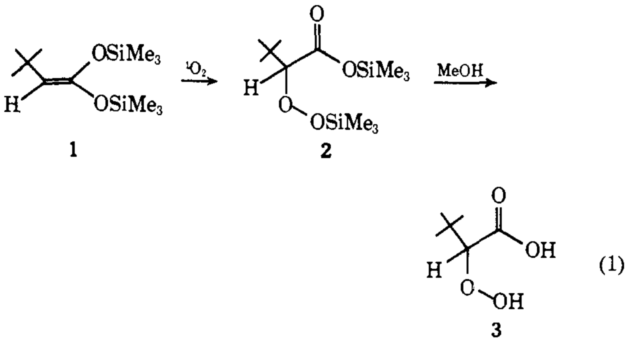
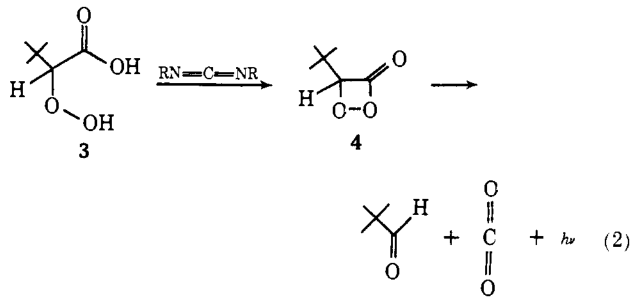
readily available by silylation of the α-lithio carboxylate,[18] gave quantitatively the α-silyl peroxy ester **2** (eq 1):



bp 67–69° (0.2 mm); 99 ± 1% pure by iodometric titration; ir (cm^{-1}, CCl_4) 1730 and 1710 (C=O), 1365 (*tert*-butyl), and 1245 (Si–O); nmr (60 MHz) δ (TMS, CCl_4) 0.30 (s, 9, OOSi-Me_3), 0.20 (s, 9, CO_2SiMe_3), 0.98 (s, 9, C*Me*), and 3.97 (s, 1, >C*H*). This novel ene reaction involving migration of a trimethylsilyl group was anticipated, since in the photooxidation of trimethylsilyl enol ethers a similar migration was observed.[19] Hydrolysis of the silyl ester **2** with methanol at 5–10° afforded the desired α-hydroperoxy acid **3** essentially quantitatively, which on recrystallization from anhydrous ether–pentane mixture gave white needles: mp 69–70°; 99.5 ± 0.5% pure by iodometric titration; ir (cm^{-1}, CCl_4) 3510–3450 (OOH), 1715 (C=O), and 1365 (*tert*-butyl); nmr (60 MHz) δ (TMS, CCl_4) 1.05 (s, 9, CMe_3), 4.30 (s, 1, >C*H*), and 9.52 (s, 2, OO*H* and CO_2H). Catalytic reduction over platinum gave the α-hydroxy acid quantitatively, mp 85–87° (lit.[20] mp 87–88°).

The cyclization of the α-hydroperoxy acid **3** into the α-peroxy lactone **4** (eq 2) was most effectively achieved



by stirring equimolar quantities of **3** and dicyclohexylcarbodiimide in CCl_4 below −10° for 30 min. Flash distillation of the reaction mixture at −10° permitted separation of the unreacted starting materials and the dicyclohexylurea, affording a clean solution of the α-peroxy lactone **4** in CCl_4, whose ir exhibited a strong carbonyl band at 1875 cm^{-1} (for comparison, α-lactones[21] absorb at 1900 cm^{-1} and β-lactones at 1830 cm^{-1}) and the characteristic *tert*-butyl at 1365, while the nmr spectrum showed singlet proton resonances at δ 1.10 (*tert*-butyl) and 5.48 (>CH). However, the infrared and nmr spectra quickly changed (the approximate lifetime of the α-peroxy lactone is 5–8 min at room temperature) to that of pivalaldehyde under vivid evolution of CO_2. The presence of pivalaldehyde, the exclusive decomposition product, was confirmed by comparison of glpc retention times and ir and nmr spectra with the authentic material. Warming of a sample to room temperature in the dark clearly displayed the expected luminescence, which could be significantly enhanced by addition of 9,10-diphenylanthracene as the photoreceptor.[8]

Efforts to isolate the α-peroxy lactone **4** in pure form have failed, since it readily codistills with CCl_4, and efforts to crystallize the compound have not succeeded. Presently we are exploring substitution patterns which should help stabilize the α-peroxy lactone structure and at the same time incorporate desirable physical properties to permit isolation. Measurements of luminescence quantum yields, the luminescence spectrum, and activation parameters, as well as synthetic utilization of this novel peroxide heterocycle, are in progress.

Acknowledgments. The generous financial support of this work by the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, the Research Corporation, and the A. P. Sloan Foundation is gratefully appreciated.

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(22) Taken in part from the Doctoral Dissertation of J. C. Liu to be submitted to the University of Puerto Rico in partial fulfillment of the requirements of the Ph.D. degree.

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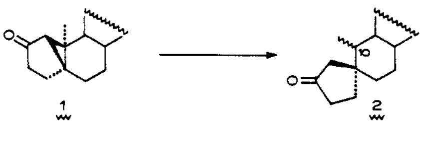
Stereochemistry of the Lithium–Ammonia Reduction of *cis*-1,7-Dimethyltricyclo[4.4.0.0^{2,6}]decan-3-one and Related Compounds

Sir:

The alkali metal–ammonia reduction of conjugated cyclopropyl ketones is now a well-known process[1–5] and has considerable synthetic potential. It has been established[1] that, in general, the cyclopropyl bond which cleaves is the one possessing the greater overlap with the π orbital system of the carbonyl group. However, one interesting and potentially useful facet of this reaction which has not yet received investigative attention is the stereochemical fate of the β carbon atom. For example, although lumicholestenone (**1**) has been reduced with lithium in liquid ammonia,[1] the stereochemistry at C_{10} in the product **2** was not determined.



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(1) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966), and references therein.

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Table I. Effect of Alcohol and Temperature on the Reduction of Compound **4**

Run[a]	Alcohol[b]	Temp, °C	Ratio (**5**:**6**)	Yield, %[c]
1	None	−33	85:15	51
2	MeOH	−33	78:22	69
3	*i*-PrOH	−33	77:23	63
4	*tert*-BuOH	−33	78:22	68
5	None	−78	94:6	55
6	MeOH	−78	90:10	62
7	*i*-PrOH	−78	90:10	66
8	*tert*-BuOH	−78	90:10	62

[a] All experiments were done at least in duplicate. [b] In each case, 5 mmol of alcohol was used. [c] As determined by glc, using an internal standard.

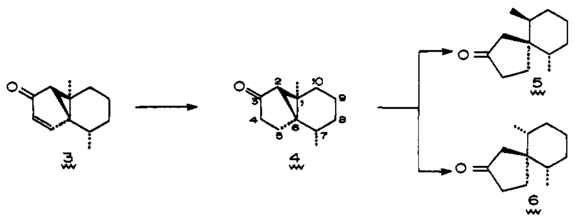
Table II. Effect of Alcohol Concentration on the Reduction of Compound **4**

Run	Alcohol (mmol used)	Temp, °C	Ratio (**5**:**6**)	Yield, %[a]
1[b]	None	−33	85:15	51
2–4[b]	ROH (5)	−33	78:22	69, 63, 68
9	MeOH (50)	−33	64:36	70
10	*tert*-BuOH (53)	−33	68:32	68
11[c]	MeOH (125)	−33	57:43	60
12	MeOH (50)	−78	85:15	60

[a] As determined by glc, using an internal standard. [b] From Table I. [c] In this experiment, lithium was added slowly to a solution of **4** in ammonia–tetrahydrofuran containing 125 mmol of methanol.

We report here our preliminary studies concerning the reduction of *cis*-1,7-dimethyltricyclo[4.4.0.0^{2,6}]decan-3-one (**4**), which was readily prepared by controlled catalytic hydrogenation of the known *cis*-1,7-dimethyltricyclo[4.4.0.0^{2,6}]dec-4-en-3-one (**3**).[6]

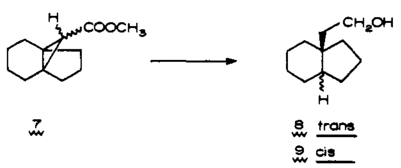
Our studies show that, under appropriate reaction conditions, the dissolving metal reduction of compound **4** occurs with a high degree (>90%) of *inversion* at the β carbon atom. For example, reduction of **4** with excess lithium in liquid ammonia–tetrahydrofuran at −78° afforded a mixture of the spiro ketones **5**[7] (inversion product) and **6**[7] (retention product), in a ratio of 94:6, respectively. This novel result is in contrast to the photoreduction of **4** in 2-propanol, which afforded the expected epimeric mixture of compounds **5** and **6**, in a ratio of approximately 2:3, respectively.[8] In view of these contrasting results, further studies were undertaken in order to determine the effect of various reaction conditions on the stereochemical outcome of the Birch reduction of compound **4**. The results of some of these studies are summarized in Tables I and II.



The typical experimental procedure employed to obtain these results was as follows. To a magnetically stirred solution of lithium metal (250 mg) in liquid ammonia (40 ml), at the desired temperature, was added a solution of the tricyclic ketone **4** (60 mg) in tetrahydrofuran or in tetrahydrofuran containing the desired amount of the appropriate alcohol. After 2 hr, the reaction was quenched by addition of ammonium chloride, the ammonia was allowed to evaporate, and water was added to the residue. The product, isolated by extraction of the resultant mixture with ether, was subjected to a modified Collins oxidation.[10] Distillation of the resulting product under reduced pressure afforded a mixture of compounds **5** and **6**, which was subjected to analysis by gas–liquid chromatography.[11]

The results summarized in Table I indicate that, in the Birch reduction of compound **4**, the extent of inversion at C$_1$ is greater at −78° than at −33°. In fact, of the experimental parameters we have thus far investigated, that of temperature appears to be the most important in determining the extent of stereoselectivity of the reaction. However, the results also show that inversion is enhanced by use of ammonia, rather than an alcohol, as the proton source. Indeed, as shown by the results outlined in Table II, as the concentration of alcohol was increased, the extent of inversion was appreciably diminished. In fact, when lithium metal was added slowly to a stirred solution of **4** in ammonia containing a large excess of methanol (run 11), the products **5** and **6** were produced in nearly equal amounts. Finally, as shown by a comparison of runs 1, 5, 9, and 12, the effect of alcohol was greater at −33° than at −78°.

Although an elucidation of the mechanistic details of these reductions must await further experimentation, the above results do demonstrate the synthetic potential of the reactions. For example, it is pertinent to mention that the reductive cleavage of the methyl ester **7** with lithium–ammonia–*tert*-butyl alcohol has been reported to afford the two alcohols **8** and **9** in a ratio of approximately 4:1, respectively.[12] In view of our results, it seems likely that a judicious choice of reaction conditions would increase the stereoselectivity of this reaction, an obviously desirable result in view of the difficulty associated with the synthesis of trans-fused perhydroindan derivatives.



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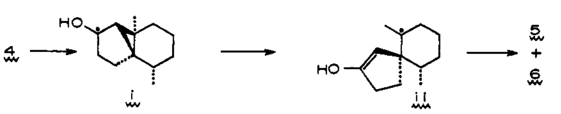
(8) In the photoreduction, the proposed intermediacy of an α-hydroxycyclopropylcarbinyl radical i,[9] followed by successive stereoelectronically controlled cleavage (i → ii) and hydrogen abstraction from solvent (2-propanol), would be expected to afford **5** and **6** in a ratio approaching 1:1.



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(10) R. Ratcliffe and R. Rodehorst, *ibid.*, **35**, 4000 (1970).

(11) The described procedure was shown to leave the ratio of **5**:**6** unchanged when a sample of known composition was subjected to the reduction–oxidation sequence and then reisolated and analyzed.

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Acknowledgments. Financial support from the National Research Council of Canada and a National Research Council of Canada Studentship (to P. W.) are gratefully acknowledged.

[13] Fellow of the Alfred P. Sloan Foundation.

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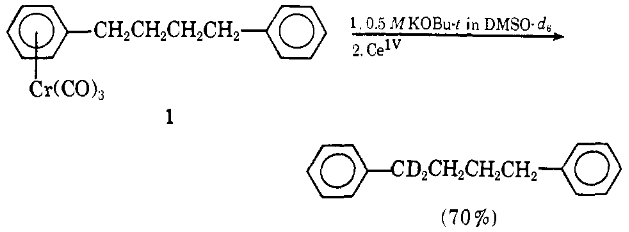
Arene-Metal Complexes. IV. Base-Catalyzed Stereoselective Hydrogen-Deuterium Exchange of Benzylic Protons of Tricarbonylchromium(0)-Complexed Alkylbenzenes[1]

Sir:

We have found that benzylic protons of tricarbonylchromium(0)-complexed alkylbenzenes undergo base-catalyzed hydrogen-deuterium exchange fairly rapidly. For example, the monotricarbonylchromium complex of 1,4-diphenylbutane (**1**) was prepared from 1,4-diphenylbutane and hexacarbonylchromium: mp 44.5-45.0°; nmr (CCl_4) δ 7.16 (m, 5), 5.10 (m, 5), 2.9-2.2 (m, 4), and 1.66 (m, 4).[2] Treatment of **1** with 0.5 *M* potassium *tert*-butoxide in dimethyl-d_6 sulfoxide (DMSO-d_6) followed by decomplexation of the arene by oxidation with ceric ammonium nitrate (CAN) gave a 70% yield of 1,1-dideuterio-1,4-diphenylbutane (**2**).

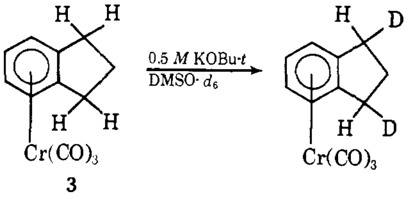


1

2

The nmr spectrum of **2** was very similar to that of 1,4-diphenylbutane except that the intensity of the downfield methylene absorption was decreased: nmr (CCl_4) δ 7.1 (s, 10), 2.6 (m, 2), and 1.65 (m, 4). The mass spectrum of **2** contained peaks at *m/e* 212 (molecular weight for **2**), 211, and 210 in ratios of 100:02:02 and peaks at *m/e* 93 and 91 in a ratio of 97:100. Thus, **2** was obtained in $\geq$96% isotopic purity.

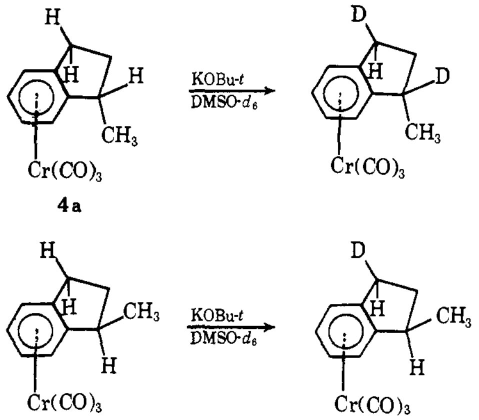
(Indan)tricarbonylchromium[2,3] (**3**) exchanged only two of its benzylic protons when placed in a 0.5 *M* potassium *tert*-butoxide-DMSO-d_6 solution. Both protons were shown to exchange within 15 min and no further exchange occurred when the complex was left in the basic solution for as long as 4 hr. The exchange was followed by observing the decrease of the nmr signal[4] of the benzylic protons which is a multiplet centered at δ 2.8. This signal decreased from a relative area of 4 to 2 while the relative areas for the signals of the complexed aromatic protons at δ 5.2 and the nonbenzylic methylene at δ 2.1 remained 4 and 2, respectively. The half-life for exchange of the two benzylic protons in a 0.013 *M* potassium *tert*-butoxide-DMSO-d_6 solution at 25° was determined to be *ca.* 15 min.



3

These results from the indan complex indicate that the base-catalyzed hydrogen-deuterium exchange is stereoselective. The results from a mixture of *ca.* 45:55 *syn*- and *anti*-(1-methylindan)tricarbonylchromium isomers indicate that only the benzylic protons which are anti to the tricarbonylchromium moiety undergo exchange.

Jackson and coworkers have shown that treatment of 1-methylindan with hexacarbonylchromium gives rise to approximately equal amounts of the syn and anti isomers.[5] These workers have separated and rigorously characterized both isomers, including their stereochemistry.[5] They report that the syn isomer has its methyl nmr absorption (δ 1.28) at lower field than the anti isomer (δ 1.16).[3] Thus, an nmr spectrum of a mixture of the two isomers shows two clearly separated methyl doublets at δ 1.28 (J = 3 Hz) and 1.16 (J = 4 Hz). A mixture of *ca.* 45:55 *syn*- (**4a**) and *anti*- (**4b**) (1-methylindan)tricarbonylchromium was submitted to conditions similar to those used to bring about hydrogen-deuterium exchange of the indan complex **3**. The nmr spectrum of the product mixture showed that the downfield methyl doublet collapsed into a broad singlet while the upfield methyl doublet remained unchanged. These results clearly demand that only the benzylic protons which are anti to the metal atom of both the *syn*-methyl (**4a**) and the *anti*-methyl (**4b**) isomers undergo exchange.



4a

4b

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(1) (a) Part III: D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 7461 (1970). (b) Based on work by R. J. C. in partial fulfillment of the requirements for the M. S. degree at Iowa State University. (c) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research by Grant No. 5261-AC.

(2) Acceptable elemental analyses were obtained for these complexes by Spang Microanalytical Laboratory, Ann Arbor, Mich., or Chemalytics, Inc., Tempe, Ariz.

(3) D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. B*, 1210 (1969).

(4) Water was added to the basic solution and the complex was extracted with ether. The yellow ethereal solution was washed with water and dried ($MgSO_4$), and the solvent was removed. The residue was dissolved in carbon tetrachloride and an nmr spectrum of the solution was taken.

(5) D. E. F. Gracey, W. R. Jackson, C. H. McMullen and N. Thompson, *J. Chem. Soc. B*, 1197 (1969).