at reflux temperature). The residue was purified by column chromatography (neutral alumina, activity I), to give 553 mg (85%) of a viscous orange liquid: $[\alpha]^{22}_D$ -308.0° ($c$ = 0.4, $CHCl_3$). The spectral data were identical in every respect with that obtained for (*S*)-(*R*)-**18**, although the lower optical rotation obtained suggests that it was in a slightly lower state of purity.

**Procedure for Relative Rate Determination (Hammett Study).** To a solution of 0.050 mmol of **3** and 0.055 mmol of (*R*)-(*S*)-**4** in 2.5 mL of 1,2-dichloroethane was added a solution of 5.0 mmol of freshly distilled **2b**, 5.0 mmol of **1a**, and 5.0 mmol of the para-substituted benzaldehyde in 2.5 mL of 1,2-dichloroethane. The reaction mixture was heated to 50 °C and the disappearance of starting materials monitored by GLC using a 25-m capillary fused-silicon DB 17/30 W column (HP Model 5890A gas chromatograph). The peak areas of the starting material were calibrated from the known starting concentration prior to addition of the catalyst. When a change in concentration of **2b** was no longer observed, the molar concentrations of unreacted aldehydes were used to calculate the relative rate constant. The $^1H$ NMR spectra and GLC results of the products were examined to insure that concurrent reactions leading to the disappearance of aldehyde did not occur.

**Ethyl 2,2-Dideuterio-α-isocyanoacetate (2b-$d_2$).** To 20 mL of deuterium oxide in a Schlenk tube, which was previously rinsed with deuterium oxide and dried, was added sequentially a solution of 1.1 mL (10 mmol) of **2b** in 10 mL of deuteriochloroform and 50 μL triethylamine. The reaction mixture was stirred at room temperature, and the exchange reaction was monitored by the disappearance of the methylene group protons at $\delta$ 4.18 in the $^1H$ NMR spectrum. After the exchange reaction was complete, the organic phase was separated and then was stirred for an additional 1 h with 20 mL of fresh deuterium oxide. The aqueous phase was separated, and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was distilled, to give 0.95 g of a colorless liquid, bp 95 °C.

**Kinetic Isotope Effect.** To a solution of 20 mg (0.029 mmol) of (*R*)-(*S*)-4 and 14 mg (0.027 mmol) of **3** in 2.5 mL of 1,2-dichloroethane was added sequentially 152 μL (1.4 mmol) of 2-$d_2$, 153 μL (1.4 mmol) of **2**, and 140 μL (1.4 mmol) of **1**. The reaction mixture was heated to 50 °C and was held at this temperature for 18 h. The solvent was removed in vacuo, and the residue was dissolved in 20 mL of diethyl ether. Any precipitate formed was removed by filtration with the aid of Hi-flow, and the solvent was removed in vacuo. The residue was bulb-to-bulb distilled (Kugelrohr) and the mixture analyzed by $^1H$ NMR (250 MHz) and MS.[98]

**Acknowledgment.** We thank Ciba-Geigy AG for support and permission to publish this work, R. Kesselring, R. Häusel, and G. Puleo for their skillful assistance in the laboratory, and Jo Behrens for preparation of the manuscript. We thank Prof. C. Floriani and Prof. G. van Koten for stimulating discussions.

(98) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley-Interscience: New York, 1984; pp 83-111.

(99) **Note Added in Proof**: The [Au((*R*)-(*S*)-4)]$BF_4$ complex was formed in methylene chloride and freed of cyclohexyl isocyanide by precipitation with diethyl ether, filtration, and washing with pentane.

(100) **Note Added in Proof**: A statistical mixture of the four possible isotopomeric oxazolines was formed, also indicating a rapid H/D scrambling of the starting materials **2b** and **2b**-$d_2$.

# *Notes*

## Properties of the Zinc-Nickel Chloride-Deuterium Oxide System: A Simple Method for Deuterium Addition to Carbon-Carbon and Carbon-Oxygen Double Bonds

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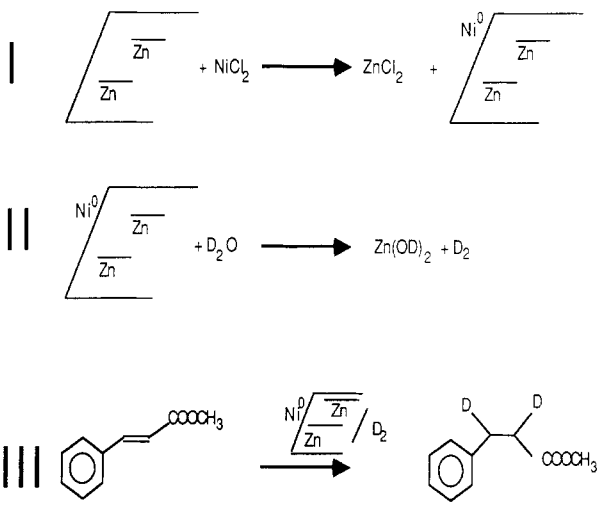
We previously reported that zinc-nickel chloride in deuterium oxide solution can be used to carry out selective deuterium addition on the olefinic bond of methyl cinnamate.[1] This incorporation is not the result of an electron transfer that is generally involved in equivalent systems.[2] In the mechanism proposed for the conjugated deuteration of methyl cinnamate (Scheme I) the nickel chloride is reduced to nickel metal, which coats the zinc surface (I). The zinc, assisted by nickel, reduces deuterium oxide to dideuterium (II). The nickel-activated surface catalyzes this reduction (III).

Several compounds have been tested and the results examined both to check the utility and validity of the method and to bring additional informations to the discussion of the reaction pathways.

**Scheme I**




### Results and Discussion

Results obtained for several compounds are displayed in Table I. Deuterated products were isolated in high yield and are characterized by a good to high degree of deuterium addition.

(1) Pétrier, C.; Luche, J.-L.; Lavaitte, S.; Morat, C. *J. Org. Chem.* **1989**, *54*, 5313-5317.

(2) House, H. In *Modern Synthetic Reactions*; W. A. Benjamin Inc.: Menlo Park, CA, 1972; pp 145-227.

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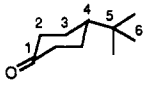
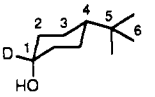
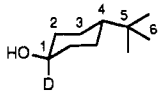
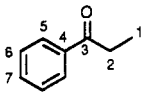
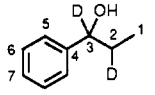
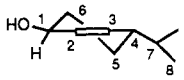
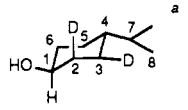
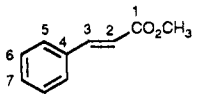
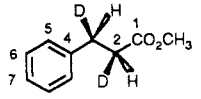
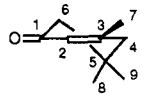
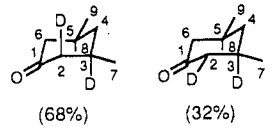
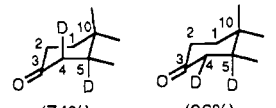
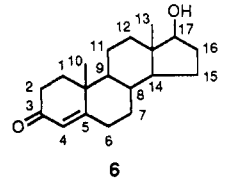
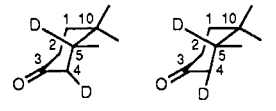
**Table I. Deuteration Content and Isolated Yields Obtained in the Deuteration of the Different Substrates**

| substrates | products (rel yields)[a] | isolated yield, % | deuterium content[b] |
|---|---|---|---|
|  1 |  1a | 60 | 98% C1 |
| |  1b | 32 | 98% C1 |
|  2 |  2a | 96 | 23% C2<br>73% C3<br>3% C1 |
|  3 |  3a | 81 | 90% C2<br>93% C3 |
|  4 |  4a | 98 | 88% C3<br>88% C4 |
|  5 |  (68%) (32%) 5a | 89 | 88% C2<br>87% C3 |
| |  (74%) (26%) 6a | 33 | 85% C4<br>83% C5 |
|  6 |  (94%) (6%) 6b | 62 | 83% C4<br>84% C5 |

[a] Based on the integration of the signal by $^2H$ NMR. [b] Measured by $^{13}C$ quantitative NMR. [c] Measured product. C2: axial/equatorial deuterium ratio = 0.93. C3: equatorial/axial deuterium ratio = 0.91.

Ketones are easily reduced. 1-Deuterio-4-*tert*-butylcyclohexanol is obtained preferentially with the hydroxyl group in the axial position, **1a**. The stereoisomer ratio is in agreement with that generally obtained for 4-*tert*-butylcyclohexanone reduction on nickel catalyst in a polar medium.[3,4] In this case, only the carbonyl carbon is affected by the reaction, but for the enolizable phenyl ethyl ketone (**2**) there is also deuteration on the adjacent carbon (23%).

Allylic alcohol **3** is reduced to a 2,3-dideuterio cyclohexanol derivative with a remarkable cis stereoselectivity. This reaction should involve the anchoring effect of the pseudoequatorial hydroxyl group, the strong oxygen affinity toward the nickel surface directing the product distribution.[5,6] The small deuterium incorporation (3%) observed at the carbon bearing the alcohol function suggests that some double-bond migration occurs in the catalytic process.[7]

$\alpha,\beta$-Unsaturated carbonyl compounds may be selectively transformed to the dideuterated saturated species. $^1H$ and $^2H$ NMR data showed (see Experimental Section) that methyl cinnamate (**4**) is reduced exclusively to the *RR*/*SS* (threo) adduct, corresponding to a cis stereoselectivity as observed for compound **3**.

Examination of the products resulting from the deuteration of isophorone (**5**) and testosterone (**6**) reveals some interesting features. Regioselectively, only the two olefinic carbons are involved in the reaction. Isophorone gives two epimeric derivatives at the $C_2$ position, and for products **6a** and **6b** the deuterium on $C_4$ is also preferentially axial. The two couple of isomers $\alpha,\alpha'$ and $\beta,\beta'$ with an excess of the later couple are observed in the reduction of testosterone.

These experimental results are consistent with Augustine's hypothesis of the four different adsorption modes of the substrate on the catalyst surface.[8] As represented

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(7) Nishimura, S.; Hama, M. *Bull Chem. Soc. Jpn.* **1966**, 2467–2470.
(8) Augustine, R. L. *Adv. Catal.* **1976**, *25*, 57–80.

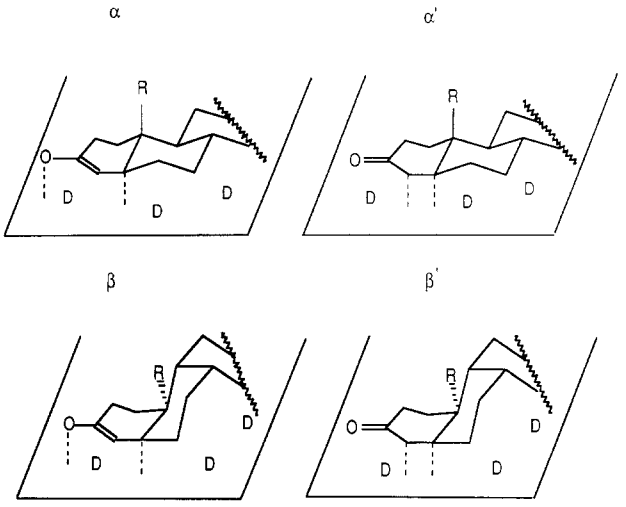


**Figure 1.** Adsorption of testosterone on the catalytic surface according to ref 8: $\alpha,\beta$, 1-4 adsorption; $\alpha',\beta'$, 1-2 adsorption; $\alpha,\alpha'$, trans adsorption; $\beta,\beta'$, cis adsorption.

(Figure 1), the enone can be on a 1-2 or 1-4 diadsorbed form ($\alpha',\beta'$ and $\alpha,\beta$, respectively). 1-2 diadsorbed species will give the cis addition of deuterium. In the other case, the carbonyl group is polarized on the catalyst surface acting as a Lewis acid to give the 1-4 diadsorbed species.[9-11] The enol forms ($\alpha,\beta$) resulting from the deuterium addition ketonize with preferentially axial deuterium, resulting in trans dideuterium products from this pathway.[8,12,13]

The two cyclohexane rings of testosterone may adopt a trans ($\alpha,\alpha'$) or a cis ($\beta,\beta'$) relative configuration on the catalytic surface. The later mode of adsorption predominates, even if the carbon $C_{10}$ is bearing a methyl group, because it involves fewer interactions between the hydrogens of the substrate and the surface of catalyst, especially for the 1-4 adsorbed form.[13] In fact, it seems that the products resulting from the **6** deuteration reflect the proportion of intermediate adsorbed species.

All of these examples are consistent with a catalytic heterogeneous deuteration mechanism. There is no doubt for compounds **3** and **4**, which show cis addition of deuterium. For compounds **1**, **5**, and **6**, the alternative reduction through an electronic transfer gives compounds with different stereochemistry. Similarly, the reduction of **1** by lithium in alcoholic medium gives **1b** in a large excess and, when **6** is reduced with sodium or lithium in ammonia, the trans adsorption product is largely predominant.[2,14,15]

## Conclusion

This simple system constitutes a cheap and efficient alternative method to add selectively deuterium atom(s) on a carbonyl or an olefinic double bond.

Deuteration results with respect to the regioselectivity and the stereoselectivity agree well with those observed for catalytic addition of deuterium in a heterogeneous system. Extension of the method to other chemical functions is in progress.

## Experimental Section

**General.** Zinc dust and nickel chloride hexahydrate were obtained from Prolabo. Anhydrous nickel chloride is prepared from nickel chloride hexahydrate by heating under vacuum at 50 °C. It is stored under argon. 1,4-Dioxane is distilled under argon over sodium benzophenone ketyl. Deuterium oxide (99.8%) was purchased from Aldrich.

Infrared spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Melting points (uncorrected) were determined with a Buchi Tottoli apparatus. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM 300 spectrometer. Typical parameters for $^1H$, $^2H$, and $^{13}C$ are listed below. $^1H$ (300.13 MHz), sweep width (SW) = 2100 Hz, pulse width (PW) = 9.3 μs, acquisition and processing data size 16K. $^2H$ (46.05 MHz), SW = 322 Hz, PW = 17 μs, data size 4K. $^{13}C$ (75.47 MHz), SW = 16 642 Hz, PW = 4 μs, data size 16K.

$^1H$ spectra were run in $CDCl_3$ or $C_6D_6$ solution. The chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard. $^2H$ spectra were run unlocked in a $C_6D_6/C_6H_6$ (1/1) mixture. Field homogeneity was obtained by shimming on deuterated solvent. Only relative measurements corresponding to different deuterated sites were made. No deuterated sites other than expected were observed. $^{13}C$ spectra were run in $C_6D_6$ or $CDCl_3$ solution. Different experiments such as distortionless enhancement by polarization transfer (DEPT)[16] and proton decoupling with and without nuclear Overhauser effect (NOE) were performed. The latter kind of experiment was used to obtain quantitative measurements of the deuterium addition with a ±5% accuracy.

**General Procedure.** Zinc dust (500 mg, 7.64 mmol) and anhydrous nickel chloride (250 mg, 1.92 mmol) were placed in an argon-flushed flask equipped with a magnetic bar. The substrate (5 mmol) in dioxane solution (8 mL) and deuterium oxide (2 mL) were then introduced. The flask was firmly stoppered and heated to 40 °C; an excess of deuterium was developed during the early stage, and this gas was consumed in the reaction. The endpoint of the reaction was checked by thin layer chromatography (TLC) (generally 14 to 16 h). After dilution with ethyl acetate, filtration through Celite, and drying ($Na_2SO_4$), the solvent was evaporated and the product was purified by chromatography on a silica gel column (Merck, 70–230 mesh).

**Analytical Data.** Deuterated compounds were compared to the nondeuterated samples in gas chromatography experiments (Erba Science chromatograph equipped with 10% Carbowax 20 M column, 2.5 m × 2 mm). Attributions corresponding to the different compounds were obtained from the homonuclear (COSY) and heteronuclear shift correlation NMR experiments on nondeuterated samples. For the following data the values in parentheses refer to the carbon or the carbon bearing proton or the deuterium (ax = axial, eq = equatorial). An asterisk indicates the carbon bearing the deuterium atom.

***cis*-1-Deuterio-4-*tert*-butyl-1-cyclohexanol (1a)**: white crystals, mp 80 °C ($CH_2Cl_2$). IR (KBr): 3300, 2940, 2100, 1380, 1180, 1010, 950, 920, 820, 800, 680, 650 $cm^{-1}$. NMR: $^1H$ ($C_6D_6$) 4.00 (C*H*OH eq, 1); 1.22 (H ax, 2); 1.67 (H eq, 2); 1.38 (H ax, 3); 1.43 (H eq, 3); 0.86 (H ax, 4); 0.84 ($CH_3$, 6) ppm. $^2H$ ($C_6D_6$): 3.86 (D eq, 1) ppm. $^{13}C$ ($C_6D_6$): 65.48, 65.01* (1); 33.81 (2); 21.31 (3); 48.43 (4); 32.84 (5); 27.76 (6) ppm.

***trans*-1-Deuterio-4-*tert*-butyl-1-cyclohexanol (1b)**: white crystals, mp 76 °C ($CH_2Cl_2$). IR (KBr): 3250, 2940, 2100, 1440, 1360, 1120, 1090, 980, 950 $cm^{-1}$. NMR: $^1H$ ($C_6D_6$) 3.46 (C*H*OH ax, 1); 1.14 (H ax, 2); 1.88 (H eq, 2); 0.85 (H ax, 3); 1,61 (H eq, 3); 0.89 (H ax, 4); 0.77 ($CH_3$, 6) ppm. $^2H$ ($C_6D_6$): 3,34 (D ax, 1) ppm. $^{13}C$ ($C_6D_6$): 70.92, 70.42* (1); 36.32 (2); 25.99 (3); 47.51 (4); 32.24 (5); 27.76 (6) ppm.

**1-Deuterio-1-phenyl-1-propanol (2a)**: colorless oil. IR (neat): 3350, 3020, 2200, 1600, 1480, 1440, 1100, 1015, 760, 700 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$) 0.98 ($CH_3$, 1); 1.80 ($CH_2$, C*H*D, 2); 4.59 (C*H*OH, 3); 7.25 (phenyl, 5,6,7) ppm. $^2H$ ($CDCl_3$): 1.75 (CHD, 2); 4.51

(9) Mc Quillin, F. J.; Ord, W. O.; Simpson, P. L. *J. Chem. Soc. C.* **1963**, 5996–6003.
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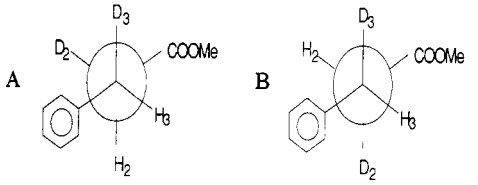
(15) Dryden, H. L. In *Organic Reactions In Steroids Chemistry*; Fried, J., Edwards, J. A., Ed.; Van Nostrand Reinhold Company: New York; 1972; Vol. 1, pp 1–60.
(16) Droddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.




A (RR/SS) B (RS/SR)

**Figure 2.**

(CDOH, 3) ppm. $^{13}C$ ($CDCl_3$): 9.95 (1); 31.56, 31.32* (2); 75.73, 75.27* (3); 144.48 (4); 125.88 (5); 128.14 (6); 127.33 (7) ppm.

***trans*-2,3-Dideuterio-4-isopropyl-1-cyclohexanol (3a)**: colorless oil. IR (neat): 3330, 2940, 2150, 1440, 1380, 1360, 1050 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$) 3.45 (*CH*OH ax, 1); 1.14 (H ax, 2,6); 1.88 (H eq, 2,6); 0.88 (H ax, 3,5); 1.63 (H eq, 3,5); 0.93 (H ax, 4); 1.35 (H, 7); 0.79 ($CH_3$, 8) ppm. $^2H$ ($C_6D_6$): 3.40 (D ax, 1); 1.21 (D ax, 2); 1.95 (D eq 2); 0.84 (D ax, 3); 1.54 (D eq, 3) ppm. $^{13}C$ ($CDCl_3$): 70.80 (1); 35.40, 34.95* (2); 27.64, 27.28* (3); 42.84 (4); 27.64 (5); 35.40 (6); 32.25 (7); 19.78 (8) ppm.

**Methyl 2,3-dideuterio-3-phenyl-1-propanoate (4a)**: colorless oil. IR (neat): 3040, 2950, 2150, 1740, 1600, 1490, 1430, 1260, 1200, 740, 706 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$) 3.66 ($OCH_3$); 2.61 (CHD, $CH_2$, 2); 2.94 (CHD, $CH_2$, 3); 7.29 (phenyl, 6,7,8) ppm. $^2H$ ($CDCl_3$): 2.52 (CHD, 2); 2.84 (CHD, 3) ppm. $^{13}C$ ($CDCl_3$): 51.35 (1); 173.07 (2); 30.67, 30.35* (3); 35.40, 35.11* (4); 140.27 (5); 128.06 (7); 126.06 (8) ppm.

**Determination of the Stereochemistry.** In $^2H$ NMR the two nuclei $D_2$ and $D_3$ exhibit a quadruplet ($J$ = 1.8 and 1.3 Hz) and a triplet ($J$ = 2.2 Hz), respectively. Among the two possible configurations, *RR/SS* (threo) and *RS/SR* (erythro) in their most stable conformation (*A* and *B*, respectively, in Figure 2), only the threo isomer could give such a pattern corresponding to $^3J_{D3H3}$(trans) $\approx$ 1.8 Hz and $^2J_{D2H2} \approx$ 3.1 Hz for $D_2$ and to $^3J_{D3H2}$(trans) $\approx {}^2J_{D3H3} \approx$ 2.2 Hz for $D_3$. Conversely, the erythro (*B*) would give only a doublet of $\approx$ 3.1 Hz ($^2J_{D2H2}$) for D2 and of $\approx$ 2.2 Hz ($^2J_{D3H3}$) for $D_3$ (neglecting the $^3J_{DH}$ gauche and $^3J_{DD}$ trans coupling values which should be less than 0.6 Hz).

$^1H$ NMR confirms these assignments. By selective irradiation of H2 and H3 successively, these two nuclei exhibit a complex pattern of lines with a mean half-height width ($\Delta\nu_{1/2}$) of $\approx$ 10 Hz. The threo configuration (*A*) could correspond to the experimental spectrum with $^2J_{HD} \approx$ 2–3 Hz and $^3J_{HD}$(trans) $\approx$ 2 Hz. The erythro configuration (*B*) would show a triplet for each proton corresponding to the $^2J_{HD}$ values, giving a $\Delta\nu_{1/2}$ of 4–6 Hz.

**3,5,5-Trimethyl-2,3-dideuterio-1-cyclohexanol (5a)**: colorless oil. IR (neat): 2150, 2940, 1710, 1440, 1160, 1260, 1225 $cm^{-1}$. NMR: $^1H$ ($C_6D_6$) 1.44 (H ax, 2); 2.17 (H eq, 2); 1.63 (H eq, 3); 0.82 (H ax, 4); 1.14 (H eq 4); 1.74 (H ax, 6); 1.95 (H eq, 6); 0.73 ($CH_3$ eq, 7); 0.71 ($CH_3$ ax, 8); 0.80 ($CH_3$, 9) ppm. $^2H$ ($C_6D_6$): 1.42 (D ax, 2); 2.13 (D eq, 2); 1.57 (D ax, 3) ppm. $^{13}C$ ($C_6D_6$): 208.7 (1); 48.60, 48.36* (2); 29.47, 28.92* (3); 47.90 (4); 34.80 (5); 53.97 (6); 22.24 (7); 31.98 (8); 25.63 (9) ppm.

**(5α,17β)-4,5-Dideuterio-17-hydroxy-3-androstanone (6a)**: white crystals, mp 180 °C (ethyl acetate). IR (KBr): 3450, 2940, 2100, 1695, 1440, 1320, 1140, 1075, 1045, 960, 915, 735 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$) 2.04 (H ax, 4); 2.20 (H eq, 4); 1.50 (H ax, 5) ppm. $^2H$ ($CDCl_3$): 2.46 (D ax, 4); 2.65 (D eq, 4); 1.89 (D ax, 5) ppm. $^{13}C$ ($CDCl_3$): 209.0 (3); 44.59, 44.12* (4); 46.77, 46.31* (5) ppm.

**(5β,17β)-4,5-Dideuterio-17-hydroxy-3-androstanone (6b)**: separated from 5α on a silica gel column, (230–400-mesh Merck) eluted with methylene chloride/ethyl acetate (85–15); white crystals, mp 140.5 °C (ethyl acetate). IR (KBr): 3450, 2940, 2100, 1700, 1440, 1370, 1260, 1060, 910, 735 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$) 1.98 (H ax, 4); 2.60 (H eq, 4); 1.77 (H ax, 5) ppm. $^2H$ ($CDCl_3$): 2.01 (D ax, 4); 2.65 (D eq, 4); 1.78 (D ax, 5) ppm. $^{13}C$ ($CDCl_3$): 212.9 (3); 42.22, 41.87* (4); 44.24, 43.97* (5) ppm.

**Registry No.** 1, 98-53-3; **1a**, 30461-16-6; **1b**, 30461-17-7; **2**, 93-55-0; **2a**, 124267-81-8; **3**, 64233-68-7; **3a**, 124267-82-9; **4**, 1754-62-7; **4a**, 39196-55-9; **5**, 78-59-1; *cis*-**5a**, 124267-83-0; *trans*-**5a**, 124267-84-1; **6**, 58-22-0; (4β,5α,17β)-**6a**, 124267-85-2; (4α,5α,17β)-**6a**, 31285-38-8; (4α,5β,17β)-**6b**, 124267-86-3; (4β,5β,17β)-**6b**, 124267-87-4; Zn, 7440-66-6; $NiCl_2$, 7718-54-9; $D_2O$, 7789-20-0.

# Some Transformations of Adducts of Dichlorocarbene and 7-Substituted Benzonorbornadienes

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## Introduction

The addition of dichlorocarbene to norbornene (**1**),[1] norbornadiene (**2**),[1] and benzonorbornadiene (**3**)[2] provides the most direct route to compounds containing the bicyclo[3.2.1]octyl ring system. The reaction involves addition of the carbene to the exo face of the bicyclic alkene to give initially a *gem*-dichlorocyclopropane, which under the rection conditions usually undergoes ring opening to afford a rearranged, ring-expanded dihalide, e.g. **6**. In the reaction involving norbornene (**1**), the initial adduct **4** has been isolated, but in the case of norbornadiene (**2**) and benzonorbornadiene (**3**), the ring-expanded products have been obtained directly.[1,2]

The stereochemical outcome of *gem*-dihalocyclopropane ring opening has been rationalized in terms of orbital symmetry constraints.[3] The reaction involves cyclopropyl to allyl cation interconversion with participation of the cyclopropyl bonding electrons from the face of the cyclopropyl ring opposite to that of the departing halide ion. Collapse of the resulting ion pair, e.g. **5**, then affords the allylic halide, e.g. **6**, of defined stereochemistry. In a converse argument, for those cases in which the *gem*-dihalocyclopropane cannot be isolated or detected, the stereochemistry of the allylic halide defines the stereochemistry of carbene addition: exo halogen orientation implies exo addition of dihalocarbene. This paper concerns the addition of dichlorocarbene to two substituted benzonorbornadienes in which a substituent shields the exo face of the double bond.

## Results and Discussion

Addition of dichlorocarbene, generated from $CHCl_3$ and NaOH under phase-transfer conditions, to *anti*-7-*tert*-butoxybenzonorbornadiene (**7**) afforded the *endo*-chloro derivative **8** and the *exo*-chloroderivative **9** in a ratio of ca. 9:1 in a total yield of 58% (based on unrecovered starting material after two sequential reactions). The endo (or β) orientation of the chloro substituent in **8** was apparent from the value $J_{5,6}$ = 5.0 Hz for the bridgehead H5 to chloromethine H6 coupling constant.[4] The corre-

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