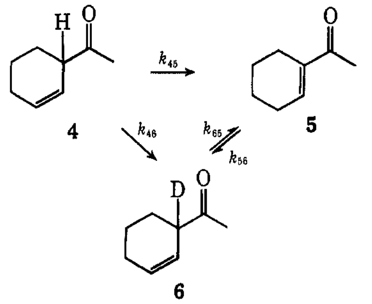

(2)

In summary, we have found that in D_2SO_4–D_2O 2-cyclohexen-1-yl methyl ketone exchanges the hydrogen at C-1 (*i.e.*, enolizes) about ten times faster than it isomerizes to 1-cyclohexen-1-yl methyl ketone. Since the C-1 D compound isomerizes at a rate which is $^1/_{4.5}$th of that of the C-1 H compound, the former compound accumulates, and the formation of the conjugated isomer shows non-first-order behavior. Because enolization is faster than isomerization, we conclude that protonation of the enol has become rate-limiting in the isomerization process, as we have observed previously for 3-cyclohexen-1-one.[4]

Because the medium can be expected to affect the enolization process and the protonation of the enol to form either the α-deuterated β,γ-unsaturated ketone or the α,β-unsaturated ketone, the observed solvent isotope effect is a complex combination of the effects on these individual processes. For enol formation we expect the usual effect (k_{D_2O}/k_{H_2O}) of about 1.4.[4] If we take the effect which has been observed on the protonation of enol ethers[12] or of acetone's enol[13] as a model, we can expect effects of 0.3–0.4 on the protonations of the enol (at the α carbon to form α-deuterated 2-cyclohexenyl methyl ketone and at the γ carbon to form γ-deuterated cyclohexenyl methyl ketone), contributing to the total observed effects on the rate of isomerization in opposing directions. Apparently in this case these contributions result in the total observed effect of 1.0. This is in contrast to the result for 3-cyclohexen-1-one, where the rate of exchange is so much faster than the rate of isomerization that the enolization process is virtually at equilibrium, which is affected comparatively little by the medium. In that case the medium effect on the protonation of the enol leading to isomerized product clearly dominates the observed solvent isotope effect.

Registry No.—**1**, 3744-02-3; **4**, 29372-98-3; **5**, 932-66-1; 1-(acetoxyethylidenyl)-2-cyclohexene, 32958-83-1.

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[12] A. J. Kresge, D. S. Sagatys, and H. L. Chen, *J. Amer. Chem. Soc.*, **90**, 4174 (1968).

[13] J. E. Dubois and J. Toullec, *Chem. Commun.*, 478 (1969).

Photoreduction of 2,4-Dimethyl-3-oxo-3,5,6,7,8,8a-hexahydro-1,8a-butanonaphthalene, a Nonphotorearranging Cross-Conjugated Cyclohexadienone

WILLIAM L. MOCK* AND KENNETH A. RUMON

Mellon Institute and Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

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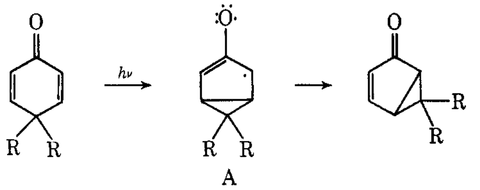
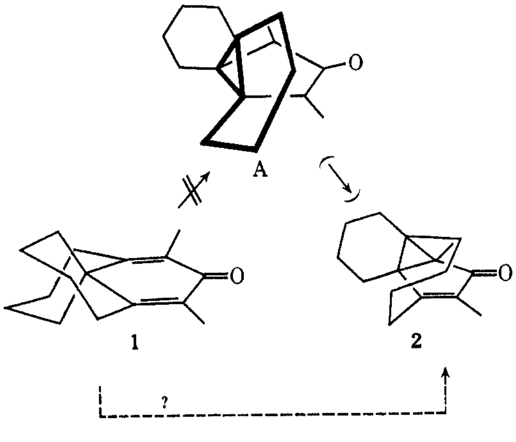
The title substance (1) was prepared from an (iodobutyl)tetrahydronaphthol by internal displacement. Failure of 1 to undergo type A photorearrangement was observed, and a low quantum efficiency for photodecomposition was noted. In 2-propanol solvent, photoreduction of one of the double bonds of 1 was achieved. Nmr examination of 1 and its di- and tetrahydro derivatives allowed stereochemical structure assignments to be made. The mechanism of photoreduction is considered to be a proton abstraction (radical) from solvent by excited 1, followed by a disproportionation.

Recent reports[1,2] examining the influence of steric factors in the type A photorearrangement of 2,5-cyclohexadienones have prompted us to record the synthesis and limited photochemical reactivity of a novel tricyclic dienone (**1**). Our original intent in preparing the ring system of **1** was to attempt to disprove the mechanistic proposals for the type A photoisomerization of cyclohexadienones advocated by Zimmerman.[3] A key intermediate in the latter scheme involves bridging between β and β' positions of the conjugated system (A). It will be observed that due to the geometric constraints imposed by the tetramethylene bridges of the spiro ring system of **1** the intermediate (containing as it would a trans-fused norcarane ring—bold face bonds) may not



A



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[1] H. E. Zimmerman and G. Jones, *J. Amer. Chem. Soc.*, **91**, 5678 (1969); **92**, 2753 (1970).

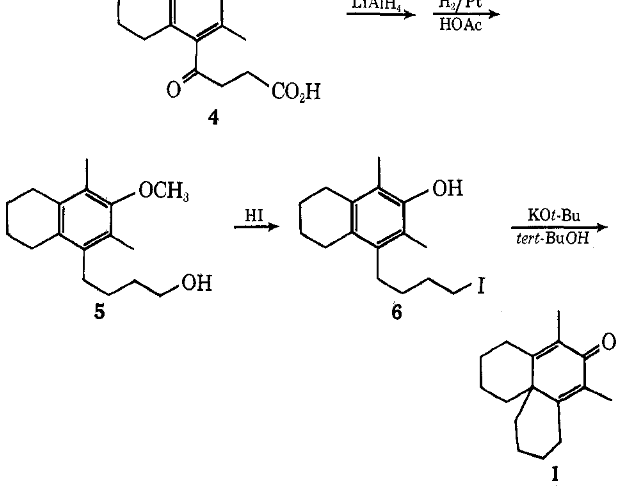
[2] T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 4845 (1969).

[3] H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967); H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

be easily formed from **1**. However, the ultimate product of a type A rearrangement (**2**) appears to be capable of existence by examination of molecular models.[4] Consequently, were the photorearrangement to proceed and to yield the normal product (**2**), a full-fledged intermediate such as that previously proposed (A) would have to be discounted and alternatives (*e.g.*, perhaps a concerted mechanism) would receive support. On the other hand, should an abnormal product arise, further insight into the properties of the excited species produced by irradiation of cyclohexadienones might be gained.

Results

Synthesis of Dienone 1.—A representative of the desired ring system was prepared from 7-methoxy-6,8-dimethyl-1,2,3,4-tetrahydronaphthalene[5] (**3**) by the sequence shown. Friedel–Crafts condensation of β-carbomethoxypropionyl chloride with **3** followed by saponification gave **4**. This was exhaustively reduced, first with lithium aluminum hydride and then catalytically with hydrogen and platinum in acetic acid in order to convert some residual intermediate aryl carbinol to **5**. Treatment with aqueous hydriodic acid then simultaneously converted the methyl aryl ether to a phenol and the primary alcohol function on the side chain to an iodide, yielding **6**. Upon treatment with potassium *tert*-butylate in *tert*-butyl alcohol, **6** gave, probably through an Ar_2^--6-assisted[6] ionization, a low conversion to the target structure **1**, mp 148°, which was isolated by column chromatography.



Photolysis in Isooctane.—When **1** was submitted to intense irradiation in degassed isooctane solution (*ca.* 0.003 *M*) at wavelengths (254 nm, from low-pressure mercury lamps) corresponding to its ultraviolet absorption, relatively slow photochemical decomposition was observed. No characterizable photolysis product could be isolated from solution after or during irradiation. A brown residue formed on the walls of the reaction vessel and had to be removed periodically, since it suppressed further photoconversion of **1**. Examination of this material revealed only tars. At the conclusion of irradiation no ultraviolet-absorbing species remained in solution.

In view of the negative preparative results obtained, a brief examination of the efficiency of the photodecomposition of **1** was undertaken. The photoreduction of benzophenone in 2-propanol is known to proceed with a quantum yield near unity,[7] and this reaction may therefore be used for crude actinometry. Qualitative experiments comparing the rate of photodisappearance of benzophenone (degassed 2-propanol) against the rate for **1** (isooctane) under otherwise identical conditions such that all incident light was absorbed in each case, indicated that **1** disappeared from solution at least 20 times more slowly than did benzophenone. It follows that the quantum efficiency for photoreaction of **1**, by whatever mechanism, must be less than 0.05.

Similar photochemical behavior for **1** was observed when it was intensively purified by sublimation–recrystallization (to remove possible adventitious quenchers), when it was irradiated in other inert (purified) solvents, when it was irradiated selectively at the $n \rightarrow \pi^*$ transition, or when photosensitization (acetophenone) was attempted. In no case was a photorearrangement product obtained.

Photoreduction of 1 in 2-Propanol.—In an effort to gain some indication of the photochemical fate of **1**, irradiation in 2-propanol was attempted.[1] Slow disappearance of dienone was again observed, but when the reaction was interrupted short of completion a new crystalline ketone, **7** (mp 123°), could be isolated by column chromatography. This was demonstrated to be a reduction product by mass spectroscopy, which revealed the addition of two atomic weight units over that of starting dienone. Additional spectroscopic evidence (ir 1655, 1615 cm^{-1}; uv 251 nm) indicated a cyclohexenone structure. Examination of the nmr spectrum revealed that the resonance from one of the methyl groups in the dienone had become split (J = 7 Hz) and had moved to higher field, as if the carbon to which it were attached had become quaternized by addition of a hydrogen nuclei. On this evidence and reasonable mechanistic considerations, the new substance appeared most probably to have resulted from the addition of a molecule of hydrogen (actually derived from the dehydrogenation of 2-propanol) across one of the double bonds of **1**.

However, some form of concurrent rearrangement could not be excluded, and therefore an independent synthesis of the new material was thought desirable. Controlled catalytic reduction of **1**, such that only 1 equiv of hydrogen was absorbed, yielded a new substance which was demonstrably *different* (tlc behavior)

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[4] The double bond of **2** should be relatively free of torsional strain, since its trans substituent positions are linked by a seven-atom chain at worst: J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970); J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970).

[5] W. Cocker, *J. Chem. Soc.*, 36 (1946).

[6] R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **84**, 788 (1962); see also S. Masamune, *ibid.*, **86**, 288 (1964); E. J. Corey, N. N. Girotra, and C. T. Mathew, *ibid.*, **91**, 1557 (1969); T. G. Crandall and R. G. Lawton, *ibid.*, **91**, 2127 (1969).

[7] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959); see also W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964); M. J. Gibian, *Tetrahedron Lett.*, 5331 (1967); N. Filipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968); S. G. Cohen and J. I. Cohen, *Israel J. Chem.*, **6**, 757 (1968). With rigorous exclusion of oxygen Φ may approach 2 for this system.

from the photoreduction product, plus a substantial amount of recovered dienone **1**. The nonidentity of the reduction products was not particularly surprising, since the catalytic procedure would be expected to yield a cis hydrogenation product, which models indicate to be sterically congested and therefore not to be the thermodynamically favored isomer. The new substance was partially separated by column chromatography; the material obtained proved to be an oil which apparently contained a small amount of unreduced **1**. In view of its noncrystallinity, the reduction product could not be assumed to be a homogeneous substance. Consequently, an attempt was made to convert it to a more easily characterizable compound, which it was hoped would turn out to be **7**. The oil was refluxed in trifluoroacetic acid, whereupon it was isomerized cleanly to a new material (**8**) which had properties (tlc behavior) quite similar to **7**. However, upon purification (column chromatography) and characterization, the new substance (mp 92°) was shown to be a *saturated* cyclohexanone (see Experimental Section). Apparently, reduction of the intermediate cyclohexenone was more facile than reduction of the dienone **1**;[8] this fits with the observation that roughly an equivalent amount of unreduced dienone **1** was recovered in the reduction even though a full mole of hydrogen was absorbed.

At this point a chemical correlation had not been established with respect to the photoreduction product **7**. However, a thorough nmr investigation of the materials in hand was undertaken at this juncture, with the result that a complete stereochemical assignment could be made for **7** as well as for the tetrahydro substance produced by catalytic reduction (**8**). This required use of high-field strength 250 MHz instrumentation in conjunction with the lanthanide shift reagent $Eu(THD)_3$[9] and spin decoupling. Consideration of the spectral data upon which the structures were based is deferred to the Discussion.[10]

Discussion

Lack of Photorearrangement of 1.—The failure of the cross-conjugated cyclohexadienone **1** to photoisomerize was until recently without precedent.[1] Negative results of the sort here obtained are open to numerous interpretations. Insofar as possible we shall avoid concocting an explanation for the failure of **1** to yield rationalizable rearrangement product. However, we do feel that some significance may be attached to the low quantum efficiency (<0.05) for the disappearance of **1** from solution. This should be contrasted with unconstrained cyclohexadienones which undergo type A photorearrangement with quantum efficiencies near unity.[1,3] While the actual mode of deactivation of photoexcited **1** remains undetermined, it is clear that type A photoisomerization has been greatly retarded, if not prevented altogether, by the tetramethylene bridges of **1**. This is entirely consistent with Zimmerman's mechanism for the latter process, in which β,β' bonding may be a requisite first step. As indicated in the introduction, access to such a mode of reactivity is effectively denied to **1** by steric considerations. Hence, our result might be taken as negative evidence in support of Zimmerman's scheme. However, regarding our original objective, the type A photoproduct (*e.g.*, **2**) is itself characteristically photolabile,[11] and therefore cannot be excluded as an intermediate which does not accumulate due to the relatively low efficiency of its formation. With this in mind it is worthwhile taking a closer look at the steric constraint upon type A photorearrangement imposed by the ring system of **1**. The extra ring strain (beyond that of a cyclopropane ring) induced upon β,β' bonding in **1** (*i.e.*, the intermediate A) would be comparable to that in *trans*-cycloheptenone, which can be produced by photoisomerization of *cis*-cycloheptenone.[12] Hence, the type A process must be regarded as feasible.[13] Consequently, for **1** the conclusions must be drawn either that (a) the driving force for β,β' bonding, etc., upon electron promotion is sufficiently powerful to overcome this steric prohibition only <5% of the time (and that the product **2** is further degraded), or (b) that the driving force is insufficient and some other mechanism operates in this specific case to give a different product. Although speculations may be drawn about other plausible modes of photoreaction, among them dimerizations, reductive hydride transfer (see later) and various types of fragmentation, we decline to do so here.

We should like to note that the photochemical inertness of **1** does allow further inference to be drawn regarding the nature of the intermediates within Zimmerman's generalized scheme. There is still some question as to whether the structure of the type A intermediate possesses a finite lifetime or whether it is merely a formalism which does not have a discrete existence within the scope of a concerted process. In the latter case, α,γ bonding would be synchronous with β,β' bonding (and with β',γ bond rupture). The conceptual alternatives are represented pictorially in the figures as path A_1 and path A_2, respectively. The geometrical distinction between the two is an exiguous one, but it has to do with the motion of the $RC_\gamma R$ group. In path A_1 this group translates to a symmetrical position above the ketone-containing ring (this corresponds to the type A intermediate) and then undergoes a transposition with rotation to give the final product. In path A_2 rotation commences immediately as the $RC_\gamma R$ group

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[8] Alternatively, it may be that the intermediate cyclohexenone was simply not desorbed from the catalyst; the stereochemistry of the double reduction is consistent with this interpretation (see Discussion).

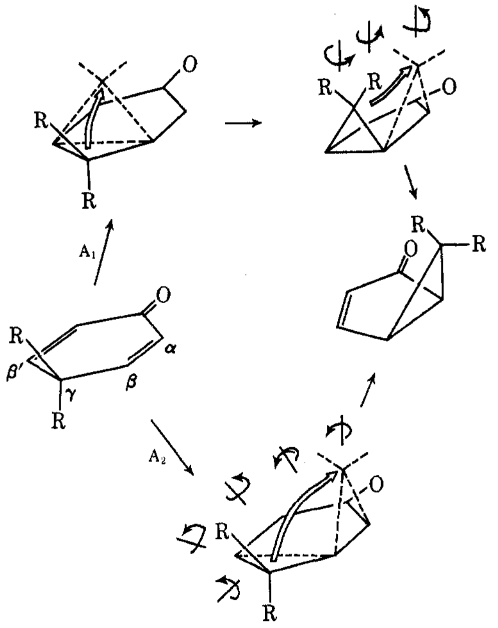
[9] Tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium.

[10] It might appear that a chemical correlation would still be feasible by catalytic hydrogenation of the photoreduction compound **7** to the corresponding saturated ketone, with subsequent comparison (after isomerization) with the tetrahydro substance (**8**). However, it is not obvious that the same stereochemistry would be obtained in the hydrogenation of **7**, since the configuration produced for the methyl group in photoreduction of **7** is the opposite to that expected for catalytic cis monohydrogenation of **1** (see Discussion). Hence, there is no reason to expect **7** to be adsorbed cleanly on the catalyst on the same face of the molecule as the intermediate in the hydrogenation of **1** (which ultimately gives **8**). Due to this uncertainty and to a shortage in the quantity of available **7**, and because there is considered to be no ambiguity in structural assignments, this reduction was not examined.

[11] H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966); F. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

[12] E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *J. Amer. Chem. Soc.*, **87**, 2051 (1965); P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965). The presumption that strain in a trans cycloalkene, $(CH)_2(CH_2)_n$, approximates that in the corresponding *trans*-bicyclo[$(n-1)$.1.0] ring system has justification in fact: W. Kirmse and C. Hase, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968); P. G. Gassman, F. J. Williams, and J. Seter, *J. Amer. Chem. Soc.*, **90**, 6893 (1968); A. J. Ashe, III, *Tetrahedron Lett.*, 523 (1969); K. B. Wiberg and A. de Meijere, *ibid.*, 519 (1969).

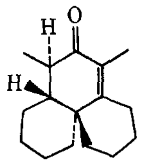
[13] There is an initial input of 75–90 kcal of excitation energy (assuming triplet manifold).



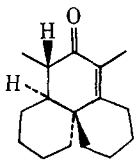
leaves the plane of the cyclohexadienone ring and continues in the course of a concerted reaction to give the product.[14] Of course, there may be a continuum of reaction paths between these conceptual extremes. The pertinent observation is that **1** would accommodate itself better to path A_2 than to path A_1, since in the former the trans-fused norcarane structural feature (introduction) tends to be avoided. From the photochemical inertness of **1** it is possible to infer that path A_1 more accurately describes the course of the *normal* type A process, and that an intermediate with a finite lifetime is required (perhaps to achieve spin inversion and electron demotion). However, this is offered as a suggestion only, since it is based upon negative evidence.[15]

Since we were chiefly interested in reactions which might be competitive with the normal type A isomerization, and especially in view of the elegant substantiation of Zimmerman's mechanism provided in his examinations of dienone photoreactivity since the inception of this work, we have not probed further into the photobehavior of this ketone in nonparticipating solvents. We have limited our discussion to the steric aspects of the molecule **1**, since electronic considerations have been adequately presented elsewhere.[1,8,14] Particular attention should be drawn to a sterically constrained system devised by Zimmerman which also failed to rearrange.[1] The latter study complements ours, since the constraint in that system was designed to prevent the second step in path A_1 (above). As noted, ours was designed to inhibit the first step. The similarity in the photochemical behavior of the two systems is probably not coincidental, since they additionally give related (but different) photoreduction products (subsequent sections).

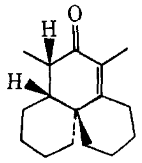
Structure of 7 and 8.—As previously indicated, the new ketone obtained in low yield upon photolysis in 2-propanol appeared to be a reduction product resulting from the transfer of two hydrogen atoms from the solvent to one of the double bonds of **1**. It must be realized, however, that a number of diastereomers can result from this operation. Of the four possibilities depicted, only the first (**7a**) is consistent with the nmr evidence. The normal (60 MHz, CCl_4 solution) spectrum consists of a broad envelope upon which is superimposed, as the only recognizable functionalities, a singlet (δ 1.77) arising from the methyl group remaining on a double bond and a doublet (δ 1.05, $J = 7$ Hz) arising from the other methyl group. Upon the addition of increments of $Eu(THD)_3$,[9] these (and other resonances) are progressively shifted strongly downfield, until at saturation the methyl groups appeared to have suffered an induced shift of *ca.* 9.7 ppm relative to TMS (δ_{Eu} 11.3 and 10.8, respectively).[16] Even more strongly affected was a single-proton multiplet which ultimately was shifted to δ_{Eu} 15.0 downfield from TMS.[16] This must be assigned[18] to H-2, adjacent to the carbonyl group and on C-2 bearing the methyl group. Less strongly affected was a one-proton *doublet*, δ_{Eu} 8.8 ($J = 12$ Hz), which was shown to be coupled to H-2 by irradiation of the latter signal. Coupling of this magnitude indicates a trans diaxial vicinal relationship for this proton (H-3) and H-2 as shown in the perspective view. Of most significance, however, is the observation that H-3 is not further coupled. It is therefore concluded that this proton must have a gauche relationship with *both* protons of the adjacent methylene group ($H_{a,e}$-4). This is only feasible for the stereochemical relationship depicted; the fusion of the C-4–C-7 annelated ring is therefore fixed as being cis relative to the octalone portion of the rest of the molecule. While trans fusion is



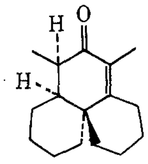
7a



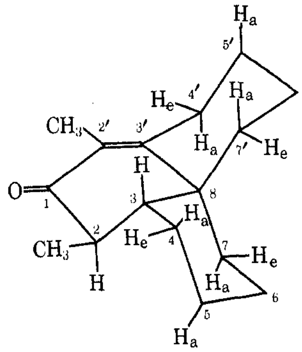
7b



7c



7d



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[14] A variation of this is to have the primary photochemical process be a twisting of one of the double bonds in the dienone. See ref 1 for a discussion on this point. See also R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), Section 6.2, for orbital symmetry aspects of the concerted pathway.

[15] Moreover, see ref 1 for contrary arguments.

[16] The chemical shifts designated by δ_{Eu} in this paper are those measured for the particular samples used in this study in which carbon tetrachloride solutions saturated with $Eu(THD)_3$ were examined. Since the induced shift is highly concentration dependent the usual meaning of δ (extrapolation to infinite dilution) should not be inferred for these measurements. For this study ΔEu values[17] were not derived, since for the majority of protons sufficient resolution was not obtainable until the end of the shifting process, when the spectrum was examined at 250 MHz; extrapolated values in the absence of shift reagent were thus not calculable. Due to the line broadening effect of the reagent, couplings of less than 2–3 Hz were not observable.

[17] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734, 5737 (1970).

[18] For purposes of discussion the positions are numbered nonsystematically according to the figures given. Full names are given in the Experimental Section.

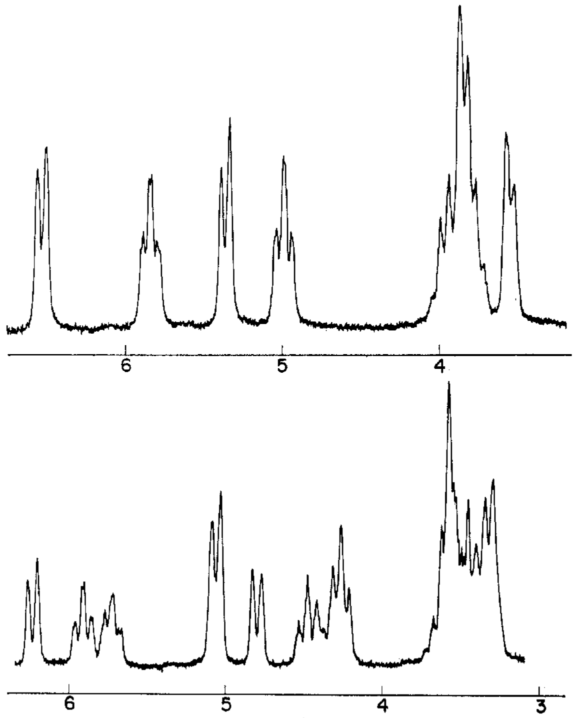
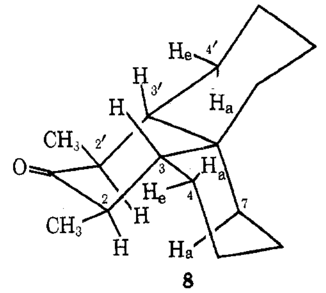


Figure 1.—Portions of Eu(THD)$_3$ shifted spectra of **1** (upper) and **7** (lower). See text and footnote 16 for interpretation.

stereochemically feasible (**7b**, above) it would definitely produce a trans diaxial relationship which should further split H-3.

However, failure to observe further coupling for the β proton (H-3) of **7** is negative evidence. It would be desirable to have an analogous structure wherein the alternative stereochemical relationship could be examined to substantiate the nmr interpretation. The saturated cyclohexanone **8**, produced by catalytic hydrogenation and acidic isomerization, fulfills this objective excellently. For this substance there are of course several more configuration possibilities than for **7**. Those which potentially contain a twofold rotation axis (as does **1**), etc., may be immediately excluded by the nmr observation that the unshifted methyl groups (δ 0.86 and 0.93, J = 7 Hz) are nonequivalent. Of the remaining isomers, only that depicted in perspective is considered to be consistent with the known relative thermodynamic stability of **8** and the Eu(THD)$_3$ shifted spectrum of this material at 250 MHz. For **8** the methyl groups undergo an induced shift of nearly the same magnitude as in **7** when a carbon tetrachloride solution is saturated with Eu(THD)$_3$ (both δ_{Eu} 9.1). Similarly, the α protons (which are also nonequivalent) are shifted to δ_{Eu} 11.7 and 12.3 (H-2 and H-2′, relative assignments undetermined) as was the corresponding proton of **7**. In addition, the β protons were found to be shifted to a similar relative position as in **7**. However, in this case one of these protons, δ_{Eu} 7.8, was a *triplet* (coupling *ca.* 12 Hz) whereas the other was a *doublet*, δ_{Eu} 7.4 (J = 10 Hz). We find this uniquely consistent with the structure pictorially represented. The latter resonance (doublet) arises from H-3, which is coupled only to H-2, since it bears a gauche relationship with both protons of the C-4 methylene group as in **7**. The triplet resonance, ascribed to H-3′, is coupled to both H-2′ and the axial proton (H$_a$-4′) of the adjacent methylene group, to both of which it bears a trans diaxial vicinal relationship (and hence experiences an equivalent coupling). The feasible structural alternatives for **8** (*i.e.*, other than that shown) either do not possess trans diaxial orientation between the α and β protons (H-2,-H-3 and H-2′,H-3′) and/or fail to display acceptable relationships between the β and γ protons (H-3,H$_{ae}$-4 and H-3′,H$_{ae}$-4′). Accordingly, the course of the catalytic hydrogenation must be as depicted (**1** → **8**).



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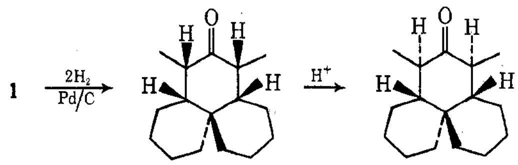

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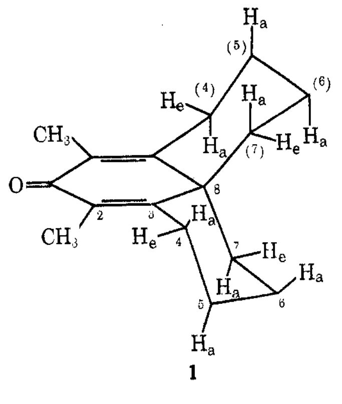
The preceding paragraphs have outlined the nmr spectral features which allow assignment of structure to **7** and **8**. In the case of the photoproduct, however, a reservation must be made that there is no proof that carbon skeleton rearrangement has not taken place. One should consider the possibility that **7** in fact possesses a different ring system. We have two reasons for discounting this prospect. One is that we are unable to formulate an isomeric structure which is consistent with the data cited. Secondly, additional features of the nmr spectrum of **7** lend confidence to the assumption that a common carbon framework is shared by all of the substances which we have identified; specifically, the annelated tetramethylene bridges are part of cyclohexane rings which in each case are *locked into chair conformations*. The 250-MHz spectrum of the dienone **1** in the presence of Eu(THD)$_3$ was also recorded and is partially presented in Figure 1. In addition to the substantial shift of the methyl groups (δ_{Eu} 12.1, not shown), four additional resonances were sufficiently moved that their coupling patterns could be discerned. It was evident that these arose from the methylene protons on C-4 and C-7. There were two



1

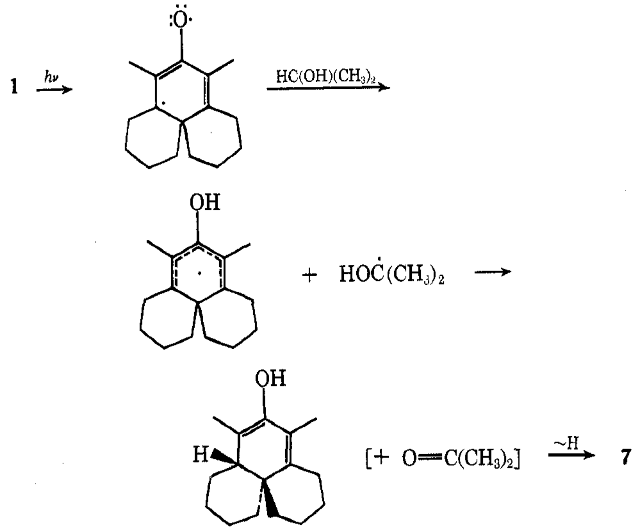
doublets (δ_{Eu} 6.6, J = 14 Hz and δ_{Eu} 5.4, J = 14 Hz) which must be assigned to positions equatorial to six membered rings (H_e-4 and H_e-7), where they experience only geminal coupling. The axial protons to which they are coupled (δ_{Eu} 5.9 and 5.0, respectively) are *triplets* (coupling *ca.* 13 Hz). This latter splitting is interpreted as the resultant of reciprocal geminal coupling to the equatorial protons *plus* trans diaxial vicinal coupling of the same magnitude to one other proton in each case. Suitable stereochemistry for this latter pattern is found for both the axial proton H_a-4 (adjacent to the double bond) and the axial proton H_a-7 (adjacent to a quaternary center); the other axial protons (H-5, H-6) should exhibit further coupling (however, they are buried in an eight-proton multiplet, δ_{Eu} 3.5–4.1). There is no internal evidence to allow relative assignments of the described resonances to the C-4 or C-7 methylene positions. (However, see the discussion of **7** which follows.)

The point of describing the nmr spectrum of **1** is that correlations may be drawn to the corresponding resonances observed in **7**, lending credence to the assumption that skeletal rearrangement has not taken place in the photoreduction. Of course, the symmetry of **1** has been destroyed in **7**, such that the tetramethylene bridges are no longer equivalent. It is apparent (Figure 1) that the downfield doublet and triplet of **1** have been split into four resonances in **7**. Furthermore, it was confirmed by spin decoupling that the furthest downfield doublet in **7** (δ_{Eu} 6.2, J = 14 Hz) is geminal to the second triplet upfield (δ_{Eu} 5.7), whereas the adjacent triplet (δ_{Eu} 5.9) is coupled to a single proton doublet 0.9 ppm upfield (δ_{Eu} 4.8, J = 14 Hz). It is our feeling that the large difference in the chemical shifts found in the equatorial protons indicates that the downfield resonances in **1** and **7** arise from the C-4 (C-4′) methylene hydrogens which are (were) adjacent to a double bond. The other methylene groups described in the spectrum of **1** are little effected by saturation of one of the double bonds. A two-proton doublet, δ_{Eu} 5.1 (J = 13 Hz, equatorial protons), in the same region of the spectrum as in the case of **1** was shown by spin decoupling to be geminal to an apparent two-proton quartet (δ_{Eu} *ca.* 4.5) which we feel is best interpreted as overlapping (axial proton) triplets. As before, these resonances are regarded as arising from C-7 (C-7′) methylene groups. It will be noted that an additional two-proton triplet (or, more likely, overlapping pair of doublets) has been shifted selectively downfield (δ_{Eu} *ca.* 4.3) from the six-proton multiplet arising from the rest of the hydrogens in the molecule (δ_{Eu} 3.1–3.8). No assignment is offered for these resonances; by irradiation they appeared to be coupled only to the high-field multiplet. The correlations which we have pointed out strongly support the conclusion that there are tetramethylene bridges existing in chair conformation cyclohexane rings in **7** (as in **1**).

The region of the spectrum exhibited in Figure 1 (and just discussed) was also examined in the Eu(THD)$_3$ shifted spectrum of the saturated ketone **8**. While resonances were observed in the same places, extensive overlapping precluded analysis of the sort given for **1** and **7**. However, one proton was selectively shifted proportionately further downfield. This resonance (δ_{Eu} 6.0) was a triplet (coupling *ca.* 13 Hz), suggesting it to be one of the axial hydrogens previously discussed. From inspection of models we believe it to be H_a-7 (see perspective representation of **8**), which is located over the cyclohexanone ring and in close proximity to the α protons (C-2, C-2′) which are strongly deshielded.

In discussing the induced shift results we have avoided speculation as to the mode of action of the europium chelate, which probably operates through coordination with the carbonyl group. We have not given a more quantitative evaluation of the magnitude of the shifts, since extrapolated ΔEu values[17] were not easily obtainable[16] and because the mechanism by which the europium nucleus accomplishes its effects is presently incompletely established.[19] Trial calculations using formulae which have been suggested[17,19,20] and which might have unambiguously settled the question of structure in **7** (or led to firm assignments of the C-4 and C-7 methylene group protons) were not fruitful, since the results depended grossly upon the orientation assumed for the carbonyl-O to Eu coordination and since the Eu to H distances were all approximately the same for the critical protons.[21]

Mechanism of Photoreduction of 1.—Clearly a hydrogen abstraction step is involved in the production of **7**, and based upon precedent, the sequence given is considered most probable. Purely on the basis of analogy,[1,3] the photochemically active state of **1** we believe to be the n → π^* triplet, although preparatively the irradiation was absorbed by the π → π^* band. Intersystem crossing is generally more than sufficiently facile to account for the observed quantum efficiency.[1,3] Moreover, hydrogen abstraction to give ketyl radicals is characteristic of the n → π^* state.[1,7] The next step is formulated as disproportionation of the radical pair to give acetone and the enol of **7**. (We disfavor the possibility that the radical from **1** abstracts another hydrogen from solvent 2-propanol, since this would seem to be an endothermic step. Disproportionation of two mole-



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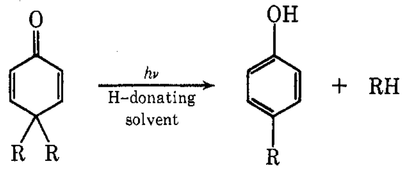
[19] In addition to the pseudocontact interaction the possibility of a contact interaction operating through the π system cannot be excluded. For pertinent references see C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971).

[20] J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970); A. F. Cockerill and D. M. Rackham, *Tetrahedron Lett.*, 5149, 5153 (1970).

[21] Z. W. Wolkowski, *Tetrahedron Lett.*, 821 (1971); T. H. Siddall, III, *Chem. Commun.*, 452 (1971).

cules of the radical from **1** is also reasonable.) This second proton appears to enter into the less hindered site of the molecule; the product which would ultimately result from attack upon the opposite (more hindered) position of the π electronic system is inconsistent with the nmr spectral evidence, as cited in the previous section.[22] The final step of the mechanism is ketonization of the enol, which preferentially should produce the substance in which a trans hydrogenation of one of the double bonds in **1** has been achieved, since this configuration is clearly the most stable (equatorial methyl group).

Finally, we would point out that this photoreduction appears to be unique among cyclohexadienones. In those few cases in which type A photorearrangement (or the diversion of intermediates therefrom) is not the exclusive reaction path, formation of a phenol by expulsion of one of the ring substituents has been the alternative reaction course.[1,23] We were able to detect



only a trace of material which may have been phenolic[1] in the reductive photolysis of **1**. It is not unreasonable that the annelated rings attached to the cyclohexadienone nucleus of **1** might suppress this mode of reactivity, especially if the expulsion step were a reversible radical fragmentation.[24,25] Alternatively, it may be that the fragmentations also proceed from the type A intermediate, and that transient β,β' bonding may be obligatory in those cases as well.

Experimental Section

Preparation of 4.—To a stirred solution of 109.75 g (0.58 mol) of **3**[5] and 132 g (0.88 mol) of β-carbomethoxypropionyl chloride[26] in 300 ml of benzene maintained at 0–6.5° was added slowly 132 g (1.0 mol) of aluminum chloride. After stirring for 16 hr at room temperature the mixture was decomposed with ice and diluted with hydrochloric acid. The oily product was extracted into ether and dried with anhydrous sodium sulfate. The residue obtained upon removal of the ether solvent was distilled at reduced pressure. There was obtained 145 g of crude methyl ester of **4**, bp 180–186° (0.01 mm), which solidified on standing. Spectral evidence indicated that the ester was impure; therefore it was saponified to the carboxylic acid. The distillate was dissolved in 500 ml of dioxane and was added to a solution of 50 g of sodium hydroxide in 1.0 l. of water. The mixture was warmed and stirred until a homogeneous solution was obtained and then was allowed to stand for 1 hr. Upon acidification a substance precipitated which was collected and recrystallized from 2.0 l. of toluene. There was obtained 123 g (73%) of β-(2,4-dimethyl-3-methoxy-5,6,7,8-tetrahydro-1-naphthoyl)propionic acid (**4**), mp 182–183°.

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.23; H, 7.73.

Preparation of 5.—To a solution of 80.8 g (0.28 mol) of **4** in 500 ml of tetrahydrofuran was added portionwise 10.0 g of lithium aluminum hydride and the mixture was refluxed for 3 hr. An additional 5.0 g of lithium aluminum hydride was then added and refluxing was continued for 2 hr. Excess hydride was destroyed with methanol and the solvent was removed under vacuum. The residue was treated with dilute hydrochloric acid and the mixture so obtained was extracted with ether. After drying over anhydrous sodium sulfate, the solvent was removed. The product at this stage was a mixture of a cyclic ether, a diol, and a hydroxy ketone, which could be separated by column chromatography. For preparative purposes, the unresolved mixture was hydrogenolyzed to **5**. Adams catalyst was prepared by reducing 0.5 g of platinum oxide in 100 ml of acetic acid. To this was added the mixture from the hydride reduction in 200 ml of acetic acid; hydrogen uptake proceeded for 24 hr under several atmospheres pressure. The filtered solution was then added to excess sodium hydroxide solution (hot) and stirred to saponify any ester which may have formed. The chilled basic solution was then extracted with ether and, after drying, the extracts were evaporated to give a residue which solidified upon standing. Recrystallization from hexane gave 34 g (46%) of 2,4-dimethyl-1-(4-hydroxybutyl)-3-methoxy-5,6,7,8-tetrahydronaphthalene (**5**), mp 66–67°.

Anal. Calcd for $C_{172}H_6O_2$: C, 77.82; H, 9.99. Found: C, 78.41; H, 10.06.

Preparation of 6.—A mixture of 20.0 g (0.076 mol) of **5** and 200 ml of 50% hydriodic acid was refluxed for 1.5 hr. The cooled solution was diluted with water and the insoluble oil was extracted into methylene chloride. The extracts were washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. After drying, the solvent was removed and the residue was recrystallized from 100 ml of hexane to give 19.9 g (73%) of 1,3-dimethyl-4-(4-iodobutyl)-5,6,7,8-tetrahydro-2-naphthol (**6**), mp 87–88°. This substance decomposed on standing.

Anal. Calcd for $C_{16}H_{23}IO$: C, 53.64; H, 6.47. Found: C, 54.06; H, 6.64.

Preparation of 1.—To a solution of 10.0 g (0.028 mol) of **6** in 150 ml of *tert*-butyl alcohol was added 10.0 g of commercial potassium *tert*-butylate and the solution was stirred until homogeneous. Upon heating a precipitate (KI) formed. After 15 min at reflux the mixture was poured into 500 ml of cold water and extracted with ether. After washing with water and saturated sodium chloride solutions, the extracts were evaporated to give a residual oil. This was submitted to column chromatography on 80 g of silicic acid with chloroform eluent. First eluted was a yellow oil, followed by **1** and then by another yellow oil. The chromatographic fractions containing **1** were combined and purified by recrystallization from 20 ml of hexane followed by sublimation at 100° (0.1 mm). A final recrystallization from hexane gave 0.77 g (12%) of 2,4-dimethyl-3-oxo-3,5,6,7,8,8a-hexahydro-1,8a-butanonaphthalene (**1**): mp 147.5–148°; ir $\nu_{\max}^{\mathrm{KBr}}$ 1650 and 1610 cm^{-1}; mass spectrum *m/e* 230; $\lambda_{\max}^{n\text{-hexane}}$ 247 nm (ϵ 16,000), 321 sh (26), 331 (32), 343 (31), 357 (20), and 371 sh (8); $\lambda_{\max}^{i\text{-PrOH}}$ 253.5 nm; nmr $\delta_{\max}^{\mathrm{CCl_4}}$ 1.85 (d, $J = 0.8$ Hz, CH_3 coupled across double bond to one methylene proton) and 0.8–3.0 ppm (m, CH_2) (see also text).

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.27; H, 9.45.

Photoreduction of 1.—A solution of 600 mg (2.6 mmol) of **1** in 550 ml of distilled 2-propanol was irradiated (Vycor flask) at 40–50° with a bank of 16 low-pressure mercury arcs (Rayonet photochemical reactor) for 185 hr, at which time the absorbance at *ca.* λ 250 nm had decreased by >60%. Solvent was removed by distillation and evaporation on a rotary evaporator and the oily residue was submitted to column chromatography on 50 g of silicic acid with carbon tetrachloride–chloroform gradient elution. Fractions were collected periodically and evaporated to dryness. From later fractions was obtained after recrystallization from hexane 106 mg of starting material dienone **1**. More rapidly eluted was a new substance which was recrystallized from hexane to give 55 mg (9% based on unrecovered **1**) of 2,*cis*-4-dimethyl-3-oxo-*cis*-3,4,4a,5,6,7,8,8a-octahydro-1,8a-butanonaphthalene (**7**): mp 123–123.5°; ir $\nu_{\max}^{\mathrm{KBr}}$ 1655 and 1615 cm^{-1}; mass spectrum *m/e* 232; $\lambda_{\max}^{\mathrm{EtOH}}$ 251 nm (ϵ 10,500); nmr (see text).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.77; H, 10.52.

No product could be isolated following relatively slow photodegradation in the following solvents: CH_3CN, *i*-C_8H_{18}, *n*-C_6H_{14}, $(C_2H_5)_2O$, and *tert*-C_4H_9OH.

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[22] The steric discrimination is between one or two 1,3-diaxial interactions in the transition state.

[23] K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

[24] We note that in the parallel study of Zimmerman previously cited,[1] explusion of a methyl group was the reaction course which was observed.

[25] The mechanism we suggest is closer to that proposed by Zimmerman[1] than to the alternative originally postulated by Schuster: D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **87**, 2515 (1965); D. I. Schuster and C. J. Polowczyk, *ibid.*, **88**, 1722 (1966); however, see D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968).

[26] J. Cason, "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 169.

Catalytic Hydrogenation of 1.—A solution of 233 mg (1.0 mmol) of **1** in 15 ml of ethyl acetate was added to a prereduced mixture of 24 mg of catalyst (10% palladium on carbon) in 5 ml of ethyl acetate in a conventional (1 atm pressure) hydrogenation apparatus. After stirring for 45 min, *ca.* 24 ml of hydrogen had been absorbed and the reduction was interrupted. Catalyst was removed by filtration and solvent was evaporated under reduced pressure. The residue was submitted to column chromatography on 17 g of silicic acid with chloroform eluent. Product was eluted first, followed by 83 mg of recovered **1**. Since the new substance could only be obtained as an oil contaminated with **1**, it was directly isomerized. Chromatographic fractions containing reduced material were combined and dissolved in *ca.* 1 ml of trifluoroacetic acid and the solution was refluxed for 1.5 hr. After removal of solvent the residue was submitted to column chromatography as before. After combination of appropriate chromatographic fractions and recrystallization from hexane, there was obtained 66 mg of *cis*-2,*cis*-4-dimethyl-3-oxo-*cis*-perhydro-*trans*-1,8a-butanonaphthalene (**8**): mp 91.5–92.5°; ir ν_{max}^{KBr} 1700 cm^{-1}; mass spectrum *m/e* 234; nmr (see text).

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.01; H, 11.23.

Registry No.—**1**, 32670-24-9; **4**, 32670-25-0; **5**, 32670-26-1; **6**, 32670-27-2; **7a**, 32653-54-6; **8**, 32653-55-7.

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Hydride Reduction of *N*-Cyclopropylimines

Carl L. Bumgardner,* Ernest L. Lawton,[1] and James G. Carver

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

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The fate of intermediates generated by hydride addition to the carbon atom of *N*-cycloalkylimines was studied to determine the stability of species which have a negatively charged nitrogen atom adjacent to a small ring. When sodium aluminum hydride or lithium aluminum hydride was used as the hydride source, cleavage of the three-membered ring accompanied reduction of the carbon–nitrogen double bond. However, only the imine group was reduced when sodium borohydride, lithium borohydride, or hydrogen and platinum were employed. Results are rationalized in terms of isomerizations analogous to the cyclopropylcarbinyl allylcarbinyl anion conversion.

The proclivity for cyclopropylcarbinyl anions to undergo ring opening to give the isomeric allylcarbinyl anions is well known.[2] For example, reactions[3,4] of cyclopropylcarbinyl Grignard and lithium reagents, Wolff–Kishner reduction[2] of certain cyclopropyl aldehydes, treatment of cyclopropylcarbinyl quaternary salts with sodium amide,[2] and addition of isopropyllithium[5] to substituted vinyl cyclopropanes all lead to products which involve ring opening of a cyclopropylcarbinyl species having some carbanoid character. In like manner, cyclopropoxides rearrange to carbonyl compounds.[6]

To determine the stability of intermediates which have a negatively charged nitrogen atom adjacent to the small ring, we examined the consequence of adding hydride to the carbon atom of a number of *N*-cycloalkylimines. The imines studied included *N*-(3-phenylpropylidene)cyclopropylamine (**1**), *N*-benzylidenecyclobutylamine (**2**), *N*-benzylidene(*trans*-2-phenylcyclopropyl)amine (**3**), *N*-(3-phenylpropylidene)benzylamine (**4**), and *N*-benzylidenecyclopropylamine (**5**). Lithium aluminum hydride, sodium aluminum hydride, lithium borohydride, and sodium borohydride were employed as hydride sources. The course of catalytic hydrogenation was also investigated.

In previous work, Kaiser, Burger, and coworkers[7] observed that reduction of *N*-(2-phenylcyclopropyl)formamide with lithium aluminum hydride gave not the expected *N*-methylamine but *N*-methyl-3-phenylpropylamine. In addition, 2-phenylcyclopropylamine was found to be unstable to lithium aluminum hydride. Our results are in accord with theirs and also establish the requirements for ring opening in a variety of *N*-cycloalkylimine–hydride reductions.

Results

Condensation reactions between the appropriate amines and aldehydes provided the desired imines. These preparations are summarized in Table I.

Imine reductions were accomplished by refluxing an ether or tetrahydrofuran (THF) solution approximately 0.05–0.5 *M* in the imine with an excess of the complex hydride. Reactions were quenched by addition of a 1:1 mixture of 10% sodium hydroxide and ethanol or 10% hydrochloric acid and methanol and the products were isolated by distillation and characterized by nmr analysis and in some cases by independent synthesis. Results are collected in Tables II and III.

Discussion

The results in Table III may be divided into two groups: those reactions in which reduction of the carbon–nitrogen bond is accompanied by ring cleavage (runs 1, 2, 5, 7, 8, 10, 11) and those examples in which reduction leaves the small ring intact (runs 4, 13–19). The aluminum-containing reagents belong to the former group, the borohydrides and catalytic hydrogenation to the latter.

Runs 1 and 5 show that ring opening is not a function of the group attached to the imine carbon atom, and run 4 demonstrates that ring cleavage is unimportant in the case of *N*-cyclobutyl compounds.

Ring-opened products can be accounted for by a scheme involving isomerization of intermediate I to

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[1] NASA Fellow.

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