

$[\Phi]_{340} + 173^\circ$, $[\Phi]_{330} - 393^\circ$, $[\Phi]_{326} - 345^\circ$, $[\Phi]_{315} - 697^\circ$, $[\Phi]_{290} - 644^\circ$.

Anal. Calcd. for $C_{11}H_{18}O$: mol. wt., 164. Found: mol. wt. (mass spec.), 164.

$\Delta^{3(9)}$ -8-Methylhydrinden-2-one (XVIIa).—Starting with *trans*-8-methylhydrindan-2-one (XIVa)³⁴ and proceeding in the same fashion as described above for the higher homolog, there was obtained the hydrindenone XVIIa, λ_{\max}^{EtOH} 230 μ ($\log \epsilon$ 3.73); n.m.r. signals (carbon tetrachloride) at 1.18, 2.05, and 5.60 p.p.m. with a ratio of 3:2:1; R.D. (Fig. 4) in dioxane (c 0.175): $[\Phi]_{589} - 15^\circ$, $[\Phi]_{350} - 1172^\circ$, $[\Phi]_{342} - 871^\circ$, $[\Phi]_{338} - 991^\circ$, $[\Phi]_{295} + 1622^\circ$, $[\Phi]_{275} + 1082^\circ$.

(+)-*trans*-1 β -Methyl-10 α -bromobicyclo[5.4.0]-9-undecanone (XVIIIb).—Bromine (210 mg.) in acetic acid (5 cc.) was added dropwise to an ice-cooled solution of 230 mg. of the ketone IXb in 5 cc. of glacial acetic acid. After stirring for 30 min. at room temperature, water was added and the product (250 mg.) filtered and recrystallized from aqueous acetone; m.p. 158–162°; λ_{\max}^{KBr} 5.80 μ ; R.D. in methanol (c 0.265): $[\Phi]_{589} + 78^\circ$, $[\Phi]_{309} + 1957^\circ$, $[\Phi]_{287} - 2877^\circ$, $[\Phi]_{285} - 2721^\circ$.

Anal. Calcd. for $C_{12}H_{19}BrO$: C, 55.61; H, 7.39; Br, 30.84. Found: C, 55.77; H, 7.35; Br, 30.60.

Δ^{10} - (XIXb) and Δ^7 - (XXb) 1 β -Methylbicyclo[5.4.0]-9-undecanone.—The dehydrobromination of 850 mg. of (+)-*trans*-1 β -methyl-10 α -bromobicyclo[5.4.0]-9-undecanone (XVIIIb) with collidine was performed exactly as described earlier^{22b} for *trans*-3-bromo-10-methyl-2-decalone (XVIIIa). Chromatography of the reaction product on 100 g. of activity I neutral alumina provided 230 mg. of the Δ^{10} - (XIXb) and 57 mg. of the Δ^7 - (XXb) isomers. The former was distilled at 100° (0.1 mm.) to give a clear oil with λ_{\max}^{EtOH} 227 μ ($\log \epsilon$ 3.99), λ_{\max}^{fil} 5.98 and 6.22 μ ; R.D. (Fig. 3) in dioxane (c 0.25): $[\Phi]_{589} 0^\circ$, $[\Phi]_{389} + 758^\circ$, $[\Phi]_{382} + 660^\circ$, $[\Phi]_{351} + 1239^\circ$, $[\Phi]_{342} + 437^\circ$, $[\Phi]_{338} + 570^\circ$, $[\Phi]_{323} - 632^\circ$, $[\Phi]_{295} - 1792$ (infl.), $[\Phi]_{287} - 1890^\circ$.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18; mol. wt., 178. Found: C, 80.50; H, 10.09; mol. wt. (mass spec.), 178.

(34) For preparation of antipode see ref. 17.

The red 2,4-dinitrophenylhydrazone of XIXb was recrystallized from ethanol-chloroform; m.p. 179.5–181.5°, $\lambda_{\max}^{CHCl_3}$ 382 μ ($\log \epsilon$ 4.40).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.24; H, 6.32; N, 15.77.

Similar distillation of the Δ^7 -bicycloundecanone XXb afforded a colorless oil, λ_{\max}^{EtOH} 240 μ ($\log \epsilon$ 4.17), λ_{\max}^{fil} 6.01 and 6.22 μ ; R.D. (Fig. 2) in dioxane (c 0.32): $[\Phi]_{589} + 267^\circ$, $[\Phi]_{378} + 2300^\circ$, $[\Phi]_{365} + 1676^\circ$, $[\Phi]_{356} + 2068^\circ$, $[\Phi]_{346} + 570^\circ$, $[\Phi]_{341} + 909^\circ$, $[\Phi]_{333} - 107^\circ$, $[\Phi]_{326} + 410^\circ$, $[\Phi]_{321} + 196^\circ$, $[\Phi]_{310} + 963$ (infl.), $[\Phi]_{270} + 5526^\circ$.

Anal. Calcd. for $C_{12}H_{18}O$: mol. wt., 178. Found: mol. wt. (mass spec.), 178.

The red 2,4-dinitrophenylhydrazone of XXb was recrystallized from ethanol; m.p. 135–136° (crystal structure change at 124°), $\lambda_{\max}^{CHCl_3}$ 391 μ ($\log \epsilon$ 4.42).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.62; H, 6.05; N, 15.90.

Catalytic Hydrogenation of Δ^7 -1 β -Methylbicyclo[5.4.0]-9-undecanone (XXb).—The catalytic hydrogenation of the enone XXb (100 mg.) was performed in methanol solution with palladium-charcoal catalyst. Under identical conditions, the corresponding octalone XXa provided^{22b} without difficulty the pure *cis*-decalone XXa. In the present instance, the hydrogenation product (absence of conjugation established by ultraviolet absorption spectrum), which could not be crystallized, was homogeneous by thin-layer chromatography and standard gas-phase chromatography. However, when the latter was performed at 200° on a 150 ft. Goulay capillary column (internal diameter 0.002 in.) packed with Carbowax and a helium flow of 15 p.s.i., two components could be observed with retention times of 23 and 24.2 min., of which the latter corresponded to the *trans*-ketone IXb. Analysis of the areas under the peaks indicated the presence of 66 \pm 5% *cis* (XXIb) and 34 \pm 5% *trans* (IXb) ketone. The optical rotatory dispersion curve (methanol) reproduced in Fig. 1 represents a calculated curve in which the contribution of the *trans* contaminant (34%) has been subtracted.

(35) See C. Djerassi and E. Ryan, *J. Am. Chem. Soc.*, **71**, 1000 (1949).

[CONTRIBUTION FROM THE CHANDLER LABORATORIES, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

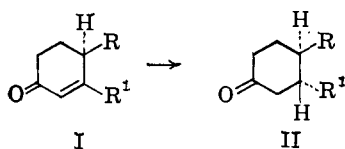
The Stereochemistry of the Lithium-Ammonia Reduction of α,β -Unsaturated Ketones¹

BY GILBERT STORK AND S. D. DARLING

RECEIVED NOVEMBER 12, 1963

The stereoelectronic requirements which have to be met in the possible transition states for the addition of a proton to the β -carbon of an α,β -unsaturated ketone undergoing reduction with lithium and ammonia are discussed. It is shown that the saturated ketone formed by such a reduction is not simply the more stable of the two possible isomers at the β -carbon. The energies of the stereoelectronically allowed transition states, rather than those of the reduction products, determine the stereochemistry of the latter.

It has been accepted since the classical investigations of Birch that the reaction of ammonia solutions of the alkali metals with α,β -unsaturated ketones involves transfer of electrons with the formation of a carbanionic species which leads, after suitable work-up, to the saturated ketone.²

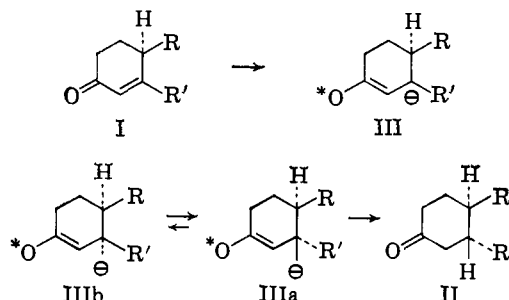


It was noted early that in many cases only one of the two possible epimers of a structure such as II was formed and, as this turned out to be the more stable isomer, it was postulated that rapid equilibration of a carbanion intermediate (*cf.* IIIa \rightarrow IIIb) must take

(1) A preliminary communication outlining some of the results in this paper has been published: G. Stork and S. D. Darling, *J. Am. Chem. Soc.*, **82**, 1512 (1960).

(2) *Cf.* A. J. Birch and H. Smith, *Quart. Rev. (London)*, **12**, 17 (1958).

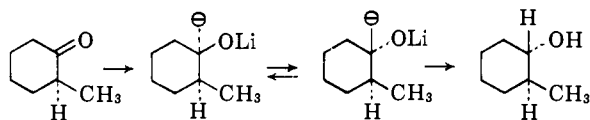
place, thus leading to the thermodynamically more stable system.³ In the case of an α,β -unsaturated ketone such as I the product normally obtained would have groups R and R' *trans* to each other (R and R' both equatorial).⁴



(3) D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954).

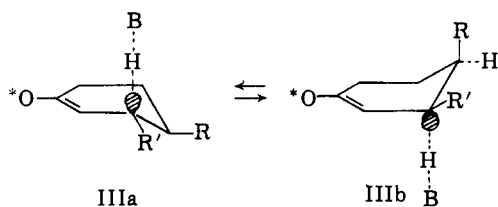
(4) In all the transition states we have written in this paper, a star is used on the oxygen of the enols to denote either one or two electrons. It is not known whether β -carbon protonation takes place at a radical anion or dianion stage.

The hypothesis that the products obtained are essentially in the ratio of their thermodynamic stabilities³ is, of course, based on a similar picture for the reduction of carbonyl compounds.⁵ For example, the reduction of 2-methylcyclohexanone leads by an analogous scheme to the anticipated more stable epimer, *trans*-2-methylcyclohexanol.

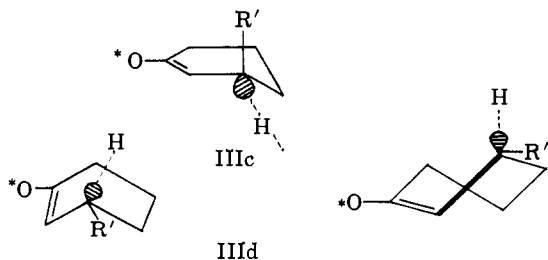


We may point out in passing that, even in the "simple" case of ketone reduction, recent work⁶ has shown the picture to be rather more complicated; and the "thermodynamic control," which certainly appears to obtain *qualitatively* with lithium and ethanol, may be greatly altered *inter alia* by varying the alkali metal.

We were led to question the validity of the assumption that in the reduction of enones, thermodynamic stability of the ketonic reduction products would determine their ratio. It would be expected that in the intermediate carbanion III rather rigid stereoelectronic requirements would have to be met in order to maintain overlap with the carbon-carbon double bond of the enolate system, and thus minimize the energy of the possible transition states for protonation. Such a requirement would in turn imply that equilibration could take place only between transition states such as IIIa and IIIb *in which overlap is maintained*.



In the usual case where R' is itself incapable of delocalizing the negative charge in the transition state, a possibility such as IIIc would be of considerably higher energy and would not have to be considered.



On the other hand, a half boat (or twist) form such as IIIId meets the stereoelectronic requirements and would have to be taken into account, although only in unusual cases will it turn out to be the lowest energy possibility.

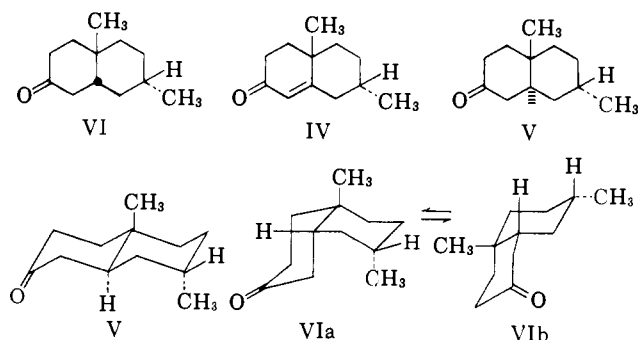
It is immediately evident that these considerations lead to the prediction that in the reduction of a simple

(5) Cf. D. H. R. Barton and R. C. Cookson, *Quart. Rev. (London)*, **10**, 44 (1956).

(6) G. Ourisson and A. Rassat, *Tetrahedron Letters*, No. 21, 16 (1960); see also J. W. Huffman, D. M. Alabran, and T. W. Bethea, *J. Org. Chem.*, **27**, 3383 (1962).

3,4-dialkylcyclohexenone such as I, the product would be expected to be derived from IIIa, and would thus be a *trans*-3,4-dialkylcyclohexanone. This is the same conclusion that would be reached immediately by the simpler, earlier statement that the product of the reduction of I should be the more stable of the two possible cyclohexanones.

It is, however, possible to construct situations in which the two points of view lead to different expectations. For example, the reduction of the octalone IV can lead to either the *trans*-decalone V or the *cis*-isomer VI. It is easy to show that the *cis*-decalone VI which can exist in the two conformations VIa and



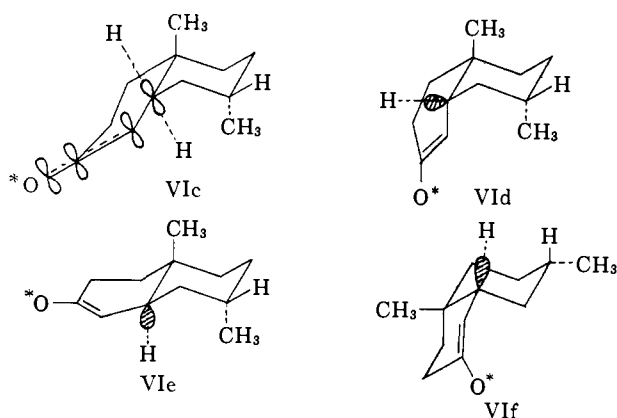
VIb should be more stable in the VIb conformation. This is essentially due to the additional very unfavorable 1,3-diaxial interaction of the 7 α -methyl group with the C₁-methylene (3.6 kcal.⁷) in VIa. Similarly, the *cis*-decalone VIb should be more stable than the *trans*-isomer V: assuming the equivalence of a 1,3-methyl-hydrogen and of a 1,3-methylene-hydrogen diaxial interaction (*ca.* 0.9 kcal.⁷), and remembering that the 1,3-interaction of the π -electrons of the carbonyl with a hydrogen (the "3-alkyl ketone effect") amounts to *ca.* 0.8 kcal.,⁸ V must be of *ca.* 1 kcal. higher energy than VIb [6(1,3-methyl-hydrogen) interactions in V and 2(methyl-hydrogen) + 2(methylene-hydrogen) + 1(carbonyl-hydrogen) in VIb]. If indeed the stereochemistry of the products of the lithium-ammonia reduction of the octalone IV were merely determined by the energy difference between the *cis* and *trans* isomers of the saturated ketone, the latter should be a mixture of 80% *cis*- and 20% *trans*-decalones.⁹

The prediction is very different, however, on the basis of our suggestion that equilibrium considerations apply not to the products of the reaction but to those transition states in which overlap of the developing p-orbital on the β -carbon is maintained during protonation. The choice now is between the two transition states which meet this restriction, *i.e.*, the two transition states which must have a geometry somewhere between that of the trigonal enolate VIc and that represented by either VIId or VIe but not by VIb (a boat-like transition state, *cf.* IIIId, would be of higher energy than VIe and need not be considered further in this case). Since now VIId is obviously much less

(7) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., p. 236.

(8) Cf. B. Rickborn, *J. Am. Chem. Soc.*, **84**, 2414 (1962).

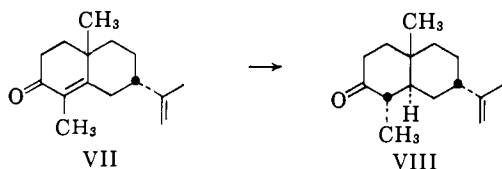
(9) It has been shown that *cis*-decalones such as VIb appear to exist with the ketone ring in a slight twist modification (*cf.* C. Djerassi, *et al.*, *J. Am. Chem. Soc.*, **86**, 465 (1964)), but this does not change the argument that VIb would be more stable than V. It merely means that there is a modification of VIb which is even more stable than all-chair VIb, and the difference in favor of the *cis* isomer would then actually be magnified.



stable than VIe, the geometry of the transition state must resemble the latter; and the product would then be expected to be the *trans*-decalone V, in spite of the fact that the *cis*-decalone VIb should be more stable than its *trans* isomer.

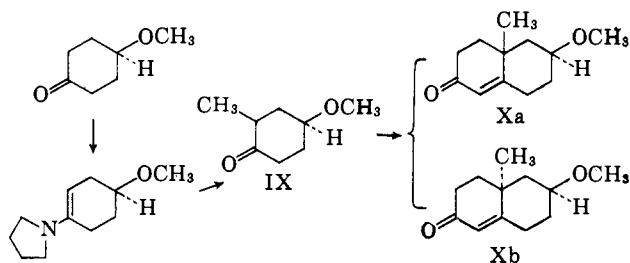
What has happened is simply that the more stable *cis*-decalone VIb would have to arise from a transition state which is not allowed because it does not permit continuous overlap during protonation.

There exists one case of octalone reduction in the literature which is germane to the present discussion. The octalone VII which corresponds to IV in its relevant features has been reduced with lithium and liquid ammonia¹⁰ and, in agreement with the discussion just given, produced the corresponding *trans*-decalone VIII apparently as the sole product of the reaction, in spite of the fact that the *cis* isomer of VIII should be the more stable. The mechanistic implication of this result was not realized at the time, but it is strong evidence for the validity of our present proposal.



We have now examined the octalones Xa, Xb, XVI, XXIIa, and XXIIb with respect to the stereochemical result of their reduction with lithium and ammonia. In all cases the results are in keeping with our generalization.

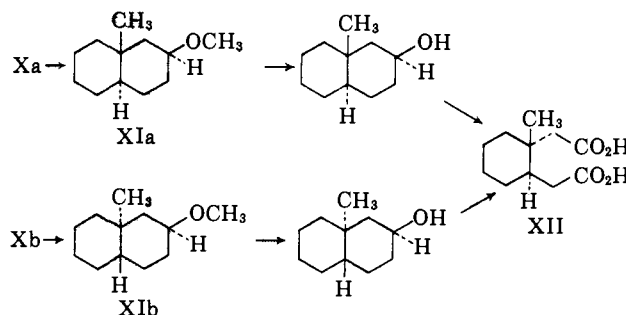
The octalones Xa and Xb were prepared starting with 2-methyl-4-methoxycyclohexanone (IX) which was itself made by the pyrrolidine-enamine alkylation¹¹ of 4-methoxycyclohexanone. Condensation with methyl vinyl ketone, as its Mannich base meth-



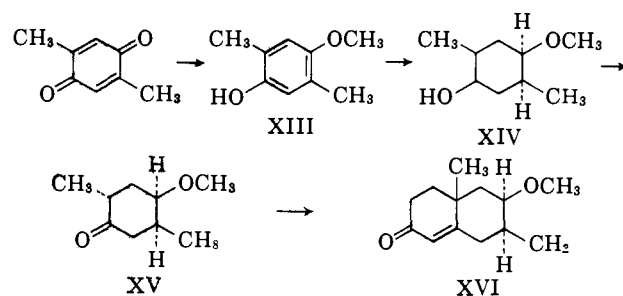
(10) R. Howe and F. J. McQuillin, *J. Chem. Soc.*, 2670 (1956).

(11) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

iodide,^{12,13} led to the desired octalone as a mixture of two epimers, Xa and Xb. The mixture consisted largely ($\sim 85\%$) of one stereoisomer. The major isomer is presumably Xa because of the expected axial introduction of the ketobutyl group, but this is of no concern with respect to the present problem since both isomers gave the same stereochemical result on reduction. Treatment of the mixture with lithium and ammonia in the presence of alcohol, followed by oxidation with chromic acid and Wolff-Kishner reduction of the resulting decalones, gave a mixture of 2-methoxy-9-methyldecalins which were separated by vapor phase chromatography into two components: XIa (84%) and XIb (16%). Both were degraded separately by cleavage with anhydrous hydrogen bromide in acetic acid to a mixture of alcohol and olefin which was then oxidized with nitric acid to give in either case *trans*-1-methylcyclohexane-1,2-diacetic acid (XII),¹⁴ the melting point of which was undepressed on admixture with an authentic sample.¹⁵



The octalone XVI, 7 β ,10 β -dimethyl-6 β -methoxy- $\Delta^{1,9}$ -2-octalone, was prepared by the usual Mannich base methiodide procedure from 2,5 β -dimethyl-4 β -methoxycyclohexanone. The latter was prepared by catalytic hydrogenation of 2,5-dimethyl-4-methoxyphenol (XIII), followed by chromic acid oxidation. The starting methyl ether XIII was conveniently prepared by the elegant method of Ramirez and Dershowitz¹⁶ from 2,5-xyloquinone and trimethyl phosphite. The cyclohexanone XV appeared homo-



geneous and was characterized as its 2,4-dinitrophenylhydrazone, m.p. 130.9–131.9°. The Robinson annelation reaction on XV gave the octalone XVI which con-

(12) Cf. E. C. Du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937).

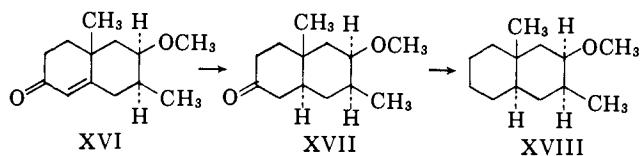
(13) Cf. Y. Ahe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi, and T. Toga, *J. Am. Chem. Soc.*, **75**, 2567 (1953).

(14) In all the cases of octalones prepared and reduced in this paper we are dealing with *d,l*-compounds and although absolute configurations are written for simplicity, it must be recalled that the mirror image is also present. This explains the apparent discrepancy of having both XIa and XIb give the diacid XII on degradation.

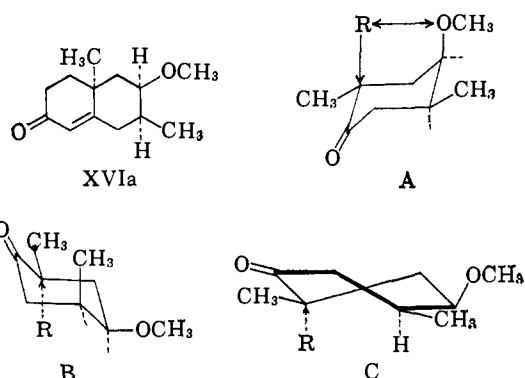
(15) R. L. Kronenthal and E. I. Becker, *J. Am. Chem. Soc.*, **79**, 1095 (1957).

(16) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

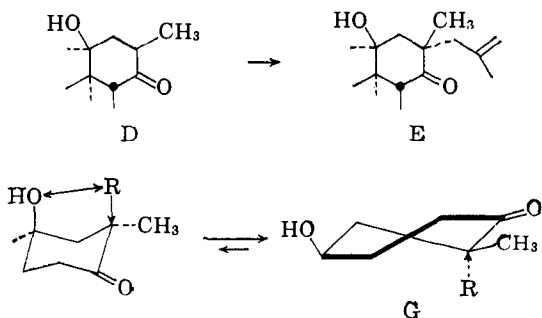
sisted essentially of only one isomer on the basis of its reduction with lithium-ammonia, and alcohol which gave a very good yield of a crystalline decalol, m.p. 104.6–105.8°. The latter was in turn oxidized to the decalone XVII, m.p. 88.4–89.1°, which was then degraded *via* the decalin XVIII (homogeneous by v.p.c.) to give again *trans*-1-methylcyclohexane-1,2-diacetic acid (XII).



Before we turn to the synthesis and reduction of the remaining octalones XXIIa and XXIIb, we will digress and comment on the stereochemistry assigned to the octalone XVI. In the first place, the cyclohexanone XV must have its vicinal methyl and methoxyl groups *cis* as shown. This might have been expected from the fact that the relative stereochemistry of the vicinal methyl and methoxyl is the result of a catalytic hydrogenation, but the anticipation was subject to caution because of the high temperature which was used. That the conclusion is valid follows from the fact that the ketone XV obtained by this route is different from the unambiguously synthesized cyclohexanone XXI in which the vicinal methyl and methoxyl groups are *trans* (*vide infra*). This point settled, there remain two possibilities for the octalone stereochemistry, XVI and XVIa. Of the two possible chair transition states for methyl vinyl ketone addition, A and B, A has considerably fewer 1,3-interactions but the approaching

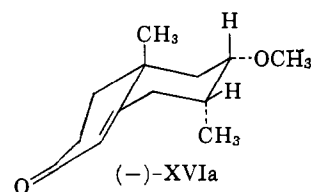


methyl vinyl ketone ("R") gets into 1,3-diaxial interaction with the methoxyl group. Such an interaction is sufficient to cause alkylation *via* a transition state which permits approach of "R" from the opposite side. See, for instance, the closely related case observed by Sarett, *et al.*¹⁷ (D → E), in which the usual

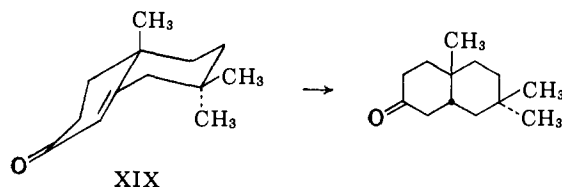


chair-axial alkylation is prevented by a similar 1,3-interaction. The result is the formation of E by what is sometimes called "equatorial" alkylation, but would be more correctly described today in terms of "twist-axial alkylation,"¹⁸ in this case *via* G. Similarly, the difficulty with the transition state A is eliminated by the involvement of the twist-axial transition state C leading to *cis* stereochemistry of the two methyls and the methoxyl in the final octalone XVI.

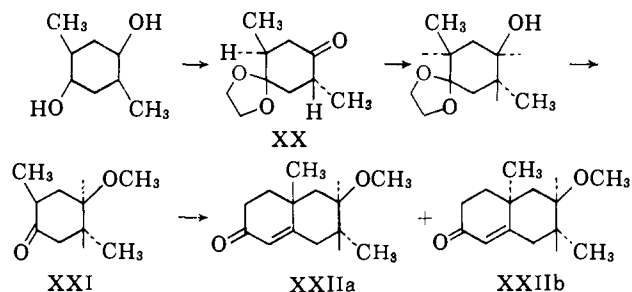
We have based the assignment of stereochemistry to XVI on a theoretical argument. What we consider good experimental evidence for the validity of this argument was brought to light in a study of the palladium-catalyzed hydrogenation of XVI. This led to a mixture of *cis*- and *trans*-decalones. Had the relative stereochemistry of XVI really been that shown in XVIa (or in its mirror image (-)-XVIa), the conformation of the octalone would be as shown in (-)-XVIa. Such a molecule would be expected to lead



exclusively to a *cis*-decalone on hydrogenation because of the shielding of the α -side of the molecule by the axial methyl group; in fact, such a prediction has already been confirmed experimentally with the apposite case of XIX which gives cleanly a *cis*-decalone on hydrogenation with palladium.¹⁹



The last octalones examined were derived from the cyclohexanone XXI in which the vicinal methyl and methoxyl groups are *trans* to each other. This was synthesized by an unambiguous route, the important feature of which consisted in the reduction of the monoketal of 2,5-dimethylcyclohexane-1,4-dione with sodium and ethanol to the more stable *trans* diequatorial alcohol which was then methylated and deketalized to the desired 2,5 α -dimethyl-4 β -methoxycyclohexanone (XXI).



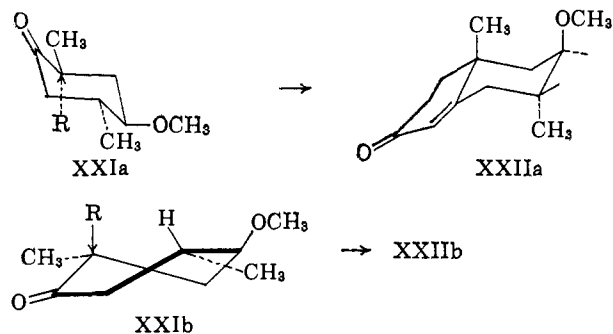
(17) L. H. Sarett, W. F. Johns, R. I. Beyler, R. M. Lukes, G. I. Poos, and G. E. Arth, *J. Am. Chem. Soc.*, **75**, 2112 (1953).

(18) For a discussion of twist cyclohexane *cf.* W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. N. Dregger, and W. N. Hubbard, *ibid.*, **83**, 606 (1961).

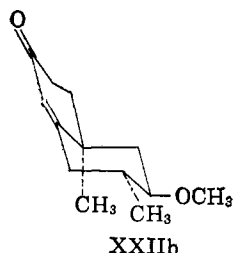
(19) T. G. Halsall and D. B. Thomas, *J. Chem. Soc.*, 2431 (1956).

The 2,4-dinitrophenylhydrazone of XXI melted at 128–128.8° and depressed the melting point of the derivative of the epimeric cyclohexanone XV.

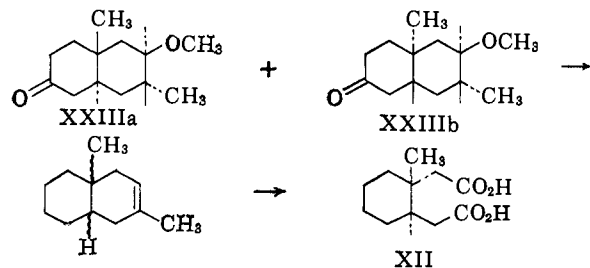
Annulation of XXI then led to a mixture of the two possible octalones XXIIa and XXIIb, formed in almost equal amounts. The formation of a mixture in this case is easily rationalized. Axial-chair alkylation of XXI is unimpeded and would be expected to lead to only one isomer (cf. XXIa), but formation of an octalone from such a substance would be expected to



be slow because it requires either that the two methyls and the methoxyl all become axial, if ring B is to remain a chair (cf. XXIIa), or that ring B take up some twist conformation. This slow formation of octalone XXIIa, coupled with the well-known reversibility of the Michael addition, then permits the alkylation to take place also via some twist-axial transition state (cf. XXIIb), thus leading to the epimeric XXIIb in which the vicinal methyl and methoxyl groups are both equatorial.



Reduction of the mixture of XXIIa and XXIIb with lithium and ammonia and degradation by the same method as used for XVII, via the decalone mixture XXIIIa and XXIIIb, led again to *trans*-1-methylcyclohexane-1,2-diacetic acid (XII) readily obtained pure; lithium-ammonia reduction there led once



more from either XXIIa or XXIIb to the *trans*-decalone series. The validity of the conclusion was checked by showing that a 50/50 mixture of the *trans*-diacid XII with its *cis* isomer could not be separated under the conditions which readily led to the pure *trans* isomer XII as the result of the above degradation

of the reduction products of the mixture of XXIIa and XXIIb.

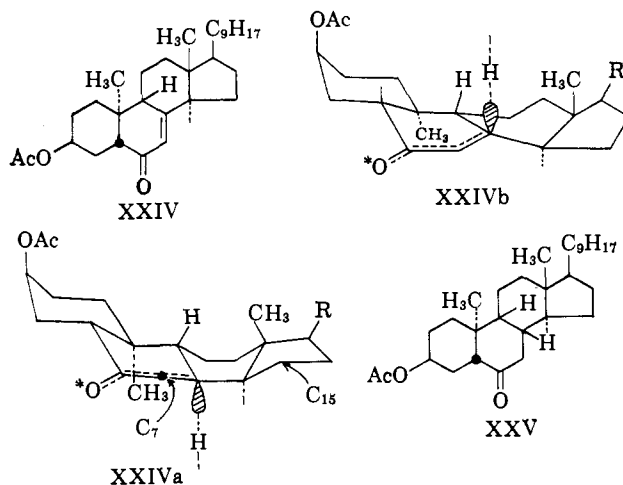
The most revealing of the new results we have now recorded are those obtained in the reduction of Xa and of XXIIa. In the first of these the *cis*-decalone should be somewhat more stable than the *trans* by ca. 0.4 kcal., while in the second the *cis*-decalone should be more stable than the *trans* by ca. 2 kcal. In either instance only the *trans* isomer appears to be formed.

In all the cases of octalone reduction we studied, regardless of the relative stability of the two possible decalones, the reduction product turned out to belong to the *trans*-decalone series, and in all cases the product was derived from the more stable of the two protonation transition states (cf. VI d and VI e) in which overlap of the β -carbanion is maintained.

Two points remain to be considered: the possible intervention of twist transition states (cf. III d) and the cases where in an α,β -unsaturated ketone undergoing reduction there is present a β -substituent which is itself capable of stabilizing a carbanionic intermediate.

As already pointed out, there will be some situations in which a boat or twist transition state may either be the only one possible or the best of the various transition state conformations which meet the requirement of protonation axial to the enolate ring. One example of this is encountered in the reduction of the polycyclic ketone XXIV.²⁰ Here the rigid requirements imposed by the *trans* fusions of rings A and B as well as C and D allow a choice between two transition states in which ring C is necessarily in a modified boat conformation. The two possible conformations which maintain overlap at C-8 in the protonation transition state are XXIVa (leading to *trans* B/C fusion) and XXIVb (giving rise to *cis* B/C fusion).

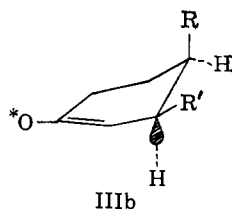
At first sight, XXIVa might seem of lower energy, but not only is ring C close to a true boat in this case, with consequent strong interference between the C-18 methyl and the C-9 hydrogen, but there is a very unfavorable eclipsed butane arrangement involving C-7 and C-15. Both interferences are relieved in transition state XXIVb which then leads to the final product, the *cis* B/C compound XXV, as is indeed found. This complex case, rather than being an exception to our generalization,²¹ actually fits well into it.



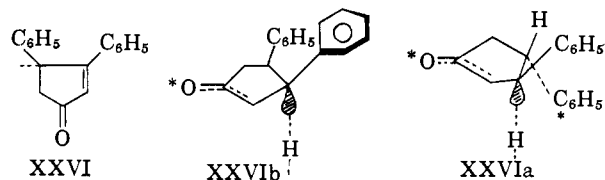
(20) P. A. Mayor and G. D. Meakins, *J. Chem. Soc.*, 2800 (1960).

(21) D. H. R. Barton and G. A. Morrison, "Fortschritte der Chemie organischer Naturstoffe," Vol. XIX, Springer-Verlag, Vienna, 1961.

The second point, the reduction of an α,β -unsaturated ketone having on the β -carbon a substituent itself capable of overlap with the developing p-orbital at that center in the transition state for protonation, has not been studied sufficiently to allow generalization. It is, however, to be expected that in the reduction of cyclohexenones of such a type transition states such as IIIb may become important because the proper orientation of R' to allow its overlap with the carb-



anionic center on the β -carbon may force R to become axial in the transition state to minimize interference between R and R'.²² Further, if R is sufficiently large and in a rigid system, the close approach required of the proton donor may also favor a *cis* arrangement of R and R' in the transition state. An illustration of the latter effect is given by the remarkable result obtained by White, who found that the lithium-ammonia reduction of 3,4-diphenylcyclopentenone (XXVI) leads to *cis*-3,4-diphenylcyclopentanone (XXVII).²³ We first note that this is one more case of the production of an isomer other than the more stable²⁴ one by the lithium-ammonia reduction of an enone. It is, however, easily rationalized. The two possible transition states here are XXVIa and XXVIb. The lower energy of the transition state XXVIb leading to *cis*-3,4-diphenylcyclopentanone reflects the strong steric hindrance to the close approach of the proton carrier which is caused by the starred phenyl group in transition state XXVIa. The occurrence of such effects and the intervention of boat or twist forms, as in the reduction of the polycyclic enone XXIV, clearly indicate the need for some sophistication in the application of the stereoelectronic concepts we have been presenting here.



Experimental

2-Methyl-4-methoxycyclohexanone (IX).—In a round-bottom flask, fitted for the azeotropic removal of water, was placed 114.8 g. (0.895 mole) of 4-methoxycyclohexanone,²⁵ 400 cc. of benzene, and 100 cc. of pyrrolidine. The solution was refluxed until no more water separated. The benzene was then removed and the product was distilled, b.p. 107–114° (3.1 mm.). The yield of enamine was 141.8 g. (87.3%). The enamine was then placed in a 1-l. round-bottom flask with 230 cc. of methanol, and 160 g. of methyl iodide was added (cautiously, as the reaction is exothermic). The solution was then refluxed 2 days and then 30 cc. of water was added and the mixture was refluxed 1 hr. The meth-

anol was removed as much as possible, and the residue was taken up in very little water and extracted very thoroughly with ether.

The ether extracts were washed successively with a little 5% hydrochloric acid, potassium bicarbonate solution, and water. Drying and concentration gave an oil which was distilled, b.p. 93.5–97.5° (18 mm.), n_{D}^{25} 1.4506. The yield was 66.8 g. (60.3%). The 2,4-dinitrophenylhydrazone had m.p. 139–140°.

Anal. Calcd. for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63. Found: C, 52.44; H, 5.91.

10 β -Methyl-6 β -methoxy- $\Delta^{1,9}$ -octalone-2 and 10 α -Methyl-6 β -methoxy- $\Delta^{1,9}$ -octalone-2 (Xa, Xb).—According to the procedure used by Abe¹³ with 2-methylcyclohexanone, 2-methyl-4-methoxycyclohexanone was condensed with methyl vinyl ketone as its Mannich base methiodide. After two distillations, 25.8% (based on unrecovered starting material) of product was obtained, b.p. 103° (0.15 mm.); λ_{max}^{EtOH} 239 m μ , ϵ 16,100. This product is a mixture in which Xa greatly predominates (*vide infra*). Derivatives, presumably from Xa, were readily obtained. The semicarbazone had m.p. 212–214° dec. (from aqueous ethanol).

Anal. Calcd. for $C_{13}H_{21}N_3O_2$: C, 62.12; H, 8.42. Found: C, 62.29; H, 8.22.

The 2,4-dinitrophenylhydrazone had m.p. 134–135.5° (from chloroform-ethanol).

Anal. Calcd. for $C_{18}H_{22}N_4O_5$: C, 57.74; H, 5.92. Found: C, 57.74; H, 6.18.

2-Methoxy-9-methyldecalin (XIa, XIb).—The octalone (5.9 g.) was reduced to the saturated alcohol by treatment of a solution in 50 ml. of anhydrous ether and 80 ml. of absolute ethanol in 200 ml. of anhydrous liquid ammonia with 5 g. of lithium until a blue color just persisted. An ammonium chloride (50 g.) was then added slowly and, after evaporation of the ammonia, water was added and the saturated alcohol was extracted with ether. Removal of the solvent left the crude saturated alcohol (94% yield) which was then oxidized by treating its solution in 100 ml. of acetone (distilled from permanganate) with 8.25 ml. of chromic acid solution added with rapid stirring during 5 to 10 min.²⁶ The solution was stirred for an additional half hour and was then decomposed with acidified bisulfite solution. The solution was taken up in ether and was extracted with saturated potassium carbonate solution. Drying and removal of ether left an oil (crude yield 91%) which was then reduced to 2-methoxy-9-methyldecalin (crude yield 76%) by the usual Huang-Minlon procedure. The methoxydecalin so obtained (65% over-all yield from the octalone mixture of Xa and Xb) was separated, by vapor phase chromatography on a 43-ft. column of 40% Dow-Corning 710 silicone on firebrick, into two fractions, A (84%) and B (16%). These were collected and separately submitted to degradation.

Degradation to *trans*-1-Methylcyclohexane-1,2-diacetic Acid (XII).—In a small glass flask was placed 1.004 g. of 2-methoxy-9-methyldecalin (fraction A) and 1.603 g. of 30% hydrogen bromide in acetic acid. The flask was stoppered tightly and allowed to stand at room temperature for 1 week (after a day or so, a second layer was noticed). The acid was then decomposed with solid potassium bicarbonate and the solution was taken up in a little water and ether. The ether solution was dried and concentrated to give an oil showing the expected acetate band in the infrared. The oil was then dissolved in 95% ethanol, 3 g. of potassium hydroxide in 95% ethanol was added, and the solution was heated gently on the steam bath for several hours. Upon working up, an oil was again obtained which had a hydroxyl band in the infrared. The yield of crude alcohol²⁷ was 0.518 g. (56.2%).

To 4.05 cc. of concentrated nitric acid cooled to 15° and stirred with a magnetic stirrer, the above crude alcohol was added slowly over half an hour, keeping the temperature at about 15°. The solution became yellow-brown and, after a while, solids separated out. After all of the alcohol had been added, the solution was allowed to warm up slowly to 30° and was kept there for 2 hr. Ice was then added and the solution was centrifuged to collect the solids. They were washed well with water and dried. The product was recrystallized from glacial acetic acid or acetic acid and water, with Norit if necessary, to give a white crystalline acid, m.p. 197.4–198.8°.

(22) Transition states of the type IIIc also would have to be considered in such cases; cf. H. E. Zimmerman and T. W. Cutshall, *J. Am. Chem. Soc.*, **81**, 4305 (1959).

(23) Private communication from Prof. W. N. White.

(24) Cf. D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and A. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

(25) Cf. A. Mandelbaum and M. Cais, *J. Org. Chem.*, **26**, 2633 (1961).

(26) Procedure of K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(27) The crude alcohols obtained in such degradations were mixtures containing variable amounts of the corresponding olefins. Since the alcohol and the olefin give the same product(s) on oxidation, separation was unnecessary.

Fraction B was degraded by the same procedure and readily gave a crystalline acid, m.p. 194–196.8°. A 1:1 mixture of either of these acids with authentic *trans*-1-methylcyclohexane-1,2-diacetic acid¹⁶ gave no depression. A mixture with authentic *cis* compound²⁸ (m.p. 191.2–192.9°) melted at 163.8–179.5°.

Authentic *trans*-1-Methylcyclohexane-1,2-diacetic Acid (XII).—The authentic acid was prepared by nitric acid oxidation as above of the crystalline *trans*-10-methyl-2-decalol²⁹ from the lithium–ammonia–ethanol reduction of 10-methyl- $\Delta^1,9$ -octalone-2. Recrystallization from acetic acid gave the *trans*-diacetic acid, m.p. 197.9–199° (reported¹⁶ 196.5–197.5°). The melting point of the 50:50 mixture with the *cis*-diacetic acid²⁸ was depressed to 158–170°.

2,5-Dimethyl-4-methoxyphenol (XIII).—A solution of 254.6 g. of 2,5-xyloquinone in 490 cc. of benzene was treated with 348 cc. of purified, freshly distilled, trimethyl phosphite. The reaction was placed under nitrogen and refluxed overnight. Care must be taken, as the reaction is often exothermic. The excess solvents were then removed under vacuum and the product was distilled from an oil-jacketed flask to give 355.8 g. (72.8%) of product, b.p. (bath temp.) 135–150° (0.28 mm.). The material solidified, giving oily, hard crystals, m.p. 50.4–57.7°. They were not purified. The product was then treated with 500 g. of potassium hydroxide dissolved in 500 cc. of water and 500 cc. of methanol and the solution was refluxed several days. Solvent was removed and enough water was added to facilitate handling. The phenol was liberated with carbon dioxide and extracted with ether. The crude yield was 155 g. of 2,5-dimethyl-4-methoxyphenol. This was recrystallized from ethanol–water; m.p. 89.5–90.5° (reported³⁰ m.p. 90°).

2,5 β -Dimethyl-4 β -methoxycyclohexanone (XV).—The above phenol was hydrogenated with W-7 Raney nickel in ethanol at a temperature of 165–190°. As hydrogenation was slow, the reaction was stopped when half finished, and the catalyst was replaced with fresh catalyst. The reaction then proceeded readily at 145–150°. The product was worked up as usual, yielding the cyclohexanone XIV as an oil, b.p. 97–105° (9 mm.), n_D^{25} 1.4630, which was readily oxidized to the corresponding ketone with chromic acid–acetone reagent. The oil so obtained was yellow, possibly due to contamination with some quinone, but the colored contaminant was readily removed by letting the product stand over potassium hydroxide pellets for a short time and distilling; b.p. 85.5° (7 mm.), n_D^{24} 1.4523.

The 2,4-dinitrophenylhydrazone, m.p. 130.9–131.9°, was prepared and recrystallized from 95% ethanol.

Anal. Calcd. for C₁₅H₂₀N₄O₅: C, 53.56; H, 5.99. Found: C, 53.73; H, 6.12.

7 β ,10 β -Dimethyl-6 β -methoxy- $\Delta^1,9$ -octalone-2 (XVI).—The above 2,5-dimethyl-4-methoxycyclohexanone (50 g.) was condensed, as in the preparation of X, with methyl vinyl ketone as its Mannich base methiodide. There was recovered 19.3 g. of starting material, and 14.6 g. (37.1% based on recovered starting material) of product was obtained, b.p. 114–116° (0.25 mm.).

The 2,4-dinitrophenylhydrazone, m.p. 176.9–178.0°, was prepared and recrystallized from ethyl acetate–95% ethanol.

Anal. Calcd. for C₁₉H₂₄N₄O₅: C, 58.75; H, 6.23. Found: C, 58.87; H, 6.02.

7 β ,10 β -Dimethyl-6 β -methoxy-*trans*-decalone-2 (XVII).—The liquid ammonia–lithium reduction of the octalone XVI (5 g.) was carried out by the same procedure used for the preparation of the mixture of XIa and XIb. After the work-up, 4.13 g. of crude solid was obtained. A sample was recrystallized from *n*-pentane to give fibrous crystals, m.p. 104.6–105.8°, of the corresponding decalol which was oxidized by the procedure outlined under the synthesis of XV above. There was obtained 3.85 g. of crude crystals, m.p. 83–86°, of which 3.14 g. was used in the next step and 0.711 g. for recrystallization from *n*-pentane; m.p. 88.4–89.1°.

Anal. Calcd. for C₁₃H₂₂O₂: C, 74.24; H, 10.54. Found: C, 74.07; H, 10.71.

3 β ,9 β -Dimethyl-2 β -methoxy-*trans*-decalin (XVIII).—The above decalone was reduced under the usual Huang–Minlon conditions to give 70–75% of crude product which was used directly. Fractionation by gas chromatography showed only one product to be present. This was proved to be the *trans*-decalin XVIII by

degradation (*vide infra*). By contrast, catalytic hydrogenation of XVI with palladium–charcoal in ethanol gave a mixture of *cis*- and *trans*-decalones, as shown by v.p.c. of the decalin mixture from their Wolff–Kishner reduction. This showed 36 ± 3% *trans*-decalin and 64 ± 3% of the *cis* isomer.

Degradation of XVIII.—The above decalin (XVIII) was placed in a tube with anhydrous sodium bisulfate, under nitrogen. The tube was then heated in an oil bath at 220° for 2.5 hr. The reaction mixture was then cooled and the tube was washed out with sodium carbonate solution and ether. The ether layer was then dried and concentrated, leaving an oil. The oil was taken up in ethyl acetate and ozonized at Dry Ice temperature. The ozonide was decomposed by mixing the ethyl acetate solution with a small amount of 30% hydrogen peroxide and water and boiling off the ethyl acetate. After heating on a steam bath an additional 15 min., the flask was cooled and the keto acid was extracted with ether. The ether solution was washed with water and concentrated. The remaining oil was then taken up in a small amount of 10% sodium hydroxide solution and treated with iodine–potassium iodide solution. An immediate precipitate of iodoform occurred, and when no more was formed the basic solution was extracted with ether several times to remove the iodoform. The water layer was then acidified with concentrated hydrochloric acid to congo red and extracted with ether. The ether extracts were washed with water, dried, and concentrated, leaving an oil which solidified. The solid was recrystallized from acetic acid and water to give white crystals, m.p. 197.6–198.8°. A mixture melting point with authentic *trans*-cyclohexane-1,2-diacetic acid showed no depression.

2,5-Dimethylcyclohexane-1,4-diol.—In a hydrogenation bomb was placed 250 g. (1.34 moles) of 2,5-dimethylquinone, 400 cc. of absolute alcohol, and 4 teaspoons of W-7 Raney nickel catalyst. The hydrogenation was carried out at about 150° and 1000 lb. of hydrogen. After the reduction, the catalyst was filtered off and the solvent removed. The product, an extremely viscous oil, was distilled, b.p. 91–95° (0.04 mm.). The yield was 191.4 g. (72.4%). (A mixture of isomers of this structure has been described as a thick oil.³¹)

2,5-Dimethyl-4-benzoyloxycyclohexanone.—According to the procedure used by Jones, *et al.*, for 1,4-cyclohexanediol,³² 2,5-dimethylcyclohexane-1,4-diol was benzoylated. The yield was 52% of a very viscous oil, which was distilled from an oil-jacketed flask, b.p. 125–140° (0.04 mm.), and was then oxidized with chromic acid–acetone–sulfuric acid to the corresponding ketone which was distilled through an oil-jacketed flask, b.p. 116–130° (0.03 mm.), n_D^{25} 1.5220 (88.1% yield).

2,5-Dimethyl-4-ethylenedioxcyclohexanone (XX).—The crude 2,5-dimethyl-4-benzoyloxycyclohexanone was changed to its dioxolane by the usual procedure. The product was distilled through an oil-jacketed flask, b.p. 136–145° (0.007 mm.), n_D^{25} 1.5188 (88.3% yield). The crude ketal 92.13 g. (0.317 mole) was then dissolved in 100 cc. of absolute ethanol, and to this was added a solution of 20.8 g. of 85% potassium hydroxide dissolved in 220 cc. of absolute ethanol. The flask was flushed with nitrogen and stoppered. The next day ether was added and the potassium benzoate was filtered off. The solution was concentrated and centrifuged to remove the remainder of the salt. The remaining solvent was then removed and the product distilled through a small column; b.p. 92–94° (0.18 mm.), n_D^{25} 1.4798 (77.4% yield).

The crude ketal alcohol (46.2 g.) was oxidized by the Sarett method³³ to give the corresponding ketone, b.p. 73° (0.12 mm.), n_D^{25} 1.4687. The yield was 26 g. (56.8%).

Anal. Calcd. for C₁₀H₁₆O₃: C, 65.19; H, 8.75. Found: C, 65.65; H, 8.88.

2,5 α -Dimethyl-4 β -methoxycyclohexanone (XXI).—In a flask fitted with a stirrer, reflux condenser, and dropping funnel, and kept under nitrogen, were placed 100 cc. of absolute ethanol and 0.6 g. of sodium. When the sodium was in solution, 26 g. of ketone XX dissolved in 40 cc. of absolute ethanol was added and the solution was refluxed for 1 hr. Sodium (9.4 g.) was added in small pieces rapidly during 15 min. to the refluxing solution. When all of the sodium was in solution, the solution was cooled and enough concentrated hydrochloric acid was added just to

(28) R. P. Linstead, A. P. Millidge, and A. L. Walpole, *J. Chem. Soc.*, 1140 (1937).

(29) A. S. Hussey, H. P. Liao, and R. Baker, *J. Am. Chem. Soc.*, **75**, 4727 (1953).

(30) E. Bamberger and J. Frei, *Ber.*, **40**, 1932 (1907).

(31) N. Zelinsky and S. Naumow, *ibid.*, **31**, 3206 (1898).

(32) Cf. E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

(33) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 425 (1953).

neutralize the base present. Ether was added to help precipitate the sodium chloride, and the precipitate was filtered off. The solvent was then removed and the residue was re-ketalized in the standard manner. The product was then worked up and distilled, b.p. 90–100° (0.15 mm.). The yield of crude ketal alcohol was 25.25 g.

In a flask fitted with a stirrer, dropping funnel, and an efficient fractionation take-off were placed, after drying under nitrogen, 500 cc. of *t*-butyl alcohol and 25.25 g. of the above ketone. Potassium (17.0 g.) was then added and the flask was heated to promote solution of the metal. When all of the metal had dissolved, about one-half of the alcohol was distilled off. Then 500 cc. of dry benzene was added and the benzene-*t*-butyl alcohol azeotrope was distilled off. Another 500 cc. of benzene was added and the distillation continued until about 700 cc. had been distilled. Methyl iodide (40 ml.) was then added and the suspension was refluxed with stirring for 3 days. The solution was cooled, and then filtered by inverted filtration. The solvent was removed and the oil was distilled, b.p. 125–128° (18 mm.), $n_{25}^{25}D$ 1.4605. The yield was 20.32 g. of product which still contained some alcohol, as shown by its infrared spectrum. The crude product was then treated with benzoyl chloride and pyridine in chloroform to react with the alcohol still present. After working up and then refluxing for 2 hr. with 5% hydrochloric acid to cleave the ketal, an oily layer remained which was taken up in ether and worked up to give an oil which was distilled, b.p. 83–87.5° (9 mm.), $n_{25}^{25}D$ 1.4506. The yield was 7.42 g.

The 2,4-dinitrophenylhydrazone, m.p. 128–128.8°, was prepared and recrystallized from 95% ethanol.

Anal. Calcd. for $C_{15}H_{20}N_4O_5$: C, 53.56; H, 5.99. Found: C, 53.82; H, 6.08.

The mixture m.p. with the derivative of the isomeric XV was 114.7–122.5°.

7 α ,10 β -Dimethyl-6 β -methoxy- $\Delta^{1,9}$ -octalone-2 (XXIIa) and 7 α ,10 α -Dimethyl-6 β -methoxy- $\Delta^{1,9}$ -octalone-2 (XXIIb).—A mixture (*ca.* 50:50) of these two octalones was prepared by two routes. The first was the same as for the octalone XVI. Starting with 3.83 g. (0.0245 mole) of ketone XXI, we obtained 1.32 g. of recovered starting material and 1.84 g. (55%) of product, b.p. 96–115° (0.01 mm.).

A 2,4-dinitrophenylhydrazone was prepared. It seemed to be a mixture, the melting point of which was raised with difficulty to 157.5–160.6°, with softening at 150.5°.

The other procedure was modeled on that of Yanagita, *et al.*³⁴ In a 10-cc. flat-bottom flask fitted with a magnetic stirrer, reflux condenser, and dropping funnel, and flamed under nitrogen, was placed 7.0 g. (0.0448 mole) of ketone XXI. The liquid was

(34) M. Yanagita, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 841 (1958).

thoroughly degassed to remove oxygen. Sodium (0.1 g.) in very small pieces was added slowly at room temperature (2 hr.), and the solution was stirred until all of the sodium had dissolved (1 hr.). Then 3.01 g. of 4-diethylamino-2-butanone, which had been previously degassed, was added rapidly. After 1 hr. the solution was slowly heated to 135° during 1 hr. and maintained there for 3 hr. The product was worked up and the oil was distilled to give 3.83 g. of recovered starting material and 2.92 g. (69.3%) of product, b.p. 95–103° (0.01 mm.).

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethyl acetate and 95% ethanol to give an erratically melting derivative, m.p. 140.5–145.3°, with softening at 137° (presumably a mixture of C_{10} -epimers (see below)).

Anal. Calcd. for $C_{19}H_{24}O_5N_4$: C, 58.75; H, 6.23. Found: C, 58.89; H, 5.96.

Mixture of 3 α ,9 β -Dimethyl-2 β -methoxydecalin and 3 α ,9 α -Dimethyl-2 β -methoxydecalin.—This decalin mixture was prepared from the octalone mixture XXIIa and XXIIb by the same procedure used for the preparation of the decalin XVIII. The corresponding decalol mixture was prepared in 94% yield; the decalone mixture XXIIa and XXIIb in 71% yield.

A pure 2,4-dinitrophenylhydrazone was obtained from the decalone mixture after recrystallization from ethyl acetate; m.p. 199.1–200.2°.

Anal. Calcd. for $C_{19}H_{26}N_4O_5$: C, 58.45; H, 6.71. Found: C, 58.91; H, 6.46.

The decalin mixture was prepared in 72% yield by the usual Wolff-Kishner reduction and the product was subjected to v.p.c. on a Craig polyester succinate column; two peaks were obtained. The first peak corresponded to $55 \pm 3\%$ and the second peak to $45 \pm 3\%$ of the mixture of decalins.

Degradation of the Decalin Mixture to *trans*-1-Methyl-1,2-cyclohexanediactic Acid (XII).—The above decalin mixture was degraded by the same procedure used to degrade the decalin XVIII. A crystalline acid was obtained which, when recrystallized once from acetic acid and water, gave a white crystalline product, m.p. 193.9–195.8°. A mixture melting point with the authentic *trans*-1-methylcyclohexane-1,2-diacetic acid gave no depression.

In order to show that if one of the components of the decalin mixture had been *ca.* 50% of the *cis* isomer the acids could not have been separated by a simple crystallization, a mixture of pure *cis*- and *trans*-acids was prepared and an attempt was made to recrystallize the mixture as in the oxidative work-ups. Pure acid(s) could not be obtained.

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The Photochemistry of α -Keto Acids and α -Keto Esters. II. Solution Phase Photodecomposition of α -Keto Esters¹

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Methyl, ethyl, isopropyl, and 2-deuterioisopropyl pyruvate, ethyl benzoylformate, and ethyl α -naphthoylformate have been irradiated at 3660 Å. in benzene solution. Products have been isolated and quantum yields for the decompositions measured. The evidence presented indicates a mechanism involving photodecarbonylation in the primary process leaving caged radicals which can disproportionate to give the aldehyde derived from the acid fraction and the aldehyde or ketone derived from the alcohol fraction of the ester. A brief discussion of the excited states involved and a novel approach to the synthesis of pyruvic esters is presented.

Introduction

In a brief communication Hammond and co-workers reported that ethyl pyruvate was a triplet excitation acceptor for benzophenone leading to relatively efficient decomposition of the ester yielding acetaldehyde and carbon monoxide as the only isolable products.²

Since those authors used this reaction only as an example of an energy transfer process, we have undertaken to study the novel photochemical reactions of α -keto esters from the organic chemist's standpoint, and have attempted to elucidate the general mechanism of the photodecarbonylation reaction.

(1) Part I of this series is P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

(2) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, **83**, 2395 (1961).