6.22 → 6.68 (m, 1, NH-CH-P), 8.30 → 8.80 (q, 3, $-CH_3$). *Anal.* Calcd for $C_4H_{11}N_2O_4P$: C, 26.37; H, 6.08; N, 15.38; P, 17.00. Found: C, 26.19; H, 5.92; N, 15.20; P, 17.10.

(3) **Gly-2-Aep:** mp 250° dec; nmr (NaOD) 6.37 (s, 2, NH_2–CH_2), 8.03 → 8.62 (m, 2, NH–CH_2), 6.30 → 6.82 (m, 2, CH_2–P). *Anal.* Calcd for $C_4H_{11}N_2O_4P$: C, 26.37; H, 6.08; N, 15.38; P, 17.00. Found: C, 26.46; H, 6.11; N, 15.33; P, 16.89.

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Registry No.—Glyamp, 30211-73-5; Gly-1-Aep, 53626-51-0; Gly-2-Aep, 53626-52-1; Phtglyamp, 38416-67-0; Phtgly, 4702-13-0; aminomethylphosphonic acid, 1066-51-9; Phtgly-1-Aep, 51814-60-9; 1-aminoethylphosphonic acid, 6323-97-3; Phtgly-2-Aep, 51814-61-0; 2-aminoethylphosphonic acid, 2041-14-7.

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Mechanism and Stereochemistry of Oxetane Reactions. I. Stereospecific Synthesis of the Diastereoisomeric 2-Phenyl-3-methyloxetanes and Study of Their Configuration and Conformation by Nuclear Magnetic Resonance Spectroscopy

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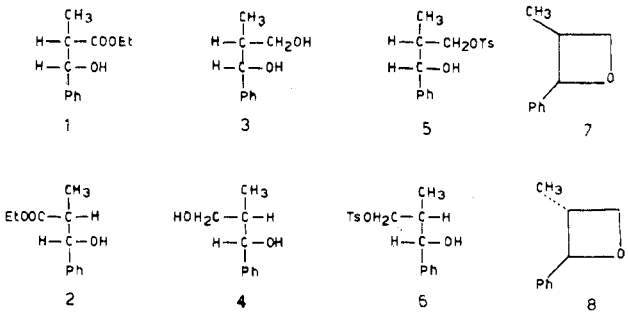
The stereospecific synthesis of the diastereoisomeric 2-phenyl-3-methyloxetanes **7** and **8** has been achieved from the corresponding 1,3-diols through their monotosylates. The relative configurations of **7** and **8** have been unequivocally established by an extensive study of their nmr spectra. The assignment of the proton resonance signals has been effected on the basis of the shielding effects and of the coupling constants, and confirmed through additive shielding parameters. By using the J_{trans}/J_{cis} ratio it has been possible to obtain some informations on the conformational preference of the oxetane ring in the examined compounds.

The stereochemistry of the ring opening of small ring heterocycles such as oxiranes[1-3] and aziridine[4,5] in acid media is well known and documented. However, practically no information is available on the steric course of the analogous reactions of oxetanes.[6] Furthermore no "stereospecific" synthesis of diastereoisomeric couples of oxetane has been reported and only a few pairs of diastereoisomeric oxetanes have been prepared.[7] Since we are strongly interested in the study of mechanism and stereochemistry of the ring opening of small ring systems,[3,5] it was thought desirable to prepare and study diastereoisomerically pure oxetanes of unquestionable configuration. Oxetanes **7** and **8** appeared as promising substrates for this purpose and their synthesis and stereochemical characterization was the aim of this work.

The Reformatsky reaction of benzaldehyde and ethyl 2-bromopropionate gave a mixture of the diastereoisomeric esters *erythro*-**1** and *threo*-**2** whose relative configurations were deduced from their nmr spectra on the basis of the higher coupling constant of the benzylic proton for the threo isomer **2**, as found for the corresponding methyl esters.[8] On the other hand reduction of **1** and **2** with $LiAlH_4$ afforded the known diols *erythro*-**3** and *threo*-**4**.[8c,9] Reaction of **3** and **4** with *p*-toluenesulfonyl chloride in pyridine gave the respective monotosylates **5** and **6**. The constitution of **5** and **6** could be inferred by the known fact that tosyl chloride should react preferentially with the primary rather than with the secondary hydroxyl group,[10] and confirmed from their nmr spectra. In fact whereas the chemical shift of the signals of the benzylic proton is almost the same for the diols **3** and **4** and the corresponding tosylates, the signals of the protons of the methylene group are shifted toward low field in the cases of tosylates. Treatment of **5** and **6** with potassium *tert*-butoxide in *tert*-butyl alcohol at room temperature led to the diastereoisomerically pure oxetanes **7** and **8**. The configurations of oxetanes **7** and **8** were



deduced from their method of synthesis. The complete stereospecificity of the formations of oxetanes **7** and **8** is in accordance with the mechanism of their formation from **5**

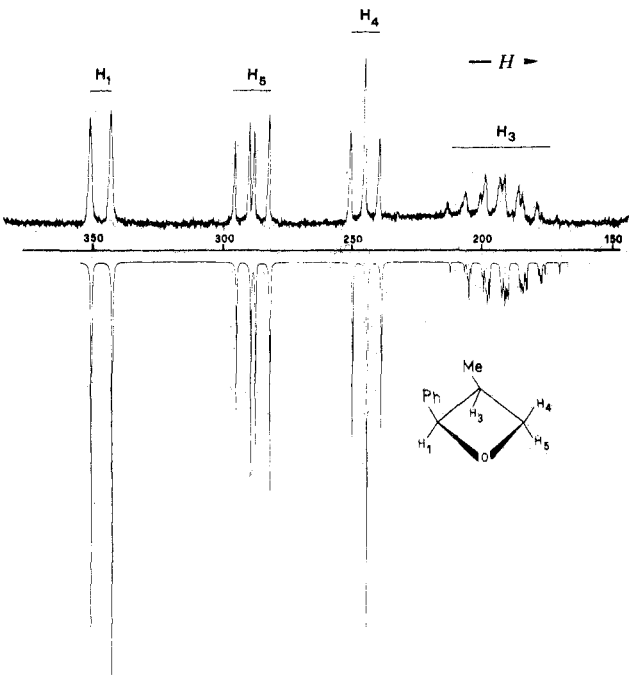


Figure 1. Observed and calculated spectrum of *cis*-2-phenyl-3-methyloxetane (7). Measured frequencies (in Hz) are relative to internal TMS.

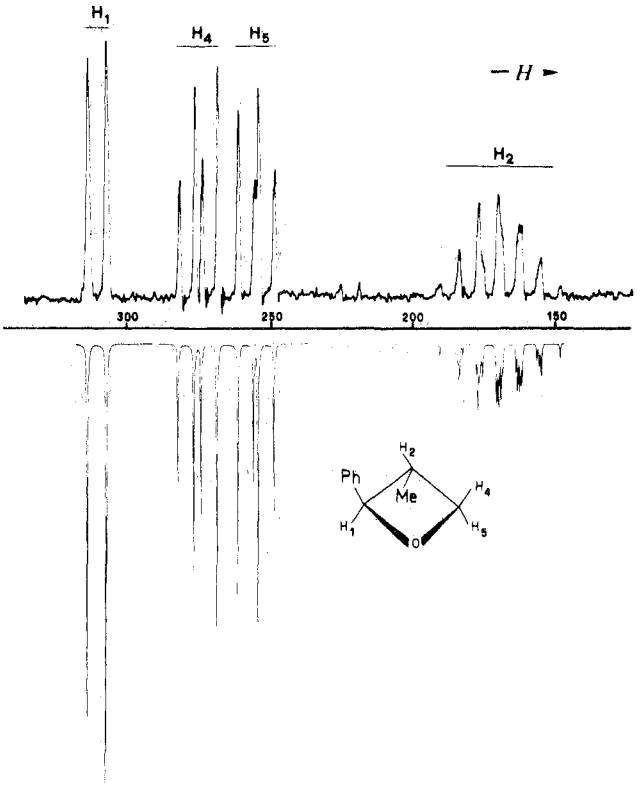


Figure 2. Observed and calculated spectrum of *trans*-2-phenyl-3-methyloxetane (8). Measured frequencies (in Hz) are relative to internal TMS.

and 6 which implies a SN2 type substitution. In this reaction the two chiral centers are not involved and oxetanes 7 and 8 should have the same relative configuration of the starting compounds. In any case the configurations of 7 and 8 have been unequivocally confirmed by an extensive study of their nmr spectra.

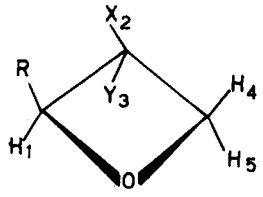
Relatively few nmr studies have been reported on the subject of oxetanes[11-17] in comparison with other four-membered ring compounds,[11,18] and just a few of those listed deal with conformational aspects.[13,14,17]

The complete analysis of the nmr spectra of *cis*-7 and *trans*-oxetane 8 should include, in addition to the oxetane ring and methyl group protons, the five protons of the phenyl ring; however, since the coupling constants between the protons of the phenyl and oxetane ring were not observable, the analyses have been performed as an $ABCDX_3$ spin system from the 60-MHz nmr spectra. The theoretical spectra were calculated using program LEQUOR, a seven-spin system modified from LAOCOON-3.[19] Figures 1 and 2 show the observed and calculated spectra of 7 and 8, respectively.

Table I gives the values of the spectral parameters of 7 and 8 obtained from the above mentioned analysis. Furthermore, the corresponding data for unsubstituted oxetane 9[16] and 2-phenyloxetane 10[12a] have also been reported for the sake of comparison.

While the attribution of the protons α to the phenyl and methyl groups of 7 and 8 is firmly established both on the basis of the known shielding effects of such substituents on the adjacent proton and from double resonance experiments, the assignment of H_4 and H_5 signals is not so straightforward. In both cases it is necessary to take into account the long-range screening effects of the methyl and phenyl group. It has been fairly well demonstrated that the use of additive shielding increments can often be a useful tool in making nmr assignments in configurational problems.[20] If one assumes that small conformational changes of the oxetane ring do not affect to a large extent the chemical shift of the oxetane protons and the substituent effects, then the evaluation of the chemical shifts through additive shielding parameters can be used with a sufficient accuracy in the present situation. The contribution to the chemical shift of the 2-phenyl group on the cis (H_4) and trans (H_5) protons can be computed by comparison of the suitable spectral parameters of 2-phenyloxetane (**10**) and of oxetane itself (**9**) ($\Delta\delta$(Ph cis) = +0.2 Hz; $\Delta\delta$(Ph trans) = +10.1 Hz). The shielding of the 3-methyl group on cis and trans vicinal protons can be, on the other hand, deduced by comparing the chemical shift of the H_1 proton of oxetanes 8 and **10** and 7 and **10**, respectively ($\Delta\delta(CH_3$ cis) = −37.1 Hz; $\Delta\delta(CH_3$ trans) = −0.2 Hz). By adding the appropriate contribution to the chemical shift of the α protons of the unsubstituted oxetane **9**, the theoretical chemical shift of H_4 and H_5 protons of 7 and 8 can be predicted (see Table I). The very good agreement between the calculated and observed chemical shifts provides unambiguous proof of the assignment of the relative proton resonance positions and clearly demonstrates the usefulness of the additivity principle also in these cyclic systems. The relative configurations of oxetanes 7 and 8 have been confirmed by the following considerations. Whereas the proton resonance position of the methyl group in the trans compound 8, when compared with the corresponding 3,3-dimethyloxetane (76.5 Hz),[12c] is practically unaffected by the presence of the phenyl group, in compound 7 it resonates at much higher field. This fact agrees with the shielding variation arising from the changes in the magnetic field caused by the ring current[21] keeping in mind that the phenyl ring should spend most of its time in a preferred conformation in which the plane of the phenyl ring lies very near the oxygen atom.[12a] Furthermore, the value of the J_{13} of 7 is higher than the J_{12} of 8 which agrees with the finding that in oxetanes vicinal cis coupling constants are of a higher value that the trans ones.[12,16] Furthermore, the values of the vicinal coupling constants of the H_4 and H_5 protons of 7 and 8 also confirm the assignment of their resonance positions made on the basis of the additive shielding increments.[22] A final confirmation came from the nuclear Overhauser effect

Table I
The Pmr Parameters for Oxetanes[a]



	Compd			
	7[b]	8[b]	9[16]	10[12a]
R	C_6H_5	C_6H_5	H	C_6H_5
X	CH_3	H	H	H
Y	H	CH_3	H	H
ν_1	347.43	310.47	277.25	347.61
ν_2	44.10	169.10	157.24	157.97
ν_3	191.97	77.90	157.24	178.73
ν_4	245.11 (240.4)	274.63 (277.3)	277.25	277.40
ν_5	288.71 (287.2)	254.89 (250.3)	277.25	287.36
J_{12}		6.67	6.60	7.31
J_{13}	8.10		8.70	7.79
J_{23}	7.10	6.80		−10.91
J_{24}		8.10	8.70	9.15
J_{25}		7.28	6.60	7.74
J_{34}	5.66		6.60	5.62
J_{35}	7.33		8.70	8.19
J_{45}	−5.59	−5.60		−5.75
J_{14}	0.0	0.0	0.14	−0.02
J_{15}	0.0	0.0	0.20	−0.03

[a] Chemical shifts (in Hz) are relative to TMS. [b] Values in parentheses have been calculated by the additive shielding parameters.

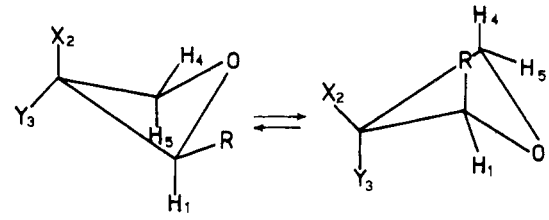
Table II
J_{trans}/J_{cis} Ratios for Oxetanes 7–10

J_{trans}/J_{cis}	7	8	9	10
J_{12}/J_{13}			0.76	0.94
J_{25}/J_{24}		0.90	0.76	0.85
J_{34}/J_{35}	0.77		0.76	0.69
J_{34}/J_{24}			0.76	0.61
J_{25}/J_{35}			0.76	0.95

(NOE); the intensities of the signals for H_4 in **7** and for H_1 and H_5 in **8** were increased respectively by 12, 18, and 11% on saturation of the methyl signal.

Even if oxetane is essentially planar,[23] it may be vibrating between two equivalent interconvertible ring-puckered conformations. However, the presence of one or more substituents on the ring can render one conformation more stable[14,24] and this could be made evident by nmr spectroscopy.

A comparison of the coupling constants of oxetanes **7, 8,** and **10** with the corresponding ones of the unsubstituted oxetane **9** shows appreciable changes in the ring vicinal coupling constants; consequently, conformational modifications must occur with the substitution of the oxetane ring. However, the variation of the single coupling constants may not be the most reliable way to reveal small conformational changes because the coupling constants can be influenced by several factors other than dihedral angle modifications.[25] In a modification of the so-called "*R*-value" method,[26] the J_{trans}/J_{cis} ratio could provide a direct route for obtaining a qualitative picture of conformational preferences in these systems (factors other than conformational ones should be minimized by using this ratio[26a,b]). Table II reports the values obtained from oxetanes **7, 8, 9,** and **10.** Deviations from the J_{trans}/J_{cis} value 0.76 obtained from the parent oxetane **9** (in which there is absolutely no conformational preference between conformer a and b)



7a (R = Ph, X = CH_3, Y = H) 7b (R = Ph, X = CH_3, Y = H)
8a (R = Ph, X = H, Y = CH_3) 8b (R = Ph, X = H, Y = CH_3)
9a (R = X = Y = H) 9b (R = X = Y = H)
10a (R = Ph, X = Y = H) 10b (R = Ph, X = Y = H)

should be indicative of conformational modifications. When the oxetane ring assumes conformation a from an ideal planar structure the increase of dihedral angle between the 2 and 4 protons (φ_{24}) and 2 and 5 protons (φ_{25}) will decrease J_{24} and will increase J_{25};[27] evidently the effect on the value (J_{trans}/J_{cis}) will be an increase. The same situation will hold for the J_{12}/J_{13}, J_{25}/J_{35} ratios. On the contrary φ_{35} and φ_{34} will decrease, thus decreasing both J_{35} and J_{34}, but the over-all effect on the J_{34}/J_{35} will be a net decrease. The same is found for J_{34}/J_{24}. The exact opposite changes in the ratios will occur for conformation b.

The high value of the J_{25}/J_{24} for trans oxetane **8** indicates that it exists largely in the dipseudoequatorial puckered conformation a. Also for 2-phenyloxetane **10** (in the original paper[12a] the conformational aspect was not discussed by the authors) the J_{trans}/J_{cis} values are consistent with conformation a having the phenyl group pseudoequatorial.[14] Evidently the higher nonbonding repulsive interactions of the substituents in the more hindered pseudoaxial positions favor conformation a. The ratio found for the cis oxetane **7** does not differ significantly from the value obtained in the unsubstituted oxetane **9;** this means that **7** likely exists as an about 50:50 equilibrium of the two conformers a and b both with a pseudoequatorial and a pseudoaxial substituent.

Experimental Section

Ir spectra were recorded on a Perkin-Elmer Infracord Model 137. Nmr spectra were determined on 10% solutions in carbon tetrachloride with a Varian DA-60 IL (operating at 60 MHz) spectrometer using tetramethylsilane as an internal standard. Peak positions were directly measured with a Marconi TF 2414 frequency meter and the mean values of five measurements were taken. Experimental line positions were determined to ±0.1 Hz. To compute the final chemical shifts, proton–proton couplings, and theoretical spectrum, an iterative program (LEQUOR) based on the method of Castellano and Bothner-By[19] was applied and solved with an IBM 370/155 computer equipped with a Calcomping plotting accessory. The parameters obtained should be correct to within ±0.1 Hz.

Glpc were run on a Carlo Erba Fractovap GV apparatus with a flame ionization detector, using a dual system with glass columns packed with 1% neopentylglycol succinate on 80–100 mesh silanized Chromosorb W. Preparative (2-mm layer) tlc were performed on silica gel F 254 plates containing a fluorescent indicator. Magnesium sulfate was used as the drying agent. Evaporations were made *in vacuo* (rotating evaporator). Petroleum ether refers to the fraction boiling at 40–70°.

***erythro*-1 and *threo*-Ethyl-3-hydroxy-2-methyl-3-phenyl Propionate (2).** A mixture of **1** and **2** (106 g, bp 102–105° (0.2–0.3 mm) [lit.[28] 107–109° (0.3–0.4 mm)]) was obtained according to the procedure of Zimmermann and English[28] from benzaldehyde (63.6 g, 0.6 mol), ethyl bromopropionate (119.4 g, 0.66 mol) and zinc (43.9 g, 0.66 g-atom) in benzene (170 ml). The above mixture (30 g) was chromatographed through a 3.5 × 82 cm column of silica gel collecting 250-ml fractions. Elution was carried out, successively, with petroleum ether (9.0 l.) and 98:2 (9.0 l.), 97:3 (2.0 l.), 96:4 (63.0

l.), 95:5 (13.0 l.), 94:6 (9.0 l.) petroleum ether–ethyl acetate. The fractions were evaporated to dryness and checked by nmr and glpc. The fractions 104–190 were combinated as pure **1** (12.8 g): ir 2.86 (OH), 5.84 μ (CO): nmr δ 4.88 (1, H, d, J = 4.6 Hz, $C_6H_5\mathbf{CH}$), 3.97 (2 H, q, $\mathbf{CH_2}$), 2.60 (2 H, dq, $CH_3\mathbf{CH}$), 1.11 (3 H, t, $\mathbf{CH_3}CH_2$), 1.09 ppm (3 H, d, $\mathbf{CH_3}CH$). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.12; H, 7.68.

The fractions 300–400 yielded pure **2** (5.5 g): ir 2.89 (OH), 5.82 μ (CO); nmr δ 4.56 (1 H, d, J = 8.55 Hz, $C_6H_5\mathbf{CH}$), 4.02 (2 H, q, $\mathbf{CH_2}$), 2.62 (2 H, dq, $CH_3\mathbf{CH}$), 1.20 (3 H, t, $\mathbf{CH_3}CH_2$), 0.91 ppm (3 H, d, $\mathbf{CH_3}CH$). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.93; H, 7.56.

***erythro*-1-Phenyl-2-methyl-1,3-propanediol (3).** To a stirred suspension of $LiAlH_4$ (6.8 g, 0.18 mol) in dry ether (150 ml) was added dropwise a solution of **1** (12.5 g, 0.06 mol) in the same solvent (150 ml). The mixture was then refluxed for 7 hr and left at room temperature for 12 hr, after which excess $LiAlH_4$ was destroyed by adding water, followed by 2 M NaOH. The organic layer was separated, filtered, dried, and evaporated to give **3**[8c,9] (9.4 g) as a liquid: ir 2.97 μ (OH); nmr δ 4.76 (1 H, d, J = 3.1 Hz, $C_6H_5\mathbf{CH}$), 3.41 (2 H, m, $\mathbf{CH_2}OH$), 1.82 (1 H, m, $CH_3\mathbf{CH}$), 0.67 ppm (3 H, d, J = 6.9 Hz, $\mathbf{CH_3}$). The nmr data agree with the previously reported ones.[8c]

***threo*-1-Phenyl-2-methyl-1,3-propanediol (4).** Reduction of **2** (5.0 g, 0.024 mol) with $LiAlH_4$ (2.7 g, 0.072 mol) as described above yielded **4**[8c,9] (3.5 g) as an oil: ir 3.00 μ (OH); nmr δ 4.29 (1 H, d, J = 9.1 Hz, $C_6H_5\mathbf{CH}$), 3.48 (2 H, m, C $\mathbf{H_2}$OH), 1.81 (1 H, m, $CH_3\mathbf{CH}$), 0.55 ppm (3 H, d, J = 6.9 Hz, $C\mathbf{H_3}$). The nmr data agree with the previously reported ones.[8c]

***erythro*-1-Phenyl-2-methyl-3-tosyloxy-1-propanol (5).** A solution of tosyl chloride (3.81 g, 0.02 mol) in anhydrous pyridine (20 ml) was added to a solution of **3** (3.00 g, 0.018 mol) in the same solvent (30 ml), while keeping the temperature below 0°. After 4 days at 5°, the mixture was poured in ice and extracted with $CHCl_3$. Evaporation of the washed (1 M aqueous H_2SO_4, saturated aqueous $NaHCO_3$, and water) and filtered extracts gave pure **5** (3.9 g) as an oil: ir 2.80 (OH) 7.40, 8.41 and 8.51 μ (OSO_2-*p*-C_7H_7);[29] nmr δ 4.68 (1 H, d, J = 4.4 Hz, $C_6H_5\mathbf{CH}$), 3.99, 3.71 (1 H each, q, $\mathbf{CH_2}O$), 1.99 (1 H, m, $CH_3\mathbf{CH}$), 0.74 ppm (3 H, d, J = 7.2 Hz, $\mathbf{CH_3}CH$).

***threo*-1-Phenyl-2-methyl-3-tosyloxy-1-propanol (6).** **4** (3.0 g) was treated with tosyl chloride under the conditions used above to give pure **6** (4.3 g) as a liquid: ir 2.81 (OH), 7.40, 8.41, and 8.51 μ (OSO_2-*p*-C_7H_7);[29] nmr δ 4.20 (1 H, d, J = 8.2 Hz, $C_6H_5\mathbf{CH}$), 4.07, 3.93 (1 H each, q, $\mathbf{CH_2}O$), 1.97 (1 H, m, $CH_3\mathbf{CH}$), 0.69 ppm (3 H, d, J = 7.2 Hz, $\mathbf{CH_3}CH$).

***cis*-2-Phenyl-3-methyloxetane (7).** A solution of **5** (3.90 g, 12.2 mmol) in *tert*-butyl alcohol (40 ml) was treated with potassium *tert*-butoxide (1.8 g, 16.0 mmol) and left 24 hr at room temperature. Dilution with petroleum ether, filtration, and evaporation of the solvent gave a residue (1.50 g) consisting of crude **7**. Purification of this product through preparative tlc (a 8:2 mixture of petroleum ether–ethyl ether being used as eluent) yielded pure **7** (0.78 g): ir 10.15 μ (oxetane ring);[30] nmr (see Table I). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.85; H, 8.05.

***trans*-2-Phenyl-3-methyloxetane (8).** Treatment of a solution of **6** (4.10 g, 12.8 mmol) in *tert*-butyl alcohol (40 ml) with potassium *tert*-butoxide (1.87 g, 16.7 mmol) as described above yielded **8** (1.70 g), which was purified through tlc to give pure product (0.95 g): ir 10.30 μ (oxetane ring);[30] nmr (see Table I). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.83; H, 8.20.

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Registry No.—**1,** 17226-82-3; **2,** 17226-81-2; **3,** 19774-62-0; **4,** 7087-77-6; **5;** 53432-97-6; **6,** 53432-98-7; **7,** 53432-99-8; **8,** 53433-00-4; **9,** 503-30-0; **10,** 4436-23-1; tosyl chloride, 98-59-9.

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