H, 10.48. Found: C, 80.98; H, 10.20.

Reduction of 9.—Reduction of 85 mg. (0.45 mmole) of **9** in the manner described for reduction of **6** yielded 65 mg. (75%) of a single alcohol (**17**), m.p. 61–62°.

2,3-Dimethyltricyclo[5.4.0.$0^{3,7}$]undec-1-en-4-ol (**17**), $C_{13}H_{20}O$, had mol. wt. 192.25[6]; $\nu_{\max}^{CCl_4}$ 3620, 3470 (broad), and 1700 cm.$^{-1}$; and τ = 8.90 (s) (3H), 8.48 (s) (3H), and 6.50 (m), (1H) p.p.m.

Anal. Calcd. for $C_{13}H_{20}O$ (192.25): C, 81.20; H, 10.48. Found: C, 81.18; H, 10.41.

Pyrolysis of 17.—Pyrolysis of 40 mg. (0.21 mmole) of **17** in a sealed, evacuated, 0.5 × 5 cm. Pyrex tube, maintained at 340–350° for 10 min. in an electric furnace, gave a yellow pyrolysate which was found by vapor phase chromatography to be a mixture of several compounds. The major component (**18**, *ca.* 40%) was isolated by gas chromatography (DEGS).

2,3-Dimethylbicyclo[5.4.0]undec-2-en-4-one (**18**), $C_{13}H_{20}O$, had mol. wt. 192.25[6]; $\nu_{\max}^{CCl_4}$ 1670 and 1625 cm.$^{-1}$; $\lambda_{\max}^{EtOH}$ 258 mμ (ϵ 8750); τ = 8.26 (s) (6H) p.p.m.; and 2,4-dinitrophenylhydrazone m.p. 147–148° from ethanol.

Anal. Calcd. for $C_{19}H_{24}N_4O_4$ (372.41): C, 61.27; H, 6.48; N, 15.05. Found: C, 61.68; H, 6.17; N, 15.28.

Degradation of 18. A. Permanganate–Periodate Oxidation.[35]—The oxidant was prepared by dissolving 200 mg. of potassium carbonate, 21 mg. of potassium permanganate, and 1.205 g. of sodium metaperiodate in 120 ml. of water and adjusting the pH to 7.7 with sodium hydroxide solution. To 95 ml. of this solution was added 61 mg. (0.32 mmole) of **18** in 3 ml. of dioxane. The solution was stirred at room temperature for 40 hr. After acidification with 5 ml. of dilute sulfuric acid and addition of 2 ml. of saturated sodium bisulfite solution, the reaction mixture was extracted with three 50-ml. portions of ether. The ethereal extracts were combined and washed with saturated sodium bicarbonate solution. The bicarbonate washings were acidified and extracted with several portions of ether. The ethereal solution was dried and then concentrated to a brown oil which has an infrared spectrum indicative of a keto acid (**19**): $\nu_{\max}^{neat}$ 3100 (broad), 1735, and 1710 cm.$^{-1}$.

B. Hypochlorite Oxidation.—The oil obtained from the Lemieux oxidation was dissolved in 3 ml. of 2 *N* potassium hydroxide and 5 ml. of 5.4% sodium hypochlorite solution was added. After the reaction mixture had been stirred for 6 hr., sodium sulfite was added to destroy excess hypochlorite. The solution was then acidified with hydrochloric acid and extracted with three 25-ml. portions of ether. After the extract was dried, the ether was distilled, leaving an oily residue which crystallized when cooled by a stream of nitrogen (25 mg., 41% from **18**). The residue was dissolved in hot water and the solution deposited white crystals, m.p. 139–140°, upon cooling. The infrared spectrum of these crystals is superimposable upon that of authentic *trans*-3-(2-carboxycyclohexyl)propionic acid (**20**).[16] Further recrystallization from hot water gave colorless crystals, m.p. 141–142°, which showed no melting point depression upon admixture with authentic acid.

Acknowledgment.—We are grateful to Mr. P. Chastagner and to Professor A. L. Burlingame for the mass spectra of our compounds. We thank the Research Corporation for a Frederick Gardner Cottrell Grant and the National Science Foundation for as institutional grant toward the purchase of a Varian A-60 n.m.r. spectrometer.

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Configurations of Epimeric 6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ols and Corresponding Aldols. Stereochemistry of the Aldol Condensation

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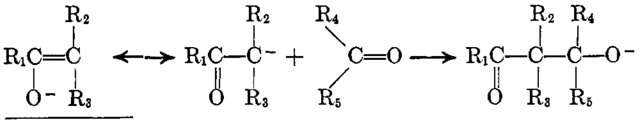
Received June 28, 1965

The configurations of four epimeric 6-hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ols (IIIa–d), derived from the corresponding aldols (IIa–d) by Cannizzaro or lithium aluminum hydride reduction, have been established. Manganese dioxide oxidation of the glycols produced the related ketols (Va and b) which were reduced with lithium aluminum hydride to regenerate the glycols having equatorial C-1 hydroxyl. The infrared frequency differences, $\Delta\nu$, between free and intramolecularly bonded hydroxyl stretching frequencies were determined for the glycols IIIa–d and their unsaturated analogs and compared with values for related substances of known configuration. The assignments of configuration and isomer distribution of the cyclic aldols (IIa–d) formed under conditions of kinetic and thermodynamic control at 25 and 110° are discussed relative to the known facts regarding aldol-condensation stereochemistry. A transition state which does not resemble products and repulsions between bulky groups in the acyclic precursor at, or removed from the bond-forming site, appear to be important features of aldol-condensation stereochemistry.

The aldol condensation is an important example of a nucleophilic addition of a carbanion (enolate anion) to a double bond (C═O). Knowledge of the stereochemistry of this[2] and other[3,4] additions of carbanions to double bonds is limited. The related Michael addition involves addition of a carbanion to an olefinic double bond of a conjugated system, *e.g.*, C═C—C═O.



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[1] Organic Chemistry Branch, Chemistry Division, U. S. Naval Ordnance Test Station, China Lake, Calif.

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TABLE I

EPIMERIC 6-METHYLOL-5-PROPYL-2,4,6-TRIETHYL-2-CYCLOHEXEN-1-OLS (IIIa–d)

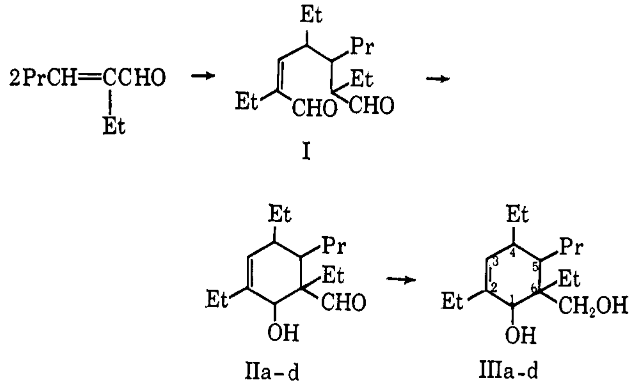
Isomer	M.p. or b.p. (mm.), °C.	Distribution at 110°,[a] % ± *ca.* 3	Hydroxyl stretching bands, ν, cm.$^{-1}$[b] ν_{free}	ν_{bonded}	$\Delta\nu$, cm.$^{-1}$	Stereochemistry OH at C-1	CH$_2$OH at C-6	OH/CH$_2$OH
IIIa	134–135 (0.4)	55[c]	3638	3606 3538	32 100	e′	a	*cis*
IIIb	62–62.5	30	3637 3541	3607	30 96	a′	e	*cis*
IIIc	90–91	10	3639	3531	108	e′	e	*trans*
IIId	112–113	5	3638	3622 (sh) 3531 (w)	16 107	a′	a	*trans*

[a] Formed in refluxing aqueous sodium hydroxide solution.[20] [b] In carbon tetrachloride (*c* 0.006 *M*). [c] Predominant isomer formed at 25° (*ca.* 99%) with 1% IIIc in methanol–water (65 to 35%).

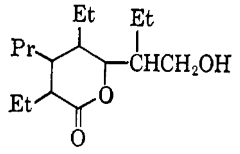
Most Michael additions to cyclic unsaturated systems produce *trans* products (*trans* disposition of bulky groups whether involved in stereochemistry of enolization or not)[5,6]; similar results are found in Michael additions leading to alicyclic systems.[7] The few examples of Michael additions leading to *cis* orientation of groups at the bond-forming site appear to involve strong repulsions between polar groups (nitro, cyano)[8] in cyclic products. The configuration of products obtained by addition of Grignard reagent (putative carbanion) to carbonyl compounds has been explained in terms of simple bulk of suitable substituents, under kinetically controlled conditions.[4,9] The repulsion of bulky groups at or near the bond-forming site in the transition state leading to products in the Michael and Grignard addition appears also to be a feature of examples of aldol-condensation stereochemistry examined in the present study.

The literature relating to the aldol condensation is voluminous.[10] The mechanism is well understood and documented,[11] but very little is known about its stereochemistry.[2] Aldols and ketols required are often susceptible to retrogression to reactants and/or dehydration to the corresponding α,β-unsaturated carbonyl compounds. Also, the facile equilibration of certain aldols through their enolate anions, as well as by retrogression, contribute to the paucity of examples of kinetically controlled aldol formation.[2,12–15] (These same problems apply to many studies of Michael-addition stereochemistry, but not to Grignard addition.) Assignments of aldol configuration and studies of related equilibria have been very limited.[2,12–18]

The present work assigns configuration to epimeric cyclic aldols (IIa–d) derived from 2-ethyl-2-hexenal by way of an intermediate dialdehyde (I) formed by Michael addition of 2-ethyl-2-hexenal to itself. This has been done by relating the configurations of the aldols to those of the corresponding glycols (IIIa–d).



The self-condensation of 2-ethyl-2-hexenal in aqueous methanolic potassium hydroxide at 25° produces epimeric aldols (IIa–d) and glycols (IIIa–d) and a lactone (IV).[19–21] The aldols are the favored products at short reaction time (maximum total yield of 45% in 30 min.) and are the precursors, by hydride transfer reactions, of the lactone and glycols. When the reaction is conducted in aqueous sodium hydroxide at reflux temperature (110°), no aldol is isolated, but there is obtained a mixture of the related glycol diastereoisomers (IIIa–d) (Table I)[20]; at 25° in aqueous methanol one of these glycol isomers (IIIa) predominates (99%). By lithium aluminum hydride reduction of the aldol mixture (IIa–d) obtained at 25° it was shown to exist principally (95–99%) as IIa, having the same configuration as glycol isomer IIIa. The con-



IV

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[15] W. S. Johnson, J. Ackerman, J. F. Eastham, and H. A. De Walt, *ibid.*, **78**, 6302 (1956).

[16] W. F. Johns, *J. Org. Chem.*, **26**, 4583 (1961).

[17] K. Tanabe and Y. Morisawa, *Chem. Pharm. Bull.* (Tokyo), **11**, 536 (1963); *Chem. Abstr.*, **59**, 7600 (1963).

[18] K. Tanabe, R. Hayashi, and R. Takasaki, *Chem. Pharm. Bull.* (Tokyo), **9**, 1 (1961); *Chem. Abstr.*, **60**, 9331 (1964).

[19] A. T. Nielsen, *J. Am. Chem. Soc.*, **79**, 2518, 2524 (1957).

[20] A. T. Nielsen, *J. Org. Chem.*, **28**, 2115 (1963).

[21] R. Pummerer and J. Smidt, *Ann.*, **610**, 192 (1957).

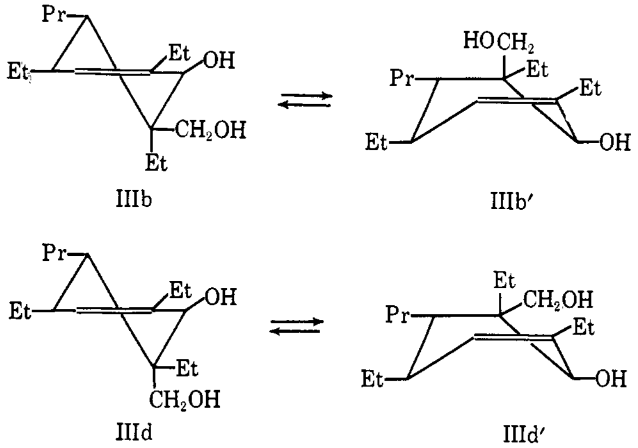


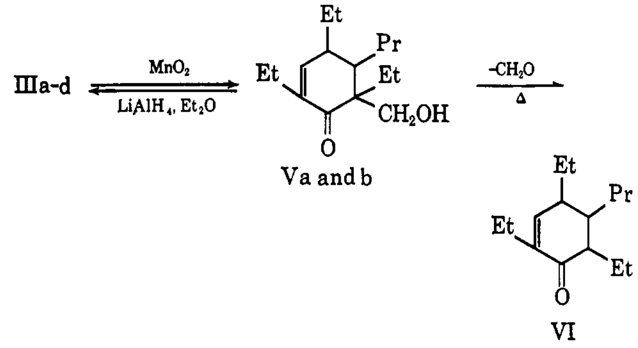
Figure 1.—Half-chair and boat forms of glycols IIIb and IIId.

figuration of lactone IV had been established previously.[19]

The configurations of C-4 ethyl and C-5 propyl in the aldols (IIa–d) and glycols (IIIa–d) are designated equatorial from previous work,[19] as well as the present finding that aldols IIa–d can be formed under equilibrium conditions which allow equilibration at C-4 and C-6 through acyclic precursor I. Three methods were employed to establish C-1–C-6 stereochemistry of the glycol isomers IIIa–d.

Configuration Assignments

Assignment of epimeric pairs at C-1 and C-6 in glycols IIIa–d was made by manganese dioxide oxidation of them in cyclohexane solvent to yield ketols, Va and b, followed by lithium aluminum hydride reduction of the ketols in ether to regenerate the glycols. Liquid glycol (IIIa) and the highest melting (112°) glycol (IIId) were found to be epimeric at C-1. Each produced a liquid ketol (Va, λ_{max} 243 mμ) which on reduction regenerated only the liquid glycol IIIa. Similarly, glycols IIIb (m.p. 62°) and IIIc (m.p. 90°) were found to be epimeric at C-1. Both produced a liquid ketol (Vb, λ_{max} 240 mμ) which on reduction formed a mixture of glycols IIIb (10%) and IIIc (90%). Each ketol (Va and b) was readily demethylolated by heating[20] to produce 5-propyl-2,4,6-triethyl-2-cyclohexen-1-one (VI), the structure of which had been established previously.[19,20]



The lithium aluminum hydride reduction of cyclohexanones[22–25] and 2-cyclohexen-1-ones[26] to the corresponding alcohols has been studied. The predominant product formed in refluxing ether solvent has an equatorial hydroxyl (*e.g.*, menthone → menthol[22]), its formation being favored by higher temperature.[25] Carvone has been reduced to carveol, 92% of the product having the *cis* pseudo-equatorial hydroxyl configuration.[26] Some exceptions to the rule of preponderate formation of equatorial hydroxyl are known[23–25]; 3,3,5-trimethylcyclohexanone affords 55% axial hydroxyl product in ether at 30°.[24,25] It has been concluded[4,22] that, when each side of the carbonyl group is equally favored for attack, the most stable (equatorial hydroxyl) product results. This situation appears to be met in reduction of ketols Va and Vb; in our experiments these ketones each produced one principal glycol, IIIa (100%) and IIIc (90%), respectively, each assigned a C-1 pseudo-equatorial hydroxyl configuration. From these results and the established epimer relationships the complete C-1–C-6 stereochemistry may be assigned (Table I).

Evidence supporting these configuration assignments accrued by measuring the infrared frequency shift ($\Delta\nu$) between free and intramolecularly bonded hydroxyl stretching frequencies in the glycols IIIa–d. Many systematic studies of this property have been reported for various diols,[27–33] but none for unsaturated cyclic diols like III.

Infrared data obtained for glycols IIIa–d in 0.006 *M* carbon tetrachloride solution (Perkin-Elmer 621 grating instrument) are summarized in Table I. Only weak intramolecularly bonded hydroxyl stretching could be detected for the high-melting isomer IIId (attributed to boat form), affirming the *trans* diaxial arrangement of the C-1 hydroxyl and C-6 hydroxymethyl[30]; its C-1 epimer, the liquid IIIa, must have the *cis* configuration.

To attempt assignment of C-1 hydroxyl configuration in the other glycol C-1 epimer pair (IIIb and c) on the basis of infrared spectra requires careful consideration. No studies of similar unsaturated diols are available for comparison with the exception of *cis*-1-hydroxy-2-hydroxymethyltetralin, $\Delta\nu$ 62[29,34,35] (see Table II). There are a few reports of dilute solution infrared spectra for substituted saturated 2-hydroxymethyl-1-cyclohexanols; these and values for *cis*- and *trans*-2-hydroxymethylcyclohexanol itself,[36] determined in the present work, are listed in Table II.

In addition to the hydrogen bonding to oxygen observed in glycols IIIa–d, there is evidence of transannu-

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[24] H. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

[25] P. T. Lansbury and R. E. Mac Leay, *J. Org. Chem.*, **28**, 1940 (1963).

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[27] (a) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); (b) *ibid.*, **76**, 4323 (1954); (c) *ibid.*, **80**, 5950 (1958).

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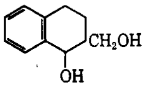
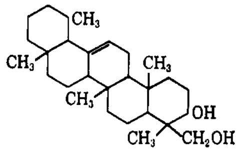
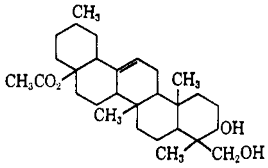
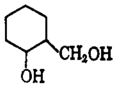
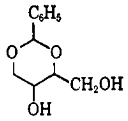
[35] In *cis*-1-hydroxy-2-hydroxymethyltetralin the hydroxymethyl group is believed to be equatorial and the hydroxyl axial. Its value of $\Delta\nu$ (62) is very low for a 1,3 glycol (usually greater than 70)[30,32] suggesting that the *trans* isomer probably has a value higher than 62.

[36] We are indebted to Professor A. T. Blomquist for samples of *cis*- and *trans*-2-hydroxymethyl-1-cyclohexanol; *cf.* A. T. Blomquist and J. Wolinsky, *J. Am. Chem. Soc.*, **79**, 6025 (1957).

TABLE II

SPECTROSCOPIC PROPERTIES OF 2-HYDROXYMETHYL-1-CYCLOHEXANOLS

Compound	No.	Stereochemistry		Hydroxyl stretching bands, ν, cm.$^{-1}$		Δν, cm.$^{-1}$	Ref.
		OH, CH$_2$OH	OH/CH$_2$OH	ν$_{free}$	ν$_{bonded}$		
	1	a′, e[a]	*cis*	3617	3555	62	29, 34
Urs-12-ene-3α,24-diol 	2	a, a	*trans*	3641	none	0	30
Urs-12-ene-3β,24-diol	3	e, a	*cis*	3629	3550	79	30
Methyl hederagenin 	4	e, e	*trans*	3643 3628 (sh)	3532	111	30
	5	(a, e)[a]	*cis*	3628	3541	87	*b*, 36
	6	e, e	*trans*[c]	3626	3539	87	*b*, 36
VIIa	7	e, a	*cis*	3636	3535	101[d]	*b*
VIIb	8	a, e	*cis*	3634	3534	100	*b*
	9	a, e	*cis*	3644	3545	99[e]	*f*
	10	e, e	*trans*	3644	3565	79[e]	*f*

[a] Probable conformation. [b] Present investigation. [c] Contains *ca.* 20% *cis* isomer. [d] Contains *ca.* 30% of ketol VIIIa. [e] Although this is not a cyclohexane derivative, the data are of interest; additional bands (3614 in 9, 3623 and 3590 in 10), attributed to hydrogen bonding to ring oxygens, complicate interpretation of these spectra. [f] S. A. Barker, A. B. Foster, A. H. Haines, J. Lehmann, J. M. Webber, and G. Zweifel, *J. Chem. Soc.*, 4161 (1963).

lar hydrogen bonding of the hydroxymethyl group to the olefinic double bond. Strong and distinct bonded hydroxyl stretching bands are observed at 3606 cm.$^{-1}$ in IIIa and 3607 cm.$^{-1}$ in IIIb (Δν 32 and 30, respectively) characteristic of nonallylic OH···π bonding.[28,29,37] These particular bands are absent in the corresponding reduced cyclohexane derivatives (VIIa and b; see below) and in isomers IIIc and IIId as well. The CH$_2$OH···π bonding occurs in the half-chair form of IIIa, but in order for such bonding to occur in IIIb, participation of its boat form (IIIb′) would appear necessary. A certain concentration of boat IIId′ evidently contributes to the small amount of OH···O bonding observed in IIId (weak band at 3531 cm.$^{-1}$, Δν 107). A band appearing as a shoulder at 3622 cm.$^{-1}$ (Δν 16) in IIId may possibly be attributed to allylic OH···π bonding in the half-chair form (expected Δν value 11–18[37]) rather than free secondary hydroxyl stretching or CH$_2$OH···π bonding. In isomer IIIc with both hydroxyl and methylol groups equatorial in the half-chair form no OH···π bonding is possible; since no such bonding is observed, there appears to be no significant contribution of a boat form with this isomer in solution. Chair forms of II and III with axial C-4 ethyl and C-5 propyl appear to be disfavored.[3,19]

The difference in free energy between the chair and boat forms of each isomer (Figure 1) is probably small, especially at higher temperatures. The equatorial arrangement of the C-1 hydroxyl in the boat forms of these isomers coupled with the additional energy of the developed hydrogen bond (CH$_2$OH···π in IIIb′ and CH$_2$OH···O in IIId′) would contribute significantly to the stability of these boat forms. In cyclohexene itself at 25° the half-chair conformation is favored over the boat by *ca.* 2.7 kcal./mole,[38,39] relative to the 5–6 kcal. difference for chair and boat forms of cyclohexane derivatives.[40] It is of interest

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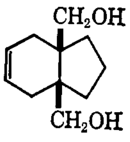
(37) P. v. R. Schleyer, D. S. Tripan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958). Compound i, for example, exhibits bands at 3635, 3480, and 3602 (w) cm.$^{-1}$ (Δν 33).[29] It has been pointed out that not all 4-methylolcyclohexenes show such bonding, even when bond angles and distances might easily accommodate it.[29]



i (*cis*)

(38) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

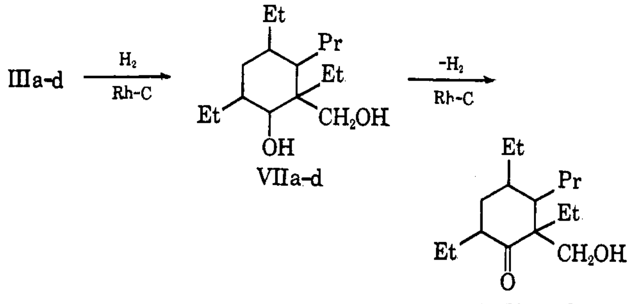
(39) Recent studies employing different methods all affirm the greater stability of the half-chair over the boat form of cyclohexene: (a) B. Rickborn and S. Lwo, *J. Org. Chem.*, **30**, 2212 (1965); (b) Z. Welvart, *Bull. soc. chim. France*, 2203 (1964); (c) A. Mc L. Mathieson, *Tetrahedron Letters*, 81 (1963); (d) E. G. Garbisch, Jr., *J. Org. Chem.*, **27**, 4249 (1962).

(40) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **82**, 2393 (1960).

that the conformation of the cyclohexene compound shikimic acid, having an allylic hydroxyl group, has been shown in a recent n.m.r. study to exist in the half-chair form with some deformation toward boat[41] (measurement in deuterium oxide at room temperature).

By making allowances for differences in ring geometry it should be possible to compare the spectra of the unsaturated glycols (Table I) with the data in Table II. Introduction of the double bond does not produce a large distortion of bond angles between the hydroxyl substituents. In cyclohexane- and cyclohexene-1,2-diols or -1,2-dimethanols, the value of $\Delta\nu$ is determined by the azimuthal angle between the vicinal substituents.[27-32] In molecules such as glycols IIIa–d the distortion in the half-chair form of the cyclohexene ring[37] forces the allylic substituents apart (111°) and the homoallylic substituents together (107°).[28,42-44] The net effect is for *trans* (C-1 and C-6, ee) substituents to have an azimuthal angle and $\Delta\nu$ value like that in a cyclohexane (net distortion, 0°), and *cis* (C-1 and C-6, ae) substituents to be forced farther apart (distortion effects additive, *ca.* 2°) leading to a larger azimuthal angle and slightly lower $\Delta\nu$ in the *cis* glycols.

Reduction of *cis* isomers IIIa ($\Delta\nu$ 100) and IIIb ($\Delta\nu$ 96) led to their cyclohexane analogs VIIa ($\Delta\nu$ 101) and VIIb ($\Delta\nu$ 100), respectively, by hydrogenation with rhodium–charcoal catalyst in ethanol solvent. [Hydrogenation of glycol IIIc led principally to a saturated ketol (VIIIb, ν 1690 cm.$^{-1}$) as a result of very facile dehydrogenation of glycol VIIc; some ketol formation (VIIIa and b) accompanied preparations of saturated glycols VIIa and VIIb (see Discussion below).] Isomer IIId was not hydrogenated, although it might be expected to behave like IIIa. Values of $\Delta\nu$ for 2-hydroxymethyl-1-cyclohexanols (60–110) are between those for cyclohexane-1,2-diols (30–50)[27] and cyclohexane-1,2-dimethanols (100–160).[28] No difference in $\Delta\nu$ could be detected between *cis*- and *trans*-2-hydroxymethyl-1-cyclohexanols (**5** and **6**, Table II, $\Delta\nu$ 87). The fused ring compounds (**1–4**, Table II) appear to be like the unsaturated glycols (Table I) in having lower $\Delta\nu$ values for the *cis* isomers. More data are needed to test these correlations. The related known spectral data, while limited, agree with configurations assigned to glycols IIIa–d on the basis of chemical evidence.



VIIa-d

VIIIa and b

A third series of experiments relating to the stereochemistry of glycols IIIa–d involved a determination of their relative rates of platinum-catalyzed oxidation to the corresponding ketols (Va and b). The reaction, including certain aspects of its stereochemistry, has been studied extensively.[45,46] Following the procedure described[46] for facile oxidation of the isomeric konduritols, employing 95% ethanol solvent, it was found that no reaction occurred within 2 hr. (complete absence of carbonyl absorption in the product, recovered reactant) *except* with isomer IIIc, which was oxidized very rapidly and quantitatively to ketol Vb.

The finding that isomer IIIc (C-1 pseudo-equatorial hydroxyl and C-6 equatorial hydroxymethyl) is notably unique in its ease of oxidation clearly implies that for the glycols IIIa–d the stereochemistry at C-1, alone, does not determine the metal-catalyzed oxidation rate. The konduritols oxidize at different rates which are not solely dependent on the configuration of the allylic hydroxyl; the fastest oxidation occurs with the isomer having an allylic pseudo-equatorial hydroxyl with an axial hydroxyl on the adjacent carbon. On the other hand, oxidation of each of the inositols occurs preferentially to convert axial hydroxyls to carbonyl.[45] With either cholestan-3-α- or -β-ol oxidation to cholestanone occurs with equal ease.[47] These observations imply that in large molecules there exists a unique manner of adsorption on the catalyst surface. A related finding[48] is that in hydrogenation of certain unsaturated compounds preferential adsorption of hydroxyl or methoxyl substituents on the catalyst surface determines stereochemistry of the hydrogenated product although this adsorption may otherwise be sterically disfavored. Dreiding models suggest that in isomer IIIc (but not in IIIa or IIId) orientation of hydroxymethyl and olefinic π electrons on the catalyst surface are such that the C-1 allylic pseudo-axial hydrogen could easily be adsorbed; in C-1 epimer IIIb the allylic pseudo-axial hydroxyl could easily be adsorbed.

The surprising finding was made that the C-1 secondary hydroxyl groups in the saturated glycols VIIa–d are much more readily oxidized than the corresponding C-1 allylic hydroxyls of the parent unsaturated glycols IIIa–d. Saturated isomer VIIb (from IIIb) in ethanol solution was oxidized, by stirring in air with rhodium–charcoal catalyst, to ketol VIIIa (*ca.* 10–15% conversion in 6 hr.), whereas the parent unsaturated glycol (IIIb) was unchanged in 24 hr. under the same conditions. The formation of saturated ketols VIIIa and b, but no unsaturated ketols Va and b, as a result of hydrogenation of unsaturated glycols IIIa–d with rhodium–charcoal catalyst is evidently due to ease of oxidation (dehydrogenation) of the related saturated glycols, VIIa–d, and failure of the newly formed carbonyl group to be reduced under these conditions. (The stereochemistry of the reduced, saturated glycols VIIa–d is thus not affected by involvement of ketol intermediates.) Both the saturated glycol VIIc and its parent IIIc are oxidized at a much greater rate than any of the other glycols. The greater ease of oxidation of the saturated glycols, compared with the unsatu-

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[41] L. D. Hall, *J. Org. Chem.*, **29**, 297 (1964).

[42] E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955).

[43] V. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, **13**, 1737 (1959).

[44] V. A. Atkinson, *ibid.*, **15**, 559 (1961).

[45] K. Heyns and H. Paulsen, "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1963, pp. 303–335.

[46] K. Heyns, H. Gottshalck, and H. Paulsen, *Chem. Ber.*, **95**, 2660 (1962).

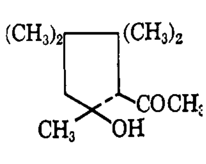
[47] R. P. A. Sneeden and R. B. Turner, *J. Am. Chem. Soc.*, **77**, 130, 190 (1955).

[48] T. J. Howard, *Rec. trav. chim.*, **83**, 992 (1964).

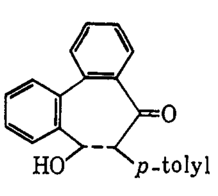
rated, may be attributed to the greater flexibility and absence of olefinic π electrons in the cyclohexane derivatives which allow better access of C-1 substituents to the catalyst surface.

Discussion

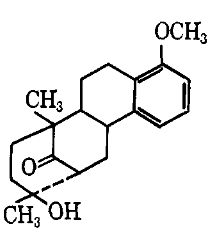
Previous studies relating to the stereochemistry of the aldol condensation[2,10-18] indicate a general lack of significant stereoelectronic control or stereospecificity in the C-C bond-forming process. Mixtures of epimers often result under kinetically controlled conditions in condensations leading to acyclic[2] or alicyclic[12-14] products. In the ketols IX,[12] X,[13] and XI[14] mild conditions and short reaction times lead to mixtures of epimers involving substituents about the bond shown by a broken line. Slightly more vigorous conditions or longer reaction times result in complete conversion to the most stable epimer in each example (retrogression required to equilibrate XI). (In formation of acyclic products equilibration may lead to mixtures of epimers.[2,49]) These observations suggest a transition state unlike the products in which the developing bond is relatively long. Ketol X epimers formed by Florisil (mild base) catalysis were, in one instance, in the ratio 60:40 *trans* to *cis;* it is not known to what extent this ratio reflects kinetic control. In one known example[7] of Michael addition leading to kinetic control of product composition, bulky groups (phenyl, isopropyl) are arranged in an *anti* configuration at the bond-forming site in the transition state leading to cyclic products. In other examples of Michael addition where stereochemistry of products has been established[5,8] it is possible that thermodynamic control is responsible for the observed product ratios.



IX



X

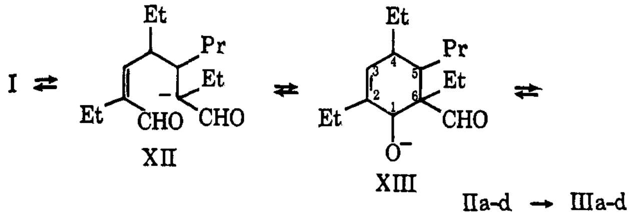


XI

The transition state of an aldol condensation is characterized by a rather low heat of activation (10-12 kcal.) and a relatively large negative entropy of activation for both the base- and acid-catalyzed reactions. For condensation of benzaldehyde with acetophenone (90% ethanol, sodium ethoxide) $\Delta H^* = 9.8$ kcal./mole and $\Delta S^* = -45$ e.u.[50] For the acid-catalyzed condensation of the same reactants (acetic acid, acid, sulfuric acid catalyst)[51] $\Delta H^* = 11.6$ kcal./mole and $\Delta S^* = -53$ e.u.; for *p*-nitrobenzaldehyde with acetophenone $\Delta H^* = 10.3$ kcal./mole and $\Delta S^* = -57$ e.u. The condensation step is rate determining in these examples. Reactions between anions and dipolar molecules are usually not characterized by such large negative entropies of activation. For example, for hydroxide ion hydrolysis of ethyl acetate in water $\Delta H^* = 11.3$ kcal./mole and $\Delta S^* = -30$ e.u.[52]; for acetaldehyde cyanohydrin formation $\Delta H^* = 22.9$ kcal./mole and $\Delta S^* = -18$ e.u.[53] The Michael addition of barbiturate anion to ω-nitrostyrene (in 67% dioxane, water) is also characterized by low heat of activation (9.8 kcal./mole) and $\Delta S^* = -31$ e.u.[54] The rather large negative entropy observed for both base- and acid-catalyzed aldol condensation relative to quite similar ion-molecule reactions suggests a transition state involving a large amount of solvent entrapment by carbonyl and enolate anion, or protonated carbonyl and enol. It could be equated with a relatively larger distance r^* between ion and molecule reflecting a relatively low steric interaction between groups at the bond-forming site and a process of low stereoselectivity. The relatively smaller negative entropy of activation observed for Michael addition[54] may be an indication of a shorter developing bond in the transition state due to less solvation about the olefinic end of the dipole; relatively more stereoselectivity appears to be observed in this process.[5-8]

Our results on the stereochemistry of the aldol cyclization provide an example wherein kinetic control is shown to be operative, at least in part. At 25° after 30-min. reaction time (65% methanol, water) one obtains a mixture of the most stable aldol (IIa, C-1 hydroxyl and C-6 ethyl equatorial, *ca.* 95%) and its C-1 epimer (IId, *ca.* 5%)[20] demonstrated by lithium aluminum hydride reduction of the aldol mixture to the corresponding glycols.[20] Practically none of the isomers epimeric at C-6 (IIb and c) were produced. However, a sample of aldol isolated after 3-hr. reaction time at 25° was found to contain only most stable isomers: *ca.* 99% of isomer IIa and *ca.* 1% isomer IIc (C-1 hydroxyl equatorial and C-6 ethyl axial); this distribution represents an equilibrium composition of the isomers at 25°.

The cyclization reaction proceeds from dialdehyde I through dialdehyde and alkoxide anions XII and XIII. Intramolecular carbonyl attack in anion XII proceeds most readily so that the C-6 ethyl is disposed *anti* to the C-5 propyl as the C-1–C-6 bond forms; thus the product consists principally of a mixture of C-1 epimers IIa and IId. The preponderance of IIa may be due in part to preference for an *anti* arrangement of largest ethyl and oxide groups in the transition state. The formation of a significant amount of the least stable isomer IId (C-1 hydroxyl axial) under kinetically controlled conditions and its absence under equilibrium conditions (at 25° in 65% methanol) clearly indicate a transition state which does not resemble products. Repulsions between bulky groups in the acyclic precursor at, or removed from the bond-forming site,



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(49) (a) A. C. Huitric and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 1147 (1956); (b) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **19**, 519 (1936).

(50) E. Coombs and D. P. Evans, *J. Chem. Soc.*, 1295 (1940).

(51) D. S. Noyce and W. A. Pryor, *J. Am. Chem. Soc.*, **81**, 618 (1959).

(52) L. Smith and H. Olsson, *Z. physik. Chem.*, **118**, 99 (1925).

(53) W. F. Yates and R. L. Heider, *ibid.* **74**, 4153 (1952).

(54) M. J. Kamlet and D. J. Glover, *ibid.*, **78**, 4556 (1956).

appear to be important features of aldol condensation stereochemistry.

The isomer distribution of glycols IIIa–d obtained at 25° by Cannizzaro reduction of the corresponding aldols (IIa–d) in aqueous methanol[19] is found to be the same as the equilibrium composition of the aldols in the same medium. At 25° after 7-hr. reaction time the glycol distribution is *ca.* 99% isomer IIIa with *ca.* 1% of isomer IIIc; some smaller amounts of isomers IIIb and d might also be expected, but these were not found. The rate of equilibration I $\rightleftarrows$ II proceeds more rapidly than Cannizzaro reduction; this fact was demonstrated previously,[19] when it was determined that formation of lactone IV (which requires acyclic intermediate I) occurs more rapidly than formation of glycols IIIa–d. It has been demonstrated that the glycols are stable under the reaction conditions and are not epimerized even at 110°; thus, it is also apparent that no epimerization of aldols at C-1 can occur without retrogression.

The composition of glycol isomers IIIa–d obtained in water at 110° (Table I) was essentially the same at 19-, 43-, and 96-hr. reaction time. Again isomer IIIa, most stable, predominates (55%) and IIId is found in smallest amount (5%). Of particular interest is the finding that at 110° the second major isomer is IIIb (30%) having C-1 axial hydroxyl and C-6 axial ethyl; the third most abundant isomer IIIc (10%) is its C-1 epimer (equatorial hydroxyl). The isomer distribution is temperature dependent; after 3 hr. at *ca.* 55–65° the composition was IIIa (81%), IIIb (9%), IIIc (10%), and IIId (<1%). Also, the product ratio of IIIb to IIIc increased as the temperature during the period of addition of the 2-ethyl-2-hexenal to the aqueous base was increased—from a value of 1.3 at 67° to 3.0 at 90°. Thus, the total percentages of isomers IIIb and IIIc, as well as the ratio of the percentages of IIIb to IIIc, increase as temperature is increased. The increase in the amount of isomer IIId with increase in temperature is less marked. Expected differences in relative rates of Cannizzaro attack on the C-6 aldehyde group in the half-chair and boat forms of IIa–d do not appear to be of much importance in determining product ratios. The predominant product is IIIa having the more hindered axial hydroxymethyl group; also, the significant change in product composition IIIa–d with temperature would not appear to be accounted for entirely on the basis of rate differences. The isomer distribution appears to be determined principally by the thermodynamically controlled retrogression of the aldols to acyclic reactant (I) since no nonretrogressive equilibration of the aldols is possible. The observed glycol isomer distribution at 110° reasonably suggests the intervention of twist or boat forms of the cyclohexene ring in IIb and IId at the higher temperature (*cf.* Figure 1).

Experimental Section[55]

Infrared Spectra.—Data recorded in Tables I and II were determined on a Perkin-Elmer Model 621 grating spectrophotometer, purged with dry nitrogen, employing a 2.0-cm. cell. Samples were prepared in carbon tetrachloride solution, *ca.* 0.006 *M*. With each sample several readings were taken directly from the instrument operated at a speed of 0.03 μ/min. and these values were averaged (accuracy ±0.5–1 cm.$^{-1}$). Most of the bands appear as closely spaced multiplets; the value recorded is that having the strongest absorption.

5-Propyl-2,4,6-triethyl-2-cyclohexen-1-ol-6-carboxaldehyde (II).—II was prepared by the procedure described previously.[19] A sample obtained at 20–29° after 185-min. reaction time was reduced to the corresponding glycol with lithium aluminum hydride.[19] A 2-g. aliquot of this product, n^{25}_{D} 1.4926, was crystallized from hexane to yield 21 mg. (1%) of glycol IIIc, m.p. 65–90°, mainly 85–90°, as the only crystalline product. The crystallization of glycol derived from an aldol sample obtained after 35-min. reaction time at 23–27° has been described[20]; there was obtained a yield of 7.5%, m.p. 90–111°, which was recrystallized for a total yield of IIId of 5.3%, m.p. 110–112°.

6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ones Va and b.—The procedure described previously[20] for oxidation of glycol IIIc to ketol Vb (shaking with active manganese dioxide catalyst in cyclohexane solvent at room temperature) was applied to the other three glycol isomers.

Ketol Va was prepared by oxidation of the liquid glycol isomer IIIa and isomer IIId (m.p. 112°). The reaction proceeded more slowly with IIIa than with any of the other isomers; a reaction time of 129 hr. gave a 53% yield of ketol Va, b.p. 114–115° (0.25 mm.), n^{25}_{D} 1.4932, $\lambda_{\max}$ 243 mμ ($\epsilon_{\max}$ 5900), ν 1710 (very weak) and 1660 cm.$^{-1}$ (strong C=O).[55] Oxidation of a liquid glycol sample derived from the corresponding aldol by lithium aluminum hydride reduction gave similar results. The glycol isomer IIId (m.p. 112°) was oxidized more readily than isomer IIIa providing a 75% yield of ketol Va in 119 hr., b.p. 117–119° (0.35 mm.), n^{25}_{D} 1.4940, $\lambda_{\max}$ 242.5 mμ ($\epsilon_{\max}$ 5700), ν 1660 (strong) and 1710 cm.$^{-1}$ (very weak).

Anal. Calcd. for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.70; H, 11.22.

Ketol Vb had been obtained previously by oxidation of glycol IIIc[20]; an 80% yield was obtained in 89 hr. It was also prepared by oxidation of glycol isomer IIIb, m.p. 60°; after 77-hr. reaction time there was obtained a 70% yield of Vb, b.p. 103–104° (0.25 mm.), n^{25}_{D} 1.4918, $\lambda_{\max}$ 240 mμ ($\epsilon_{\max}$ 6900), ν 1712 (weak) and 1660 cm.$^{-1}$ (strong C=O). *Anal.* Found: C, 76.48; H, 11.48. The sample of Vb prepared from glycol IIIc (m.p. 90°), described previously,[20] had b.p. 107° (0.4 mm.), n^{25}_{D} 1.4917, $\lambda_{\max}$ 239.5 mμ ($\epsilon_{\max}$ 8900), ν 1715 (very weak) and 1660 cm.$^{-1}$ (strong). *Anal.* Found: C, 76.12; H, 11.4. Attempts to prepare *p*-nitrophenylurethan derivatives of the ketols were unsuccessful.

5-Propyl-2,4,6-triethyl-2-cyclohexen-1-one (VI).—A 1.09-g. sample of ketol Vb (obtained by oxidation of glycol IIIb, m.p. 62°) was demethylolated by heating for 2.5 hr. in an oil bath at 200° in a stream of nitrogen; the formaldehyde produced was trapped and isolated as its 2,4-dinitrophenylhydrazone derivative, m.p. 161–163°, as previously described.[19,20] The residue, 0.71 g., n^{25}_{D} 1.4790, was distilled to yield ketone VI, b.p. 85–88° (0.35 mm.), n^{25}_{D} 1.4770, $\lambda_{\max}$ 240 mμ ($\epsilon_{\max}$ 8800), ν 1660 cm.$^{-1}$. A sample derived from ketol Va (preparation described previously)[20] had b.p. 85–90° (0.25 mm.), n^{25}_{D} 1.4774, $\lambda_{\max}$ 241 mμ ($\epsilon_{\max}$ 7630), ν 1660 cm.$^{-1}$. Attempts to prepare carbonyl derivatives of VI were unsuccessful.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.01; H, 11.90.

Lithium Aluminum Hydride Reduction of 6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ones (Va and b) to 6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ols (III).—A 1.0-g. sample of ketol Va (derived from liquid glycol IIIa), 1.0 g. of lithium aluminum hydride, and 60 ml. of ether were heated at reflux, with stirring, for 21 hr. Decomposition in the usual manner with dilute hydrochloric acid led to a viscous product which was dissolved in petroleum ether (b.p. 60–70°) and seeded successively with each of the three crystalline glycol isomers (IIIb–d). No crystalline glycol could be isolated. Distillation of the product gave the liquid glycol, IIIa, b.p. 139–140° (0.55 mm.), n^{22}_{D} 1.4935 (carbonyl absorption absent). Identical results were obtained in parallel runs employing other samples of ketol Va prepared from various liquid glycol samples or from glycol IIId, m.p. 112°.

Ketol Vb derived from glycol IIIc (m.p. 90°) was reduced similarly. A 1.0-g. sample provided 0.77 g. (91% of total glycol isolated) of glycol IIIc, m.p. 85–90° (recrystallization from

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[55] Melting points were determined on a Kofler block. Ultraviolet spectra were determined in 95% ethanol and infrared spectra (other than data in Tables I and II) were determined in chloroform solution unless otherwise stated.

hexane gave 0.70 g., m.p. 90–91°), and 0.07 g. (9% of glycol isolated) of glycol IIIb, m.p. 45–57°. In a parallel experiment reduction of a sample of ketol Vb derived from glycol IIIb (m.p. 62°) gave 89% glycol IIIc, m.p. 85–90°, and 11% glycol IIIb, m.p. 54-60°.

The glycols (III) were shown to be stable to epimerization under the reaction conditions of formation. A 1.0-g. sample of glycol IIIc, m.p. 88-90°, 2.0 g. of sodium hydroxide, 4 ml. of water, and 2 ml. of ethanol were heated at reflux for 29 hr.; the product was crystallized from hexane to yield 0.84 g., m.p. 85–89°, of recovered IIIc; no other isomer could be crystallized from the solution. In separate experiments, glycol isomers IIIa (liquid) and IIIb (m.p. 62°) were also heated under the same conditions and recovered unchanged without formation of other isomers.

6-Hydroxymethyl-5-propyl-2,4,6-triethyl-1-cyclohexan-1-ols (VIIa and b).—A 1.0-g. sample of glycol isomer IIIb (m.p. 62°) in 25 ml. of absolute ethanol and 1.0 g. of 5% rhodium–charcoal catalyst were stirred in hydrogen (700 mm., 25°) until hydrogen uptake practically ceased (4 hr., 1.0 mole equiv. absorbed). The mixture was filtered and concentrated; the product and that from a second run of 2.0 g. were combined (total recovery, 2.5 g.). Distillation through a short column at 0.1 mm. gave (1) 0.7 g., b.p. 120–123°, $n^{25}\mathrm{D}$ 1.4845; (2) 1.3 g., b.p. 123–125°, $n^{25}\mathrm{D}$ 1.4870; and (3) 0.1 g., b.p. 125°, $n^{25}\mathrm{D}$ 1.4865. The infrared spectra of all fractions were examined (smear). All showed no C=C stretching band at 1640 cm.$^{-1}$, but some nonconjugated, hydrogen-bonded carbonyl absorption at 1685 cm.$^{-1}$ [absorbance values for fractions 1, 2, and 3 were 0.38, 0.06, and 0.03, respectively, at 1685 cm.$^{-1}$ and 0.53, 0.65, and 0.65 respectively, at 3300 cm.$^{-1}$ (hydroxyl); CH absorbance, 1.3 in each sample]. Fraction 2 (principally VIIb) was submitted for analysis. Adams catalyst was ineffective for the hydrogenation of IIIb at 3.5 atm., 60°, the reactant being recovered.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58; mol. wt., 256. Found: C, 75.08; H, 12.63; mol. wt., 254.

The hydrogenation procedure just described (rhodium–charcoal catalyst) was applied to the reduction of liquid glycol isomer IIIa (19 hr.). The undistilled product had carbonyl absorption at 1685 cm.$^{-1}$ (absorbance 0.63), hydroxyl absorption at 3300 cm.$^{-1}$ (absorbance 0.85), and CH absorbance 1.5 (smear). These absorbance values and those in 0.006 *M* solution (2.0-cm. cell) indicate the crude product to be a mixture of *ca.* 30% saturated ketol VIIIa and 70% saturated glycol VIIa; this product was used without purification for the measurement of infrared spectra reported in Table II.

Application of the rhodium–charcoal-catalyzed hydrogenation procedure to glycol IIIc (m.p. 90°) gave principally saturated ketol VIIIb (7-hr. reaction time); the undistilled product had carbonyl absorption at 1680 cm.$^{-1}$ (absorbance 1.5), hydroxyl absorption at 3400 cm.$^{-1}$ (absorbance 0.60), and CH absorbance 1.5 (smear). Adams catalyst was ineffective for hydrogenation of IIIc and gave principally unchanged reactant.

A 0.1-g. sample of the unsaturated glycol IIIb (m.p. 62°) was stirred with 5% rhodium–charcoal catalyst (0.2 g.) in 15 ml. of 95% ethanol for 24 hr. After removal of the catalyst the product was recovered unchanged (carbonyl absorption absent). A parallel experiment with the saturated glycol VIIb derived from glycol IIIb (6-hr. reaction time) provided a product with carbonyl absorption at 1690 cm.$^{-1}$ (absorbance 0.29), OH absorbance 1.8, and CH absorbance 1.9 (smear).

Platinum-Catalyzed Oxidation of 6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ol (IIIc).—In separate experiments samples of each of the four glycol isomers (IIIa–d) (0.1–0.2 g.) in 95% ethanol and equivalent weights of Adams catalyst, prereduced before use, were stirred in air for 2 hr. The products were recovered reactants (carbonyl absorption absent)—except with isomer IIIc (m.p. 90°) which produced ketol Vb [carbonyl absorption at 1650 cm.$^{-1}$ (absorbance 0.40), hydroxyl (absorbance 0.45), C=C absorption at 1680 cm.$^{-1}$ (absorbance 0.11), and CH absorbance 0.81 (smear)].

Acknowledgment.—The author is indebted to Dr. A. L. Olsen for assistance in securing the infrared spectra and for helpful discussions and to Professor A. T. Blomquist for providing some of the samples employed in this study. He wishes to thank Dr. Lester P. Kuhn for helpful comments and suggestions.

Reactions of Nitrogen Dioxide with Organic Halogen Compounds.
III.[1] Oxidation of Some Cyclic Chloro Olefins to Cyclic Chloro Ketones

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Received March 12, 1965

Hexachlorocyclopentadiene undergoes a novel reaction with nitrogen dioxide at 60° to afford tetrachlorocyclopentene-1,2-dione (**1**) in about 90% yield. Another conjugated chloro olefin, decachlorobis(cyclopentadienyl) (**4**), reacts with nitrogen dioxide at 100° to give two isomeric diketones, $C_{10}Cl_8O_2$, in approximately equal amounts and in a total yield of about 85%. Spectral data show that these two diketones must have two of four possible structures: octachloro-*cis,trans,cis*-tricyclo[5.3.0.$0^{2,6}$]deca-4,9-diene-3,8-dione (**5a**), octachloro-*cis,trans,cis*-tricyclo[5.3.0.$0^{2,6}$]deca-3,9-diene-5,8-dione (**5b**), octachloro-*cis,cis,cis*-tricyclo[5.3.0.$0^{2,6}$]deca-4,9-diene-3,8-dione (**5c**), or octachloro-*cis,cis,cis*-tricyclo[5.3.0.$0^{2,6}$]deca-3,9-diene-5,8-dione (**5d**). Physical measurements, a partial resolution, and mechanistic considerations indicate that the preferred structures are the *cis,trans,cis* isomers, **5a** and **5b**. Trichloroethylene reacts with nitrogen dioxide at 80° to afford trichloronitroethylene in about 32% yield.

Relatively little has been reported about the reactions of nitrogen dioxide with chloro olefins. In 1869, Kolbe[2] described the synthesis of 1,2-dinitrotetrachloroethane by reaction of nitrogen dioxide with tetrachloroethylene. Burrows and Hunter[3] later reported that di- and trichloroethylene react with nitrogen dioxide to "undergo partial oxidation to oxalic acid, yielding also small amounts of lachrymatory substances of uncertain constitution." This appears to be the extent of published work on the reactions of nitrogen dioxide (or nitrogen tetroxide) with chloro olefins.

We now report (1) some interesting reactions of nitrogen dioxide with two cyclic chlorodienes and (2) a brief re-examination of the reaction of nitrogen dioxide with trichloroethylene.

Hexachlorocyclopentadiene reacts smoothly with nitrogen dioxide at 60°[4] to produce a yellow solid (m.p.

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(1) Parts I and II: R. M. Scribner, *J. Org. Chem.*, **29**, 279, 284 (1964); *cf.* also *ibid.*, **29**, 3429 (1964).

(2) H. Kolbe, *Ber.*, **2**, 326 (1869); *cf.* also H. Blitz, *ibid.*, **35**, 1528 (1902), and W. L. Argo, E. M. James, and J. L. Donnelly, *J. Phys. Chem.*, **23**, 578 (1919).

(3) R. B. Burrows and L. Hunter, *J. Chem. Soc.*, **134**, 1357 (1932).

(4) At 120° reaction of hexachlorocyclopentadiene with nitrogen dioxide gave dichloromaleic anhydride in small yield as the only identifiable product (*cf.* Experimental Section).