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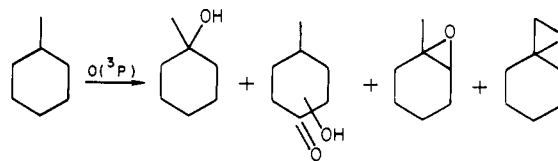
Preparative Oxidation of Cycloalkanes with O(³P) Atoms. Microwave Discharge of CO₂ as a Source of O(³P) Atoms

Summary: Reaction of O atoms produced by CO₂ discharge with cycloalkanes leads to their hydroxy, keto, and epoxy derivatives. The main products of oxidation of isomeric 1,2-dimethylcyclohexanes and *cis*-decalin were their respective tertiary alcohols formed with a high retention of configuration. This oxidation proceeds via radical mechanism, and the alcohols are formed by radical combination in a solvent cage. The influence of temperature and of O₂ on the relative product distribution was investigated.

Sir: Low-pressure photolysis of CO₂ produces O(¹D) atoms which are deactivated, resulting in O(³P) atoms.¹ It was proposed that microwave discharge of CO₂ also produces O(³P) atoms.^{2,3} We have used this method as a convenient source of O(³P) atoms for oxidation of organic compounds. The formation of O(³P) atoms by CO₂ discharge is inferred by the fact that identical results are obtained by this method and by N₂O/N₂ discharge.⁴ Moreover, the new technique is an improvement over the latter one,^{4,5} since it is simpler and easier to perform and proved to be advantageous over O₂ discharge as the oxygen atoms formed are free from oxygen molecules.⁵

We have utilized the CO₂ discharge to oxidize a number of cycloalkanes in neat liquid using a technique similar to that recently described.⁵ The reactions were performed in a flow system at 2 torr with the substrate placed in a flask with an efficient cooling condenser.⁶ The reaction times varied between 15 min and 2 h, the reaction temperatures between -78 and 25 °C, and the conversions between 20% and 50%. The main reaction products were hydroxycycloalkanes accompanied by epoxy derivatives and ketones. Thus oxidation of methylcyclohexane results in methylcyclohexanols, methylcyclohexanones, and two tertiary epoxides (Scheme I). The oxidations proceeded with a high degree of regioselectivity as indicated in Table I. This is in contrast to oxidations of cycloalkanes with O(¹D) atoms which result in a statistical distribution of primary, secondary, and tertiary alcohols.⁷

Scheme I



The relative yields of O(³P) oxidation products were independent of the reaction time but dependent on reaction temperatures: the yield of epoxides was lowest at low temperature and that of alcohols (including the derived ketones) highest (Table I). On the other hand, the regioselectivity of the formation of tertiary alcohols did not change appreciably with temperature.

The main products of the oxidation of isomeric 1,2-dimethylcyclohexanes and *cis*-decalin were the respective tertiary alcohols formed with high retention of configuration, which was temperature dependent: the highest retention was observed at low temperatures.

Since the reaction of O(³P) with saturated hydrocarbons proceeds via a radical mechanism,⁸ the formation of alcohols with high retention of configuration requires a radical combination in a solvent cage.⁹ The formation of epoxides may be explained, on the other hand, by the escape of radicals from the cage, leading to olefins which undergo a fast reaction with O(³P) atoms to give epoxides.^{5,10} This assumption was substantiated by the results of oxidation in the presence of O₂, i.e., when the source of O(³P) atoms was O₂ discharge. In this case the yield of epoxides was considerably lowered, and hydroperoxides were formed.¹¹ Their reduction with Ph₃P led to secondary and tertiary alcohols, the latter being formed with lowered stereoselectivity.

However, the fact that the yields of epoxides are not completely suppressed by O₂ points to an alternative pathway for their formation, namely, disproportionation inside the solvent cage.¹²

The following reaction scheme for O(³P) atom oxidations is suggested (Scheme II): O(³P) atoms abstract H atoms from the substrate, forming a pyramidal cycloalkyl and hydroxyl radical pair (in a triplet state) in a solvent cage. Direct combination (after intersystem crossing) leads to alcohols with retention of configuration. In addition, pyramidal radicals may undergo pseudorotation to give more planar radicals, which after cage combination result in partially inverted alcohols.¹³ Disproportionation inside the cage leads to olefins (and H₂O), which in turn react efficiently with O(³P) atoms to give epoxides. Another competing process involves diffusion of radicals out of cage to form cycloalkyl and hydroxyl free radicals, which in turn abstract H atoms from the substrate, also forming cycloalkyl radicals. Disproportionation of the latter results in olefins, the precursors of epoxides.¹⁴

(8) Andersen, P.; Lunz, A. C. *J. Chem. Phys.* 1980, 72, 5842, 5851. Paraskevopoulos, G.; Cvetanovic, R. J. *J. Phys. Chem.* 1977, 81, 2598. Wright, F. J. *J. Chem. Phys.* 1963, 38, 950.

(9) Koenig, T.; Fischer, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, pp 157-190. The intermediacy of a solvent cage in the reactions of O(³P) atoms with alkanes was originally proposed in ref 7a.

(10) Small amounts of ketones may also be formed via H migration.⁵ (11) Mayo, F. R. *Acc. Chem. Res.* 1968, 1, 193. Ingold, K. V. *Ibid.* 1969, 2, 1.

(12) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* 1970, 92, 867.

(13) (a) Greene, F. D.; Lowry, N. N. *J. Org. Chem.* 1967, 32, 875. (b) Miyajima, S.; Simamura, O. *Bull. Chem. Soc. Jpn.* 1975, 48, 526.

(14) No dimers were detected among the reaction products of O(³P) with tertiary hydrocarbons. However, a small yield of bicyclopentyl was found in the oxidation of cyclopentane (Table I).

(1) Moll, N. G.; Clutter, D. R.; Thompson, W. E. *J. Chem. Phys.* 1966, 45, 4469.

(2) Gollnick, K.; Schade, G. *Tetrahedron Lett.* 1973, 857.

(3) In addition to the O(³P) atoms, O₂(¹Δ_g) is formed (ref 2).






(4) Ung, A. Y.-M. *Chem. Phys. Lett.* 1975, 32, 351.

(5) Zadok, E.; Amar, D.; Mazur, Y. *J. Am. Chem. Soc.* 1980, 102, 6369.

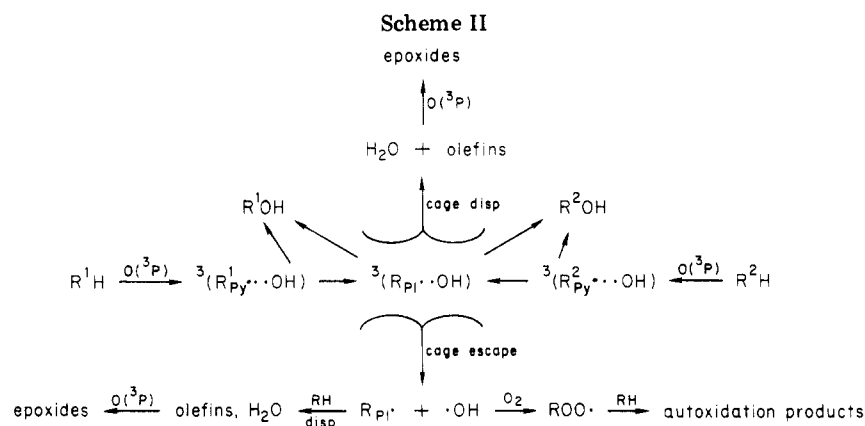
(6) He/CO₂, 12:1; total flow rate, 0.7 L/min.

(7) (a) Varkony, T. H.; Pass, S.; Mazur, Y. *J. Chem. Soc., Chem. Commun.* 1975, 457. (b) DeMore, W. B. *J. Phys. Chem.* 1969, 73, 391. This behavior is explained by the fact that the excited O(¹D) atom is much more reactive and, hence, less selective than the ground-state O(³P) atom. The difference in energy between the two species amounts to 45 kcal/mol (cf. Wagner, H. S.; Wolfrum, J. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 604).

Table I. Product Distribution from the Reaction of O(³P) Formed by CO₂ and O₂ Discharge

substrate	temp, °C	product distribution ^a (%)				
		tertiary alcohols	epoxides	secondary alcohols and ketones	retent of config	tert/sec products per H
	-30	39 (46)	36 (4)	25 (49) ^b		16 (9)
	-78	53 (53)	13 (9)	34 (37) ^b		16 (14)
	-5	54 (46)	23 (14)	23 (35) ^c	87 (72)	19 (10)
	-40	57	22	21 ^c	93	22
	0	47 (61)	35 (10)	12 (27) ^d	85 (65)	17 (9.5)
	-40	53 (64)	31 (12)	13 (12) ^d	90 (73)	17 (12)
	0	42	35	18 ^d	96	11
	-50	56	23	19 ^d	>98	12.5
	-78	68 (66)	16 (12)	15 (20) ^d	>98 (94)	19 (13)
	-78		27	65 ^e		

^a In parentheses: product yields from reaction of O(³P) formed by O₂ discharge and after Ph₃P treatment. ^b In addition, primary alcohols and aldehydes (<1%). ^c In addition, cyclodecanone (<1%). ^d In addition, 2-methylcyclohexanone (2-4%). ^e In addition, bicyclopentyl (8%).



R¹H = *cis*-1,2-dimethylcyclohexane, R³H = *trans*-1,2-dimethylcyclohexane, PI = planar, Py = pyramidal

In the presence of O₂ scavenger, cycloalkyl free radicals are trapped to give peroxy radicals, which, by autoxidation mechanism, are converted to hydroperoxides, alcohols, and β-cleavage products.¹¹ This mechanism accounts for the lower regioselectivity observed in the O₂ discharge reaction and the decrease in the retention of configuration of the tertiary alcohols formed after reduction of the hydroperoxides with Ph₃P. On the basis of this decreased retention we have estimated the yield of hydroperoxides formed in the reaction of 1,2-dimethylcyclohexanes and *cis*-decalin to be, at 0 °C, 50% and 15%, respectively. At -78 °C the calculated amount of hydroperoxides formed from 1,2-dimethylcyclohexanes was considerably lower (10%).¹⁵

The temperature dependence of the product distribution and of the retention of configuration may be explained by the change in viscosity of the substrates with temperature.⁹ At low temperature (relatively high viscosity) the diffusion of the cycloalkyl radicals out of the solvent cage is of less significance, resulting in lower relative yields of epoxides. The viscosity effect also explains the comparable larger influence of O₂ on product distribution at higher temperatures (Table I). In addition, high viscosity restricts radical pseudorotation, leading to higher retention of

configuration. This was corroborated by performing the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes in solvent of comparatively high viscosity. Thus in diethyl adipate at -10 °C the yields of alcohols formed by cage combination were considerably higher than in neat liquid at the same temperature but were similar to those at -30 °C. The retention of configuration of the alcohols at -10 °C in the viscous solvent was also higher compared to that at the same temperature in the neat liquid and similar to that at -45 °C.

It is of interest to note that γ radiolysis of liquid CO₂ solutions of cycloalkanes¹⁶ forms alcohols with regioselectivity and retention of configuration comparable to those found by us, indicating possibly the presence of O(³P) in the radiolysis. On the other hand, the reaction of O(³P) with alkanes in the absence of solvent, in the gas phase, takes a completely different course, the alcohols being formed in traces only.⁸

Registry No. Methylcyclohexane, 108-87-2; *cis*-decalin, 493-01-6; *cis*-1,2-dimethylcyclohexane, 2207-01-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; cyclopentane, 287-92-3; carbon dioxide, 124-38-9; oxygen, 7782-44-7; oxygen atom, 17778-80-2.

Supplementary Material Available: Additional tables concerning the dependence of product distribution on the discharged gas and on temperature and viscosity of the substrate or solvent used. Experimental and analytical details are also given

(15) We performed the calculations assuming a random attack of O₂ on the 1,2-dimethylcyclohexyl free radicals, yielding the corresponding *cis* and *trans* hydroperoxides in about 1:1 ratio (see ref 13b). In the case of *cis*-decalin, the corresponding ratio of *trans* and *cis* hydroperoxides was assumed to be 15:1 (ref 13a).

(16) Hori, A.; Takamuku, S.; Sakurai, H. *J. Org. Chem.* 1977, 42, 2318.

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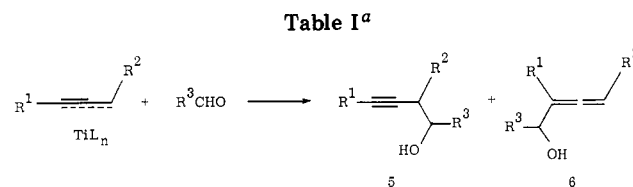
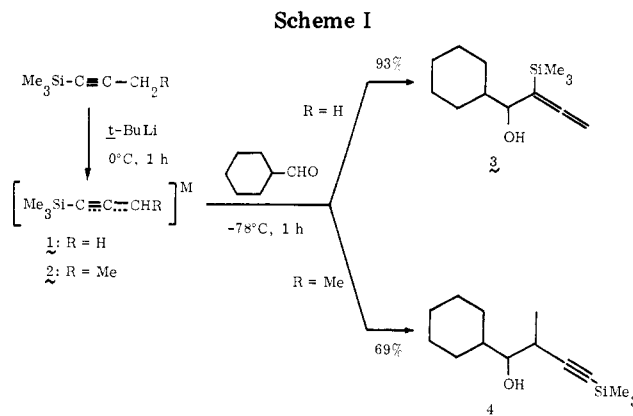
Propargylic Titanium Reagents. Regio- and Stereocontrolled Synthesis of Allenic and Acetylenic Alcohols

Summary: The highly selective condensations of propargylic titanium reagents and aldehydes are described.

Sir: The role of the propargylic anions in synthetic chemistry has become increasingly apparent.¹ An efficient and useful method for the extension of the carbon chain by means of such reactive species has recently been described.² In our continuing investigations we have studied the reaction of propargyltitanium reagents with aldehydes and have found unprecedented ambident behaviors of considerable synthetic interest.

The propargyllithium derivative 1³ (Scheme I), which was generated from 1-(trimethylsilyl)propyne and *tert*-butyllithium (THF, 0 °C, 1 h), was transformed into the corresponding titanium reagent by subsequent treatment with 1 equiv of titanium tetraisopropoxide (-78 °C, 10 min).⁴ The condensation with cyclohexanecarboxaldehyde was carried out at -78 °C for 1 h to produce the α -allenic alcohol 3 in 93% yield without contamination of any β -acetylenic alcohol (99% regioselectivity).⁵ A dramatic alteration in the product distribution occurred when the reaction of the homologous titanium reagent 2 was conducted with the same aldehyde. Thus, none of the corresponding α -allenic alcohol was detected, and instead the β -acetylenic alcohol 4 was obtained exclusively (69% yield, >99% regioselectivity).⁵ The high regioselectivity appears to be general for a range of acetylenes and aldehydes (Table I).^{6,7}

Since β -acetylenic alcohols are the main products obtained from allenic organometalics and carbonyl compounds,¹ it is currently assumed that they result from an allylic rearrangement of the organometallic by a chelate transition state of type 7 (S_Ei' process). Indeed, the IR spectrum of the titanium reagent 2 showed a strong absorption at 1898 cm⁻¹ characteristic for allenic structure,⁸ while that of the reagent 1 revealed only acetylenic absorption at 2092 cm⁻¹,⁸ in accord with the above speculation. Pioneering work by Chodkiewicz and co-workers

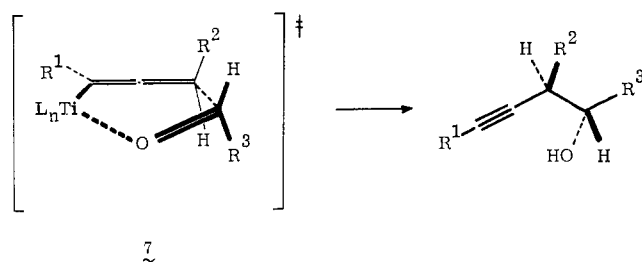


R ¹	R ²	R ³	5/6 ^{b-d} ratio	% isolated yield of 5 + 6
Si(CH ₃) ₃	H	cyclohexyl	1:99 (58:42) ^e	93 ^f
Si(CH ₃) ₃	H	phenyl	<1:99 (65:35)	87 ^g
CH ₃	H	cyclohexyl	1:99 (53:47)	90 ^h
CH ₃	H	phenyl	1:99 (49:51)	80 ⁱ
Si(CH ₃) ₃	CH ₃	cyclohexyl	>99:1	69 ^j
Si(CH ₃) ₃	CH ₃	phenyl	>99:1	79 ^k
CH ₃ CH ₂	CH ₃	cyclohexyl	>99:1 (84:16)	42 ^l
phenyl	CH ₃	cyclohexyl	94:6 (93:7)	89 ^m
phenyl	CH ₃	phenyl	>99:1 (98:2)	92 ⁿ

^a All reactions were carried out at -78 °C for 1 h.

^b Both products have been isolated and fully characterized. ^c Determined by GC analysis. ^d Values in parentheses refer to ratios of 5/6 from the reactions with lithium reagents. ^e 56:44 using Mg ion; 75:25 using Zn ion. ^f IR (liquid film) 5.18 μm; NMR (CCl₄) δ 4.38 (d, 2 H, J = 2 Hz). ^g IR 5.18 μm; NMR δ 4.45 (d, 2 H, J = 3 Hz). ^h IR 5.08 μm; NMR δ 1.62 (d, 3 H, J = 3 Hz), 4.63 (m, 2 H). ⁱ IR 5.10 μm; NMR δ 1.47 (3 H), 4.68 (m, 2 H). ^j IR 4.63 μm; NMR δ 1.18 (d, 3 H, J = 7 Hz), 2.60 (dq, 1 H). ^k IR 4.59 μm; NMR δ 1.07 (d, 3 H, J = 7 Hz), 2.67 (dq, 1 H). ^l NMR δ 1.21 (d, 3 H, J = 7 Hz), 2.57 (m, 1 H). ^m NMR δ 1.30 (d, 3 H, J = 7 Hz), 2.77 (dq, 1 H). ⁿ IR 4.44 μm; NMR δ 2.80 (q, 1 H).

established the stereoregulation of condensation between allenic organometalics and carbonyl compounds, and the transition state of type 7 permits a rationalization of their



results.⁹ It was of considerable interest to us to determine whether the titanium reagent would exhibit enhanced diastereoselection for the *threo*- β -acetylenic alcohol syn-

(1) For a recent review, see: Moreau, J.-L. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; pp 363-414.

(2) Yamakado, Y.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* 1981, 103, 5568.

(3) Corey, E. J.; Kirst, H. A. *Tetrahedron Lett.* 1968, 5041.

(4) Recently, several titanium reagents were reported as useful synthetic reagents. Weidman, B.; Widler, L.; Olivero, A. G.; Maycock, D. D.; Seebach, D. *Helv. Chim. Acta* 1981, 64, 357. Reetz, M. T.; Peter, R. *Tetrahedron Lett.* 1981, 4691 and references cited therein.

(5) Both acetylenic and allenic alcohols have been isolated and fully characterized. Satisfactory spectra and elemental analyses were obtained on all new compounds reported herein.

(6) The condensations of the titanium reagent 1 and 2 with ketones were unsuccessful, and starting ketones were recovered. Similar chemoselectivities for the titanium reagents were reported (see ref 4).

(7) Recently, Daniels and Paquette reported interesting regioselectivities at the carbonyl for additions of reagent 1 (M = Zn and Al): Daniels, R. G.; Paquette, L. A. *Tetrahedron Lett.* 1981, 1579. See also: Mukaiyama, T.; Harada, T. *Chem. Lett.* 1981, 621.

(8) See pp 367-368 of ref 1.

(9) (a) Saniere-Karila, M.; Caprau, M. L.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* 1973, 3371. (b) Favre, E.; Gaudemar, M. *J. Organomet. Chem.* 1975, 92, 17. (c) See also references cited in ref 1.