complexes (0.38 g, 0.89 mmol) obtained from hydrolysis of the epoxide complex **6** in 10 mL of dry methylene chloride was cooled to −78 °C and treated with 0.07 mL of pyridine and 0.098 mL (0.89 mmol) of trichloroacetyl chloride. After stirring for 2 h at −78 °C, the solution was poured into saturated $NaHCO_3$ and extracted with ether. The organic phase was washed with water and dried over $MgSO_4$. The oily residue obtained after solvent removal was subjected to preparative TLC; development with 15% ether/petroleum ether produced two red bands. One of these yielded the trans complex **16**: IR (CS_2) 2100, 2030, 2010 cm^{-1} (metal carbonyl), 1765 cm^{-1} ($OCOCCl_3$); ^1H NMR (CS_2) δ 6.1 (s, 1 H, complexed acetylenic), 4.5 (m, 1 H, $w_{1/2}$ = 6 Hz, $CHOCOCCl_3$), 1.7–2.1 (br m, 9 H, ring + OH). The other band yielded impure cis complex **17**. The latter was most conveniently obtained by the following method.

Preparation of [η-[1-Ethynyl-*c*-2-(trichloroacetoxy)-*r*-1-cyclohexanol]]hexacarbonyldicobalt. To an ice-cooled stirred solution containing 0.17 g (1.20 mmol) of *syn*-1-ethynyl-*r*-1,*c*-2-cyclohexanediol in 5 mL of benzene was added 0.41 g (1.2 mmol) of $Co_2(CO)_8$ and the resulting mixture stirred for 4 h. The solution was then filtered through alumina, washing with ether, and the solvent evaporated. A portion of the resulting crude diol complex (0.075 g, 0.18 mmol) was trichloroacetylated as above to yield pure cis complex in 97% yield following column chromatography, eluting with 5% ether/petroleum ether: IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl), 1770 cm^{-1} ($OCOCCl_3$); ^1H NMR (CS_2) δ 6.1 (s, 1 H, complexed acetylenic), 4.7 (br m, $w_{1/2}$ = 12 Hz, **CHOH**), 1.7–2.22 (br m, 9 H, ring + OH).

Acknowledgment. We are grateful for financial support provided by the Public Health Service (GM 26760).

Registry No. **5**, 88036-46-8; **6**, 88056-71-7; **7**, 88036-47-9; **8**, 88036-48-0; **9**, 88036-49-1; **10**, 88036-50-4; **11**, 88036-51-5; **12**, 88036-52-6; **13**, 88036-53-7; **14**, 88036-54-8; **15**, 88036-55-9; **16**, 88036-56-0; **17**, 88082-55-7; $Me_3SiCH_2CH{=}CH_2$, 762-72-1; MeOH, 67-56-1; PhOMe, 100-66-3; $CH_2{=}C(OAc)CH_3$, 108-22-5; $Co_2(CO)_8$, 10210-68-1; Cl_3CCO_2H, 76-03-9; 1,2-epoxy-3-octyne, 88036-58-2; 1-octen-3-yne, 17679-92-4; 1,2-epoxy-1-ethynylcyclohexane, 932-03-6; *cis*-2-ethynyl-2-methylcyclohexanol, 75476-40-3; *trans*-2-ethynyl-2-methoxycyclohexanol, 75476-39-0; *cis*-2-ethynyl-1,2-cyclohexanediol, 75476-42-5; *trans*-2-ethynyl-1,2-cyclohexanediol, 75476-41-4; *cis*-[2-ethynyl-1,2-cyclohexanediol]hexacarbonyldicobalt, 88036-57-1; *trans*-[2-ethynyl-1,2-cyclohexanediol]hexacarbonyldicobalt, 88082-56-8; trichloracetyl chloride, 76-02-8; 1-ethynylcyclohexene, 931-49-7.

Alkylation of Allylic Derivatives. 8.[1] Regio- and Stereochemistry of Alkylation of Allylic Carboxylates with Lithium Methylcyanocuprate

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Received August 26, 1983

Alkylation of 5-methyl-2-cyclohexenyl acetate (1-OAc) with lithium methylcyanocuprate (LiCu(CN)Me) is regiospecific (>90% excess γ-alkylation) and stereospecific (>95% anti alkylation). In the bicyclo[3.2.1]oct-3-en-2-yl system (**3**), alkylation is stereoselective (both isomers give exo alkylation) and regiospecific (excess γ-alkylation). Alkylation of *trans*-α-methyl-γ-mesitylallyl acetate (8-OAc) with LiCu(CN)Me gives 57% α- and 43% γ-alkylation as compared to >97% α-alkylation with $LiCuMe_2$. Mechanistic implications are discussed.

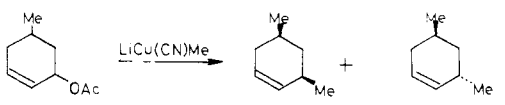
Rudler and co-workers[3] have reported that there is a striking difference in regiochemistry for alkylation of acyclic allylic acetates with lithium dimethylcuprate ($LiCuMe_2$) and lithium methylcyanocuprate (LiCu(CN)Me). They found that geranyl, neryl, and linalyl acetates react with $LiCuMe_2$ regioselectively to give alkylation at the terminal carbon. On the other hand, these three acetates react with LiCu(CN)Me regiospecifically to give γ-alkylation products.[4]

More recently, Trost and Klun[5] observed that reaction of γ-vinyl γ-lactones with alkylcyanocuprates results in anti γ-alkylation. Thus in this case the reaction is stereospecific as well as regiospecific (or regioselective).[6]

In this work we have examined the regio- and stereochemistry of alkylation of (a) *cis*- and *trans*-5-methyl-2-cyclohexenyl acetates (1-OAc) with LiCu(CN)Me and (b) *exo*- and *endo*-bicyclo[3.2.1]oct-3-en-2-yl carboxylates (**3**) with LiCu(CN)Me and $LiCuMe_2$. These systems, unlike those in the earlier work,[3,5] are unbiased with regard to substitution with and without allylic rearrangement. We also have investigated the alkylation of *trans*-α-methyl-γ-mesitylallyl acetate (**8**) with the two cuprates. This system is both sterically and thermodynamically biased against γ-alkylation.

Reaction of 5-methyl-2-cyclohexenyl acetate (1-OAc) with 2.5 equiv of LiCu(CN)Me in ether gave 60–80% yields of 3,5-dimethylcyclohexene (**2**). The crude product contained unreacted 1-OAc (0–15%), 1-OH (5–20%), and *tert*-butyl alcohol. The last two result from carbonyl attack by LiCu(CN)Me or by a decomposition product derived from the cuprate. With both isomers of 1-OAc, the configuration of the unreacted acetate and of the 1-OH is unchanged.

Results of the stereochemical studies are presented in eq 1. In these experiments isomeric compositions were



(1)

1-OAc	*cis*-2	*trans*-2
99.2 ± 0.1% cis	1.2 ± 0.5%	98.8 ± 0.5%
96.6 ± 0.1% trans	94.1 ± 0.3%	5.9 ± 0.3%

(1) Previous paper in this series: Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 3986.
(2) National Science Foundation Fellow, 1977–1980.
(3) Levisalles, J.; Rudler-Chanvin, M.; Rudler, H. *J. Organomet. Chem.* **1977**, *136*, 103–110.
(4) The terms regioselective and regiospecific are used as defined in footnote 3 of: Goering, H. L.; Singleton, V. D., Jr. *J. Org. Chem.* **1983**, *48*, 1531.
(5) Trost, B. M.; Klun, T. P. *J. Org. Chem.* **1980**, *45*, 4256.
(6) In such cases one cannot distinguish between regiospecificity and regioselectivity.

0022-3263/84/1949-0422$01.50/0

Table I. Stereochemistry of the Reaction of Bicyclo[3.2.1]oct-3-en-2-yl Carboxylates (3) with $LiCuMe_2$ and LiCu(CN)Me

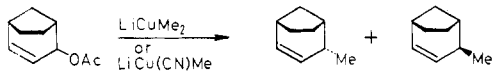
starting ester 3	cuprate	product olefin 4
100% *exo*-3-OAc	$LiCuMe_2$	99.5 ± 0.2% exo[a]
100% *exo*-3-OAc	LiCu(CN)Me	99.5 ± 0.3% exo[b]
100% *exo*-3-OTMB	$LiCuMe_2$	90.6% exo[c]
100% *exo*-3-OTMB	LiCu(CN)Me	96.9% exo[c]
93% *endo*-3-OTMB	$LiCuMe_2$	97.5 ± 0.3% exo[b]
93% *endo*-3-OTMB	LiCu(CN)Me	97.4 ± 2.0% exo[b]

[a] Average and mean to two independent experiments. [b] Average and mean of three independent experiments. [c] Results from one experiment.

determined by capillary GC. The data are averages of two (for *trans*-1-OAc) and five (for *cis*-1-OAc) independent experiments. These results demonstrate that the reaction is stereospecific (>95% excess anti alkylation) and is identical in this respect with alkylation with $LiCuMe_2$.[7]

The regiochemistry was examined with *cis*-α- and -γ-D-1-OAc.[7,8] In these experiments the alkylation product (2) was isolated by preparative GC, and the deuterium distribution at C-1 and C-3 was determined by 30.6-MHz ^2H NMR. In all cases unreacted *cis*-1-OAc remained discretely labeled. Alkylation of α-D-*cis*-1-OAc gives 2 with 96% of the label at C-1 (γ-alkylation) and 4% of the label at C-3 (α-alkylation). Similar results were obtained with γ-D-*cis*-1-OAc (97% γ- and 3% α-alkylation). The high regiospecificity observed with this reagent (>90% excess γ-alkylation) is in sharp contrast to the absence of regiospecificity with $LiCuMe_2$ in this unbiased system.[4,7] Evidently in the latter case a symmetrical (π-allyl)copper(III) complex is a precursor for essentially all of the product.[4] The observation that alkylation is regiospecific with LiCu(CN)Me but not with $LiCuMe_2$ is in agreement with the earlier report.[3]

The stereochemistry of alkylation of the bicyclo[3.2.1]oct-3-en-2-yl system (3) with LiCu(CN)Me and $LiCuMe_2$ was of interest because of the steric bias favoring bonding on the exo side.[9] Reaction of *exo*-3-OAc with 2.5 equiv of LiCu(CN)Me gave 65–80% yields of 2-methylbicyclo[3.2.1]oct-3-ene (4, eq 2). Similarly, alkylation with



(2)

3-OAc *exo*-4 *endo*-4

2.5 equiv of $LiCuMe_2$ gave 75–90% yields of 4. Under the same conditions *endo*-3-OAc gave only low yields (~15%) of 4 together with substantial amounts of *endo*-3-OH which results from carbonyl attack. Evidently the reduced reactivity of *endo*-3-OAc[10] allows carbonyl attack to become the dominant reaction. This problem was circumvented by using the mesitoate (*endo*-3-OTMB) instead of the acetate.[11] Reaction of *endo*-3-OTMB with $LiCuMe_2$ under the conditions used for *exo*-3-OAc gave 70–90% yields of 4. However, reaction with the less reactive LiCu(CN)Me stops at about 50% completion after 3 or 4 days at 0 °C. An 8-fold excess of cuprate does not improve the yield, and increasing the temperature lowers the yield. Apparently the LiCu(CN)Me decomposes at a rate comparable to the rate of alkylation. By adding additional LiCu(CN)Me midway through the reaction, 80–95% yields of 4 can be obtained. The stereochemical results are presented in Table I. Isomeric compositions of 4 were determined by capillary GC, and isomers were identified by comparison with authentic samples.[12a] These data show that in this bicyclic system alkylation is stereoselective. Both isomeric esters lead primarily to the exo-alkylation product (*exo*-4).

The results for *endo*-3-OTMB (anti alkylation) are as expected from earlier work[1,7] and from the data for 1-OAc presented in eq 1. However, syn alkylation of the exo-3 esters is anomalous. In this case steric hindrance on the endo side results in change in stereochemistry from anti to syn. A similar syn alkylation has been reported for alkylation of a [3.2.0] bicyclic allylic bromide with an alkylcuprate.[13]

It is noteworthy that somewhat more anti alkylation is observed with *exo*-3-OTMB than with *exo*-3-OAc (<1%). Evidently the bulkier leaving group causes greater steric constraints on syn alkylation so that anti alkylation becomes more competitive. This probably also accounts for the small amounts of apparent syn alkylation with *endo*-3-OTMB. This ester contains 7% of the exo isomer, and the observed *endo*-4 in the product may be derived by anti alkylation of the exo isomer.

Optically active *exo*-3-OAc[12] and α- and γ-D-*endo*-3-OTMB were used to investigate the regiochemistry. In this unbiased system α- and γ-alkylation products are enantiomers. Reaction of (+)-*exo*-3-OAc with $LiCuMe_2$ gives essentially racemic *exo*-4 as shown in Table II. On the other hand, alkylation with LiCu(CN)Me gives *exo*-4 with an optical purity about 80% that of the starting acetate. From correlations reported earlier,[12a] it can be seen that this results from 80% excess γ-alkylation.[12b] The regiochemistry for the two cuprates for syn alkylation of *exo*-3-OAc is remarkably similar to that for anti alkylation of *cis*-1-OAc. In each case there is essentially no preference for α- or γ-alkylation with $LiCuMe_2$ and a strong preference for γ-alkylation with LiCu(CN)Me.

Similar results were obtained for alkylation of *endo*-3-OTMB. As shown in Table III, alkylation with LiCu(CN)Me is regiospecific (76–88% excess γ-alkylation). With $LiCuMe_2$, α- and γ-D-*endo*-3-OTMB give essentially the same mixture of *exo*-4-2-*d* (54%) and *exo*-4-4-*d* (46%). Thus in this case the reaction is nonregiospecific. The reason for the slight excess bonding to the deuterium bearing carbon is not clear, but this was also observed for alkylation of α- and γ-D-*cis*-1-OAc with $LiCuMe_2$.[7] Presumably this results from a secondary isotope effect for the $sp^2 \rightarrow sp^3$ transformation of the allylic carbon atom. The observed k_H/k_D ratio (46/54 = 0.85) is about the magnitude expected for a reaction of this type.[14]

The above results provide insight into mechanistic details of these reactions. The observation that the steric bias in the exo bicyclic system (*exo*-3) changes stereochemistry without changing regiochemistry is particularly informative. This shows that stereochemistry and regiochemistry are controlled at different stages in the reaction pathway.

A mechanism that accounts for these and earlier[1,3] observations is presented in Scheme I. This is a refinement

(7) Goering, H. L.; Singleton, V. D., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7854.
(8) Goering, H. L.; Kantner, *J. Org. Chem.* **1981**, *46*, 2144.
(9) Goering, H. L.; Vlazny, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1801.
(10) In other work we have determined the relative rates of reaction of a number of allylic acetates with $LiCuMe_2$. The studies show that *exo*-3-OAc is slightly more reactive than *cis*-1-OAc and over 10 times more reactive than *endo*-3-OAc.
(11) Mesitoate derivatives were used previously by: Kreft, A. *Tetrahedron Lett.* **1977**, 1035. In this work we found that mesitoates are more effective than pivalates for preventing carbonyl attack.
(12) (a) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1981**, *46*, 4605. (b) The absolute rotation for *exo*-4 is correct in the Experimental Section of ref 12a, but the value in Scheme I is in error.
(13) Chapleo, C. B.; Finch, M. A. W.; Lee, T. V.; Roberts, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 676.
(14) Baldwin, J. E.; Kapecki, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4874 and references therein.

Table II. Regiochemistry of the Reaction of Optically Active *exo*-Bicyclo[3.2.1]octen-2-yl Acetate ((+)-*exo*-3-OAc) with $LiCuMe_2$ and LiCu(CN)Me[a]

cuprate	isomeric composition of 4,[b] % exo	$[\alpha]^{25}_D$, deg	$[\alpha]^{25}_{365}$, deg	optical purity, %	% γ-alkylation
$LiCuMe_2$	99.8	+0.32	−1.28	0.15[c]	50.3
$LiCuMe_2$	99.6	−0.77	−2.31	0.26[c]	50.5
LiCu(CN)Me	99.5	−54.1	−188.5	21.1[d]	91.9[e]
LiCu(CN)Me	99.8	−51.8	−175.9	20.8[d]	89.6[e]

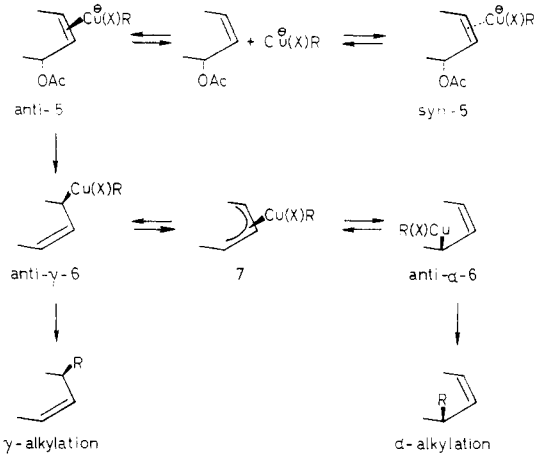
[a] The acetate optical purity was 26.3% in all cases. [b] After purification. [c] Based on the more accurate rotation at 365 nm. [d] Based on the average of the rotations for the sodium D line and 365 nm. [e] In such unbiased systems, excess γ-alkylation = 100% − 2(100 − % γ-alkylation).

Table III. Regiochemistry of the Reaction of α- and γ-D-*endo*-Bicyclo[3.2.1]oct-3-en-2-yl Mesitoate (*endo*-3-OTMB) with $LiCuMe_2$ and LiCu(CN)Me

endo-3-OTMB	cuprate	% distribution 4-2-*d*[a]	4-4-*d*
α-D	$LiCuMe_2$	53	47
γ-D	$LiCuMe_2$	55	45
α-D	LiCu(CN)Me	6	94
γ-D	LiCu(CN)Me	88	12

[a] This isomer results from α-alkylation of α-D-*endo*-3-OTMB and γ-alkylation of γ-D-*endo*-3-OTMB.

Scheme I. Mechanism of Alkylation of Allylic Carboxylates with Alkyl Cuprates



of our earlier mechanisms[8,4,15]. In this scheme, X in the cuprate is either a second alkyl group (dialkylcuprate) or a cyano group (alkylcyanocuprate).

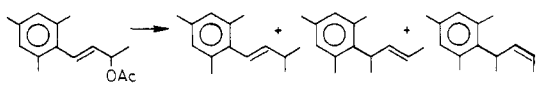
The unique feature of this mechanism is that the initial oxidative addition product is the S_N2' (σ-allyl)copper(III) complex γ-6. The stereochemistry of alkylation is determined by the stereochemistry of this initial intermediate, i.e., *anti*-γ-6 gives anti products as shown and *syn*-γ-6 gives syn products (not shown). Evidence for the S_N2' regiochemistry for this step was presented earlier.[8,15]

The reason for the S_N2' regiochemistry is not clear but presumably has something to do with prior coordination of the cuprate with the double bond to give **5**. Evidently stereochemistry is controlled by steric factors. Coordination on the least hindered side of the double bond is favored, and evidently for similar reasons this arrangement leads to the more stable transition state for the **5** → **6** transformation. In unbiased systems the anti side of the double bond is the least hindered side, and formation of *anti*-γ-6 is favored.[1] This is the stereochemistry shown in Scheme I. However, the present work shows that if the anti side is sterically hindered, as in *exo*-**3**, syn alkylation results. In this case the syn transition state for the **5** → γ-**6** transformation is favored. Syn alkylation also occurs in special cases in which the cuprate is complexed to the leaving group and the oxidative addition is a cyclic process.[16]

The regiochemistry is thought to depend on partitioning of the σ-allyl complex **6** between reductive elimination to give regiospecific γ-alkylation and reversible isomerization to the π-allyl complex **7** in which regiochemistry is lost. As noted earlier,[8] evidently the nontransferred ligand (X) in the σ complex **6** has a profound effect on this partitioning. When X = CN, reductive elimination is fast relative to isomerization to the π-allyl complex **7**, and regiospecific alkylation dominates (excess γ-alkylation). On the other hand, when X = R the **6** ⇄ **7** transformation is fast relative to reductive elimination, and regiochemistry is lost. It should be noted that stereochemistry is preserved for the **6** ⇄ **7** transformation, and reductive elimination is stereospecific (retention)[17] as indicated.

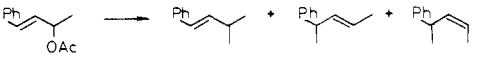
A mechanism with important similarities to Scheme I was recently proposed for reaction of lithium palladates with allylsilanes to give (π-allyl)palladium(II) complexes.[18] There is evidence that palladium(II) bonds to the anti side of the γ-carbon to give the anti S_N2' (σ-allyl)palladium(II) complex which subsequently isomerizes to the more stable π-allyl complex. Thus the pathway to the π-allyl complex and the stereochemistry are the same as for the cuprate reaction in Scheme I. Moreover, it seems likely that the initial bonding of palladium(II) to the γ-carbon involves an oxidative addition mechanism.

The effect of the steric and thermodynamic bias in the *trans*-α-methyl-γ-mesitylallyl system (**8**) was also investigated. Results for alkylation of **8**-OAc with $LiCuMe_2$ and LiCu(CN)Me are presented in eq 3. Product compositions



(3)

	8	**9**	(*E*)-**10**	(*Z*)-**10**
$LiCuMe_2$		97.5%	2.5%	
LiCu(CN)Me		57%	35%	8%



(4)

	11			
$LiCuMe_2$		95%	5%	
LiCu(CN)Me		49%	39%	12%

were determined by capillary GC, and components of the product mixtures were identified by comparison with authentic samples.[16] These results are remarkably similar

(15) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1983**, *48*, 721.

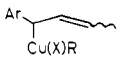
(16) Goering, H. L.; Kantner, S. S.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 715.

(17) Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7783.

(18) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1983**, 736.

to those reported earlier for alkylation of the phenyl analogue α-methyl-γ-phenylallyl acetate (11) with $LiCuMe_2$[19] and LiCu(CN)Me.[1] The results for 11 are show in eq 4.

The similar results for 8-OAc and 11 show that partitioning of the initial γ σ complex 12, between reductive



12

elimination to give the unconjugated product and isomerization to the conjugated isomer via the (π-allyl)copper complex is about the same for 8 and 11. The only significant effect of the additional hindrance in the mesitylallyl system 8 is to lower reactivity. In other work we have found that 8-OAc is at least 20 times less reactive than 11. This suggests that oxidative addition to give the σ complex 12 is rate determining and that steric hindrance in 12 has only a minor effect on the ratio of the subsequent reductive elimination and isomerization to a (π-allyl)copper complex.

Experimental Section

General Methods. Satisfactory spectral data were obtained for all new compounds. Proton NMR spectra were determined with a JEOLCO MH-100 or Bruker WH-270 instrument. Proton-decoupled ^2H NMR spectra were obtained with a JEOLCO FX-200 (30.6 MHz) spectrometer. Mass spectra were determined with an AEI MS-902 high-resolution mass spectrometer. Optical rotations were determined with a Perkin-Elmer 141 polarimeter equipped with thermostated (jacketed) cells. Peak areas for analytical capillary GC were determined with an electronic integrator. Purification of ethyl ether and cuprous iodide and standardization of methyllithium have been described previously.[8] Cuprous cyanide was prepared by a standard procedure.[20] All reactions were carried out under an atmosphere of dry nitrogen.

Materials. *cis*- and *trans*-5-Methyl-2-cyclohexenyl acetate (1-OAc)[21] and α- and γ-1-OAc[7,8] were prepared as described earlier.

***exo*-Bicyclo[3.2.1]oct-3-en-2-ol (*exo*-3-OH)** was prepared and resolved as previously described.[22] A sample of (+)-*exo*-3-OH [$[\alpha]^{25}_D$ 57.6° (*c* 1.24, $CHCl_3$) (ee 26 ± 1%)] was converted to **(+)-*exo*-bicyclo[3.2.1]oct-3-en-2-yl acetate ((+)-*exo*-3-OAc)** [$[\alpha]^{25}_D$ 74.3° (*c* 1.56, $CHCl_3$); 26% optically pure[12]] with acetic anhydride.[19] The spectral properties of (+)-*exo*-3-OAc were the same as those for racemic *exo*-3-OAc: bp 84–85 °C (6.4 mm); IR (neat) 3020 (w), 2940 (m), 2860 (w), 1740 (s), 1660 (w), 1375 (m), 1250 (s), 1025 (m), 970 (m); NMR (CCl_4) δ 6.18 (dd, 1 H, *J* = 9, 7 Hz), 5.48 (ddd, 1 H, *J* = 9, 4, 2 Hz), 4.39 (dd, 1 H, *J* = 4, 3 Hz), 2.6–2.4 (m, 2 H), 1.98 (s, 3 H), 1.9–1.1 (m, 6 H).

***exo*-Bicyclo[3.2.1]oct-3-en-2-yl mesitoate (*exo*-3-OTMB)**, mp 64–66 °C, was prepared from *exo*-3-OH and mesitoyl chloride[23] and purified by column chromatography (Woelm neutral alumina, activity III, hexane/ether eluent) followed by recrystallization (hexane): IR ($CHCl_3$) 3020 (w), 2940 (m), 2860 (w), 1710 (s), 1610 (w), 1270 (s), 1170 (m), 1090 (s); NMR ($CDCl_3$ δ 6.80 (s, 2 H), 6.21 (br dd, 1 H, *J* = 9.5, 7 Hz), 5.60 (ddd, 1 H, *J* = 9.5, 4, 2 Hz), 5.12 (br dd, 1 H, *J* = 4, 4 Hz), 2.7 (m, 2 H), 2.30 (s, 6 H), 2.25 (s, 3 H), 2.0–1.2 (m, 6 H); high-resolution mass spectrum, calcd for $C_{18}H_{22}O_2$ *m/e* 270.1619, found *m/e* 270.1616.

***endo*-Bicyclo[3.2.1]oct-3-en-2-ol (*endo*-3-OH)** was prepared by cerium chloride catalyzed borohydride reduction[24] of bicyclo[3.2.1]oct-3-en-2-one.[22] This reduction gave a mixture of 93% *endo*- and 7% *exo*-3-OH. The α-deuterated sample, α-D-*endo*-3-OH, was prepared in a similar manner with sodium borodeuteride.

γ-Deuterio-*endo*-bicyclo[3.2.1]oct-3-en-2-ol (γ-D-*endo*-3-OH) was prepared by the above reduction of γ-deuteriobicyclo-[3.2.1]oct-3-en-2-one. The latter was prepared as follows. Ozonization of 2-methylbicyclo[2.2.1]hept-2-ene-*3-d*[25] in methanol followed by reduction of the ozonide with dimethyl sulfide[25] gave a 67% yield of the deuterated dimethyl acetal of *cis*-3-acetylcyclopentanecarbaldehyde, bp ~90 °C (0.6 mm). A solution of 8.77 g (47 mmol) of the keto acetal in a mixture of 30 mL of water, 10 mL of acetic acid, and 3 mL of concentrated HCl was refluxed 18 h. The resulting solution was neutralized (K_2CO_3) and extracted with ether. Fractional distillation of the dried ($MgSO_4$) ether extract gave a 41% yield of γ-deuteriobicyclo[3.2.1]oct-3-en-2-one. Integration of the C-3 and C-4 proton signals showed the pure ketone to be ~70% deuterium labeled at C-4.

***endo*-Bicyclo[3.2.1]oct-3-en-2-yl acetate (*endo*-3-OAc) and mesitoate (*endo*-3-OTMB) and α- and γ-D-*endo*-3-OTMB** were prepared from the corresponding alcohols as indicated above for the exo isomer. The *endo*-acetate (*endo*-3-OAc) had the following: bp 81–83 °C (6 mm); IR (neat) 3035 (w), 2940 (m), 2870 (w), 1740 (s), 1655 (w), 1370 (m), 1245 (s), 1035 cm^{-1} (m); NMR (CCl_4) δ 5.99 (dddd, 1 H, *J* = 10, 6, 2, 2 Hz), 5.5 (m, 1 H), 5.25 (ddd, 1 H, *J* = 10, 2, 2 Hz), 2.7–2.3 (m, 2 H), 1.98 (s, 3 H), 1.9–1.5 (m, 6 H). Unlabeled ***endo*-3-OTMB**: bp 155–160 °C (0.45 mm); IR (neat) 3030 (w), 2940 (m), 2860 (w), 1720 (s), 1615 (w), 1270 (s), 1175 (m), 1090 cm^{-1} (s); NMR ($CDCl_3$) δ 6.84 (s, 2 H), 6.07 (dddd, 1 H, *J* = 9.5, 6, 1.5, 1.5 Hz), 5.9 (m, 1 H), 5.39 (ddd, 1 H, *J* = 9.5, 2, 2 Hz), 2.9 (m, 1 H), 2.5 (m, 1 H), 2.32 (s, 6 H), 2.27 (s, 3 H), 2.2–1.6 (m, 6 H); high-resolution mass spectrum, calcd for $C_{18}H_{22}O_2$ *m/e* 270.1619, found *m/e* 270.1616. The ^2H NMR spectrum of α-D-*endo*-3-OTMB had a single signal at δ 5.9, and that of γ-D-*endo*-3-OTMB had a single signal at δ 6.1.

***trans*-α-Methyl-γ-mesitylallyl acetate (8-OAc)** was prepared[19] from the corresponding alcohol (8-OH)[16] and acetic anhydride: bp 102–108 °C (5.5 mm); IR (neat) 2980 (m), 2920 (m), 2860 (w), 1740 (s), 1615 (w), 1380 (m), 1255 (s), 1055 (m), 960 cm^{-1} (m); NMR (CCl_4) δ 6.62 (s, 2 H), 6.40 (d, 1 H, *J* = 15 Hz), 5.48 (dd, 1 H, *J* = 15, 7 Hz), 5.32 (dq, 1 H, *J* = 7, 7 Hz), 2.16 (s, 9 H), 1.90 (s, 3 H), 1.33 (d, 3 H, *J* = 7 Hz).

Alkylation products for 1-OAc (*cis*- and *trans*-2),[7] 3-OAc (*exo*- and *endo*-4),[12a] and 8-OAc ((*E*)- and (*Z*)-9 and -10)[16] have been characterized previously. Authentic samples were available from the earlier studies.

Alkylation of Allylic Carboxylates with $LiCuMe_2$. (A) *exo*-Bicyclo[3.2.1]oct-3-en-2-yl Acetate (*exo*-3-OAc). In a typical experiment a flask equipped with a mechanical stirrer and septum was charged with 0.95 g (5 mmol) of CuI, 0.24 g (2 mmol) of mesitylene (internal standard), and 10 mL of ether. After the mixture was chilled to 0 °C, 6.45 mL of 1.55 M MeLi was added, and the mixture was stirred 15 min until a homogeneous solution was obtained. A solution of 0.33 g (2 mmol) of (+)-*exo*-3-OAc in 5 mL of dry ether was added over a 2-min period after which stirring was continued for 5 h at 0 °C, and then the reaction was quenched by addition of 5 mL of saturated aqueous NH_4Cl. After the mixture was stirred 10 min, the solids were removed by filtration and washed well with ether. The organic layers were combined, shaken with brine, dried ($MgSO_4$), and carefully concentrated by fractional distillation. Yields and product distributions were determined by capillary GC (200 ft, UCON LB-550-X). A sample of product was purified by preparative GC (10 ft × $^3/_8$ in. column, 20% UCON LB-550-X on Chromosorb W). Results of these experiments are presented in Tables I and II.

(B) *endo*-Bicyclo[3.2.1]oct-3-en-2-yl Mesitoate (*endo*-3-OTMB). Reaction mixtures were prepared as described for *exo*-3-OAc except that only 0.27 g (1.0 mmol) of *endo*-3-OTMB was used; hence a 5-fold excess of $LiCuMe_2$ was present. After being stirred 3.5 h at 0 °C, the reaction mixture was stirred overnight at room temperature. The product was isolated and

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analyzed as described above. Results of these experiments are presented in Tables I and III.

(C) *trans*-α-Methyl-γ-mesitylallyl Acetate (8-OAc). These experiments were carried out as described above for *exo*-3-OAc except that the reaction time was 1.5 h at 0 °C, and only a 2-fold excess of $LiCuMe_2$ was used.

Alkylation of Allylic Carboxylates with LiCu(CN)Me. (A) *endo*- and *trans*-5-Methyl-2-cyclohexenyl Acetate (1-OAc). In a typical experiment a flask equipped with a stirrer and septum was charged with 1.79 g (20 mmol) of CuCN and 30 mL of dry ether. After the mixture was cooled to 0 °C, 16.2 mL of 1.23 M MeLi was added, and the mixture was stirred 45 min at room temperature to obtain a homogeneous solution. The resulting solution was cooled to 0 °C, and 1.16 g (7.5 mmol) of *cis*-1-OAc was added dropwise to the stirred solution. The mixture gradually became a suspension of a yellow precipitate, after 23 h at 0 °C the solution became clear, and a gummy green-black precipitate coated the flask. The reaction was quenched with 15 mL of saturated aqueous NH_4Cl, and the precipitate was removed by filtration and washed well with ether. The ether layers were combined, dried (brine followed by $MgSO_4$), and carefully concentrated by fractional distillation. Yields and product distributions were determined by capillary GC (230-ft column, UCON LB-550-X).

Reactions of α- and γ-D-*cis*-1-OAc were carried out in the same way. The product (2) was isolated from the concentrated reaction mixture by preparative GC (10 ft × $^3/_8$ in. column, 20% UCON LB-550-X on Chromosorb W).

(B) *exo*-Bicyclo[3.2.1]oct-3-en-2-yl Acetate (*exo*-3-OAc). The procedure was the same as described above for 1-OAc except that a 5-fold excess of LiCu(CN)Me was used, and the reaction was stirred for an additional 10 h at room temperature. In addition to the black precipitate, a copper mirror was formed on the sides of the flask. Isolation and analysis were the same as described above for alkylation of *exo*-3-OAc with $LiCuMe_2$. The results of the experiments are included in Tables I and II.

(C) *endo*-Bicyclo[3.2.1]oct-3-en-2-yl Mesitoate (*endo*-3-OTMB). In a typical experiment a flask equipped with stirrer and septum was charged with 0.69 g (8 mmol) of CuCN, 0.12 g (1 mmol) of mesitylene (internal standard), 15 mL of dry ether, and 6.4 mL of 1.26 M MeLi. The mixture was stirred for 45 min at room temperature after which the homogeneous solution was cooled to 0 °C, and a solution of 0.27 g (1 mmol) of *endo*-3-OTMB in 5 mL of dry ether was added. After being stirred 1 h at 0 °C, the mixture was stirred for 4 days at room temperature. Analysis (capillary GC) showed the reaction had stopped at 50% conversion. An additional 5 mmol of ethereal LiCu(CN)Me was added and stirring continued 6 days at room temperature. The reaction was quenched, worked up, and analyzed as described for reaction of *endo*-3-OTMB with $LiCuMe_2$. Results for these experiments are included in Tables I and III.

(D) *trans*-α-Methyl-γ-mesitylallyl Acetate (8-OAc). The procedure was the same as for 1-OAc, and product distributions were determined by capillary GC (94 ft column, UCON LB-550-X).

Acknowledgment. This work was supported by the National Science Foundation (Grant GHE 8108535).

Registry No. *cis*-1-OAc, 61221-47-4; *trans*-1-OAc, 61221-48-5; α-*d*-*cis*-1-OAc, 88158-64-9; γ-*d*-*cis*-1-OAc, 73964-42-8; *cis*-**2**, 17516-95-9; *trans*-**2**, 56021-63-7; *endo*-**3**-OH, 32222-49-4; *exo*-**3**-OH, 4802-43-1; (+)-*exo*-**3**-OH, 68629-26-5; α-*d*-*endo*-**3**-OH, 88158-59-2; γ-*d*-*endo*-**3**-OH, 88158-60-5; *exo*-**3**-OAc, 4802-37-3; *endo*-**3**-OAc, 39762-77-1; (+)-*exo*-**3**-OAc, 79027-20-6; *exo*-**3**-OTMB, 88158-52-5; *endo*-**3**-OTMB, 88158-53-6; α-*d*-*endo*-**3**-OTMB, 88158-54-7; γ-*d*-*endo*-**3**-OTMB, 88158-55-8; (±)-*exo*-**4**, 88199-20-6; *endo*-**4**, 88199-21-7; (+)-*exo*-**4**, 88199-22-8; *exo*-**4**-*2*-*d*, 88158-56-9; *exo*-**4**-*4*-*d*, 88158-57-0; *trans*-**8**-OH, 84473-23-4; **8**-OAc, 88158-58-1; **9**, 16204-62-9; (*E*)-**10**, 84473-25-6; (*Z*)-**10**, 84473-26-7; **11**, 74457-38-8; (*E*)-3-methyl-1-phenyl-1-butene, 15325-61-8; (*E*)-4-phenyl-2-pentene, 42461-65-4; (*Z*)-4-phenyl-2-pentene, 76807-04-0; γ-*d*-bicyclo[3.2.1]oct-3-en-2-one, 88158-61-6; 2-methylbicyclo[2.2.1]-hept-2-ene-*3*-*d*, 88158-62-7; *cis*-3-acetylcyclopentanecarboxaldehyde-α-*d* dimethyl acetal, 88158-63-8; bicyclo[3.2.1]oct-3-en-2-one, 3212-77-9; $LiCuMe_2$, 15681-48-8; LiCu(CN)Me, 41753-78-0; CuCN, 544-92-3; MeLi, 917-54-4.

Micellar Effects upon Dephosphorylation by Peroxy Anions

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Received August 5, 1983

Dephosphorylation of *p*-nitrophenyl diphenyl phosphate (pNPDPP) by the anions of hydrogen peroxide or *m*-chloroperoxybenzoic acid (MCPBA) is markedly speeded by cationic micelles of the cetyltrimethylammonium ion. For reaction with H_2O_2 in cetyltrimethylammonium chloride (CTACl) in dilute OH^- (10^{-4} to 2.5×10^{-3} M), first-order rate constants, k_ψ, go through maxima with increasing [CTACl] and increase with increasing [OH^-] but decrease on addition of Cl^-. Added borate ion markedly speeds reaction, but carbonate ion has little effect. Reaction with *m*-chloroperoxybenzoate ion is rapid in CTA^+ micelles with chloride, mesylate, or benzenesulfonate counterion. The micellar rate enhancement is reduced by added *m*-chlorobenzoate or *p*-toluate ion. *tert*-Butylperoxy anion is an ineffective nucleophile in either water or micellized CTACl. These peroxy anion reactions were examined at high pH, and reaction with [OH^-] was studied for comparison. The rate data over a wide range of [OH^-] were fitted quantitatively to the pseudophase ion-exchange model, but this model fitted the rate data only qualitatively for reactions of the peroxy anions.

Peroxy anions are effective α-effect nucleophiles and their reactions with a variety of electrophiles have been studied mechanistically.[3] Large micellar effects upon acylation were observed by Brown and Darwent,[4] even at submicellar concentration of cetyltrimethylammonium

(1) Supported by the Apprenticeship Program of the U.S. Army Research Office administrated by the Academy of Applied Sciences.

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