2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—To a suspension of 1 (5.0 g, 0.0125 mol) in methanol (125 ml) was added 30% methanolic potassium hydroxide (25 ml), and the red mixture was refluxed for 0.5 hr. The hot solution was filtered and the filtrate was treated with dry hydrogen chloride until it became yellow. The mixture was filtered and the filtrate was cooled. The yellow precipitate was collected, washed free of acid, and dried to give crude 9 (2.754 g), mp 113–120°. Crystallization from methanol gave pure 9 (2.283 g, 44.3% yield), mp 122–123°.

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.95; H, 5.31; OCH_3, 7.49. Found: C, 86.88; H, 5.19; OCH_3, 7.80.

Oxidation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9) with Nitric Acid.—To a stirred suspension of 9 (0.09 g, 0.00022 mol) in glacial acetic acid (0.5 ml) was added a mixture of nitric acid (concentrated, d ~1.42, 0.1 ml) in glacial acetic acid (0.3 ml). The mixture became clear in 0.25 hr. After 0.5 hr a white solid precipitated from solution. Stirring was continued for another 0.5 hr. After excess ice-water had been added, the precipitate was collected, washed free of acid, dried, and crystallized from ethanol to give 1,2-dibenzoyl-1-(9'-methoxy-9'-fluorenyl)ethylene (10, 0.079 g, 85%), yellow crystals, mp 159–160°.

Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.72; H, 5.11. Found: C, 83.71; H, 4.97.

Oxidation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9) with Potassium Permanganate.—A solution of 9 (0.2 g, ~0.0005 mol) and potassium permanganate (0.40 g, ~0.0025 mol) in acetone-water-acetic acid (26–3–0.5 ml) was stirred at room temperature for 2 hr. Sodium bisulfite was added and the mixture was made strongly acidic with dilute hydrochloric acid. After most of the acetone had been removed under reduced pressure, the residue was extracted with excess ether, washed with saturated sodium bicarbonate, dried ($MgSO_4$), and evaporated. The residual oil (~0.2 g) on trituration with ether gave 10 (0.1 g, 48% yield), mp 160–161°.

Ozonolysis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—A solution of 9 (0.40 g, ~0.001 mol) in methylene chloride was ozonized at 40° for 20 min. The ozonide was reduced with zinc dust and a trace of hydroquinone. The crude product on trituration with ether gave 10 (0.064 g, 15.2% yield), mp 159–161°.

2,5-Diphenyl-3-(9'-hydroxy-9'-fluorenyl)furan (13).—To stirred magnesium turnings (0.15 g, ~0.006 g-atom) and dry ether (20 ml) was added dropwise a solution of 3-bromo-2,5-diphenylfuran (1.5 g, ~0.005 mol) in dry ether (20 ml). A crystal of iodine was added and the stirred suspension was held at 38° for 22 hr. A solution of fluorenone (11, 0.9 g, 0.005 mol) in dry ether (20 ml) was then added dropwise and the mixture was heated for another hour. The reaction solution was poured onto crushed ice–dilute sulfuric acid and then extracted with ether. The ethereal extract was washed with water and with saturated sodium bicarbonate, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel. Elution with benzene-hexane gave nearly pure 13 (0.34 g, 17% yield) as a pale yellow solid which was crystallized from hot benzene, mp 163–164°.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.0. Found: C, 87.06; H, 5.1.

Synthesis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—A solution of 2,5-diphenyl-3-(9'-hydroxy-9'-fluorenyl)furan (13, 0.075 g, ~0.0002 mol) in methanolic hydrochloric acid (7–8 ml) was stored overnight. The filtrate was poured into cold water (100 ml) and the yellow solid was filtered to yield additional 9, mp 116–117°. The crude products were combined and crystallized from methanol to give pure 9 (0.068 g, 88%), mp 122–123°. This material was identical (analysis, tlc, mixture melting point, ir, and nmr) with 9 as obtained from 1 and methanolic potassium hydroxide.

Reduction of *trans*-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Zinc–Acetic Acid–Hydrochloric Acid.—A stirred suspension of 1 (0.25 g, 0.0006 mol) and zinc dust (0.25 g, ~0.0035 g-atom) in acetic acid (3 ml) was kept at 75–80° for 0.5 hr. Concentrated hydrochloric acid (3 ml) was added in one lot and heating was continued for an additional hour. The yellow mixture was decanted and diluted with saturated sodium chloride solution (15 ml). The resulting mixture and the zinc residue were extracted with ether. The ether extracts were washed with aqueous sodium carbonate and with saturated sodium chloride, dried ($MgSO_4$), and evaporated. The crude product on crystallization from benzene gave 1,2-dibenzoyl-1-(9'-fluorenyl)ethane (14, 0.99 g, 39.4% yield), mp 212–213°.

Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47. Found: C, 86.64; H, 5.50.

Reduction of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9) with Zinc–Acetic Acid–Hydrochloric Acid.—Under conditions described for 1, 9 (0.26 g, ~0.0006 mol) was reduced to give 2,5-diphenyl-3-(9'-fluorenyl)furan (15, 0.048 g, 20% yield), white crystals, mp 158–159°.

Anal. Calcd for $C_{29}H_{20}O$: C, 90.62; H, 5.21. Found: C, 90.82; H, 5.55.

Reaction of *trans*-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Methanolic Potassium Hydroxide Followed by Hydrogen Chloride at 0°. Isolation of 1,2-Dibenzoyl(1-fluorenylidene)ethane (6).—To a suspension of 1 (1.0 g, 0.0025 mol) in absolute methanol (25 ml) was added 30% methanolic potassium hydroxide (5 ml) and the mixture was refluxed for 0.5 hr. The blood-red solution was filtered, cooled in ice, and treated with dry hydrogen chloride until precipitation of yellow 6 was complete. The reaction mixture was filtered, washed free of acid and salt, and dried, and the resulting crude product (0.4 g, mp 195–196°) was crystallized from benzene to give pure 6, mp 198° (0.382 g, 38.2% yield).

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.04. Found: C, 86.84; H, 5.29.

Reduction of 1,2-Dibenzoyl(1-fluorenylidene)ethane (6) with Zinc–Acetic Acid. Isolation of 1,2-Dibenzoyl-1-(9'-fluorenyl)ethane (14).—Under conditions described for 1, 6 (0.125 g, 0.0003 mol) was reduced to 14 (0.025 g, 20% yield), mp 213–214°. This product was identical (mixture melting points, tlc, ir) with that obtained from 1.

Transformation of 1,2-Dibenzoyl(1-fluorenylidene)ethane (6) to 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (9).—A suspension of 6 (0.075 g, 0.00018 mol) in absolute methanol (8 ml) was refluxed for 0.25 hr. The hot suspension was saturated with dry hydrogen chloride. The mixture became clear in 2 min. After 0.1 hr excess methanol was removed under reduced pressure and the residue was cooled. The yellow crystals were collected and crystallized from hot methanol to give pure 9, mp 122–123° (0.030 g, 30.8% yield).

The compound was identical (tlc, mixture melting point, ir) with that prepared from 1.

Registry No.—**1**, 31684-96-5; **6**, 31684-97-6; **9**, 31684-98-7; **10**, 31684-99-8; **13**, 31685-00-4; **14**, 31685-01-5; **15**, 31685-02-6; zinc, 7440-66-6; nitric acid, 7697-37-2; acetic acid, 64-19-7; hydrochloric acid, 7647-01-0; potassium permanganate, 7722-64-7.

Acknowledgment.—We acknowledge support of this research by the Kettering Foundation and the National Science Foundation.

Solvent Steric Effects. V. Azobis-2-methyl-3-phenyl-2-butane. The Absolute Configuration of Some Derivatives of 2-Methyl-3-phenylbutane[1]

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A stereoselective memory effect has been reported for the coupling of 3-methyl-2-phenyl-2-butyl radical

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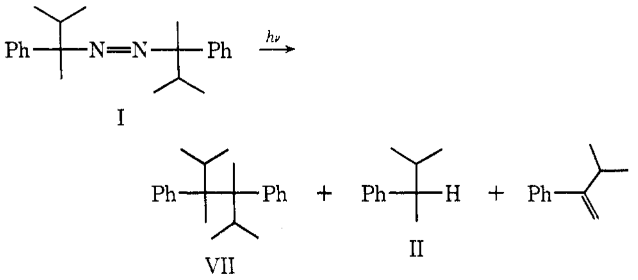
[2] Proctor and Gamble Fellow, 1969–1970; IBM Fellow, 1970–1971.

[3] Alfred P. Sloan Foundation Fellow.

pairs generated by photolysis of meso and chiral azobis-3-methyl-2-phenyl-2-butane (I) in rigid media.[4,5] We have observed substantial optical activity in 2-methyl-3-phenylbutane (II) from disproportionation of such a radical pair from partially resolved I.[6] The optical rotation of enantiomerically pure II is needed to use this result for elucidating details of the behavior of radical pairs within a rigid solvent cage. The *S* absolute configuration has previously been assigned to (−)-II on the basis of synthesis from (*R*)-hydratropic acid.[7]

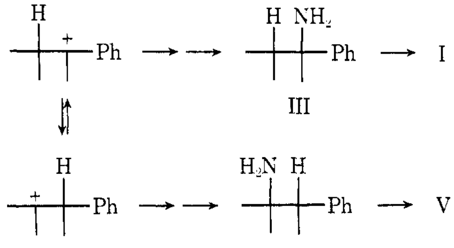


I

VII

II

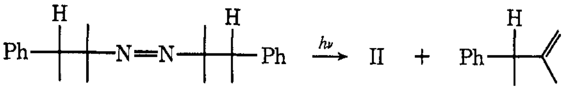
The optical purity of this sample was, however, questionable because of the intermediacy of the 2-methyl-3-phenyl-2-butyl cation in the synthesis and the possibility of its racemization through equilibration with the 3-methyl-2-phenyl-2-butyl cation.[8] Our original synthesis of I involved preparation of 3-methyl-2-phenyl-2-butylamine (III) by a Ritter reaction, and this same equilibration plagued the synthetic reaction resulting in amine mixtures containing as much as 40% of 2-methyl-3-phenyl-2-butylamine (IV).[4,9]


III

IV

Results and Discussion

In part because of the availability of substantial amounts of IV as a by-product from synthesis of III, we have used it as a source of optically pure II by way of resolution with tartaric acid, oxidative coupling to azobis-2-methyl-3-phenyl-2-butane (V), and homolysis of this azoalkane with disproportionation of the radicals to II and 2-methyl-3-phenyl-1-butene (VI). This scheme has several advantages for preparing optically pure II. (1) The oxidative coupling provides a check on the resolution of IV. (2) Resolved chiral V is crystalline allowing reinforcement of partial resolution by recrystallization. (3) Racemization should not occur in the intermediate radicals[11] as it may well do for the corresponding cation.[8]



V

VI

The diastereomers of V may be readily distinguished by pmr spectroscopy. Oxidation of racemic IV with iodine pentafluoride[12] resulted in negligible asymmetric induction in coupling to V, since equal peak heights were found for the corresponding methyl signals of the diastereomers of V both in the crude product and in that purified by preparative tlc. Coupling of resolved (−)-IV gave (+)-V with no detectable *meso*-V (<5%). Amine IV must thus have been >95% optically pure. Three recrystallizations from ether at Dry Ice temperature gave (+)-V which was presumably optically pure. An ORD curve for this azo compound showed a Cotton effect at slightly longer wavelength than the absorption maximum as was reported by Kosower and Severn for other azoalkanes.[13]

Differential scanning calorimetry confirmed the expectation of a high (∼200°) thermolysis temperature for V. Photolysis in benzene at room temperature gave rapid decomposition to equal parts of the disproportionation products II and VI, which were stable to the reaction conditions. An identical photolysis with thiophenol scavenger gave II and VI in the ratio 3.5:1 indicating a 45% cage effect.

For preparation of optically pure II recrystallized (+)-V was photolyzed at room temperature without scavenger to avoid the possibilities of high temperature racemization of the radicals during thermolysis and of racemization through reversible atom abstraction from II by scavenger radical. The resulting products purified by gas chromatography were (−)-II and (+)-VI.

The absolute stereochemistries and rotations of II, IV, V, and VI are presented in Table I. We include comparable data for I, III, and 2,3,4,5-tetramethyl-3,4-diphenylhexane (VII) with absolute configurations based on the assumption that retention predominates in both coupling and disproportionation within the solvent cage.[4,14,15]

Experimental Section

Rotations at 589 nm were obtained using an O. C. Rudolph & Sons Model 80 polarimeter[16] and those at 546 nm using a Bendix Ericsson automatic polarimeter. The ORD curve was obtained using a Cary 60 ORD-CD instrument.[16] Pmr spectra were measured with Varian A-60 A and HA-100 and Jeolco Minimar 100 instruments.

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(4) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(5) In the polyazane nomenclature system [see P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 2362 (1968)] I and V would be named 1,2-bis(3-methyl-2-phenyl-2-butyl)diazene and 1,2-bis(2-methyl-3-phenyl)-diazene, respectively.

(6) M. J. Tremelling, unpublished work.

(7) O. Červinka and L. Hub, *Collect. Czech. Chem. Commun.*, **33**, 1911 (1968).

(8) The assignment of ref 7 was based on work with partially resolved materials. Comparison of this data with ours suggests that about 22% racemization occurred at the cation stage of this preparation.

(9) It has been reported that 3-methyl-2-phenyl-2-butanol, 2-methyl-3-phenyl-2-butanol, and 2-methyl-3-phenyl-2-butene all give III from Ritter reaction in *n*-butyl ether,[10] but in our hands the amine mixture was about 90% IV under these conditions.

(10) H. Christol, A. Laurent, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 2319 (1961).

(11) C. Walling in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Wiley, New York, N. Y., 1963, Chapter 7.

(12) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961); *cf.* S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).

(13) E. M. Kosower and D. J. Severn, *ibid.*, **91**, 1710 (1969).

(14) F. D. Greene, M. A. Berwick, and J. C. Stowell, *ibid.*, **92**, 867 (1970), and references cited therein.

(15) Details of this work will be published separately.

(16) We are grateful to Professors J. A. Berson and J. M. Sturtevant, respectively, for use of the Rudolph and Cary instruments.

TABLE I

ABSOLUTE CONFIGURATIONS AND ROTATIONS

		Rotation[a]			
Compd	Configuration	[α]	λ, nm	c, g/100 ml	Solvent
$PhCH(CH_3)CH(CH_3)_2$ (II)	*S*	−36.2	546	1.6	CCl_4
		−30.0	589	1.6	CCl_4
		−24.5	589	0.7	CH_3OH
$PhCH(CH_3)C(CH_3){=}CH_2$ (VI)	*S*	94 ± 2	546	1.9	CCl_4
		79 ± 2	589	1.9	CCl_4
$(PhCH(CH_3)C(CH_3)_2N{=})_2$ (V)	*R,R*	60.2	546	0.86	CH_3OH
$PhCH(CH_3)C(CH_3)_2NH_2$ (IV)	*R*	−30.4[b]	546	3.95	CH_3OH
$PhC(CH_3)(i\text{-}Pr)NH_2$ (III)	*R*	−22.1[c]	546	1.8	CH_2Cl_2
$(PhC(CH_3)(i\text{-}Pr)N{=})_2$ (I)	*R,R*	10.5[d]	546	1.6	CCl_4
$(PhC(CH_3)(i\text{-}Pr))_2$ (VII)	*R,R*	4[e]	546	0.59	CCl_4

[a] Samples greater than 98% optically pure except as noted. [b] Greater than 95% optically pure, see text. [c] Judged to contain 8.5% (*S*)-III from meso/nonmeso ratio of oxidation product I. [d] Sample from oxidative coupling of III. 84.4% nonmeso of which 83.7% is *R,R* and 0.7% is *S,S*, since statistical coupling is observed for *rac*-III. [e] Optical purity unknown.

2-Methyl-3-phenyl-2-butylamine (**IV**) was collected as a forerun during a spinning band distillation used to remove this by-product from amine III after alkaline hydrolysis of the product from a Ritter reaction of 2-methyl-3-phenyl-2-butanol.[17] Combined foreruns from several distillations (115 g) were dissolved in 100 ml of ethanol and added to a hot solution of 160 g of *d*-tartaric acid in 600 ml of ethanol with cooling and stirring. The resulting salt was recrystallized five times from methanol to give 8.3 g of salt which was converted to 4.1 g of amine and distilled [bp 93° (8 mm)]. The resulting (*R*)-(−)-IV had $[\alpha]_{546}$ −31.1° (*c* 3.25, methanol); pmr (20% in CCl_4, 60 MHz) δ 7.30 (5 H, s, Ar H), 2.65 (1 H, q, J = 7.3 Hz, $CHCH_3$), 1.28 (3 H, d, J = 7.3 Hz, $CHCH_3$), 1.03 (2 H, s, NH_2), 1.00 (3 H, s, $C(CH_3)CH_3$), 0.86 (3 H, s, $C(CH_3)CH_3$).

Azobis-2-methyl-3-phenyl-2-butane (**V**) was prepared as a mixture of diastereoisomers by oxidative coupling of 11 g of amine mixture containing 85% IV and 15% III with 5 ml of IF_5 in 150 ml of CH_2Cl_2–18 ml of pyridine at −20 to −30°. Washing through Florisil with pentane gave 3.6 g of a yellow oil shown by pmr to contain the diastereomers of V (in equal amounts by peak heights) and a small amount of what are presumably the cross coupling products between III and IV. Preparative tlc (Merck F-254 developed five times with pentane) gave a mixture of the diastereomers of V as a yellow oil free of impurities and showed negligible fractionation of the diastereomers between early and late fractions confirming the absence of asymmetric induction in the coupling reaction. Pmr (CCl_4, 100 MHz): *meso*-V, δ 7.20 (5 H, s, Ar H), 3.19 (1 H, q, J = 7.5 Hz, $CHCH_3$), 1.22 (3 H, d, J = 7.5 Hz, $CHCH_3$), 1.02 (3 H, s, $C(CH_3)CH_3$), 0.98 (3 H, s, $C(CH_3)CH_3$); *rac*-V, 7.20 (5 H, s, Ar H), 3.17 (1 H, q, J = 7.5 Hz, $CHCH_3$), 1.22 (3 H, d, J = 7.5 Hz, $CHCH_3$), 1.05 (3 H, s, $CH(CH_3)CH_3$), 0.96 (3 H, s, $C(CH_3)CH_3$). The racemate peaks were identified by comparison with the spectrum of (*R,R*)-V.

(*R,R*)-(+)-V was prepared by a similar oxidation of 2.74 g of the resolved (−)-amine. Crude chromatography on Florisil gave 1.07 g of a yellow-brown liquid shown by pmr to be IV with less than 5% *meso*-IV. This material was recrystallized three times from ether in a Dry-Ice–acetone bath to give yellow crystals: mp 61.2–61.8°; $[\alpha]_{546}$ 60.2° (*c* 0.86, CH_3OH); $\lambda_{\max}^{\mathrm{MeOH}}$ 373 nm ($\epsilon_{\max}$ 30); pmr as above. ORD showed a Cotton effect at 393 nm.

Anal. Calcd for $C_{22}H_{30}N_2$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.62; H, 9.18; N, 8.46.

Thermolysis of V was investigated using a Perkin-Elmer DSC-1b calorimeter with a 2.9-mg sample of mixed diastereomers of V sealed in an aluminum volatile sample capsule. A scan from 107 to 257° at 10°/min showed an exotherm beginning near 185° and peaking at 217°.

Photolysis of mixed diastereomers of V was investigated with 30-mg samples degassed by freezing and thawing in benzene solution under vacuum and sealed in nmr tubes. One tube contained 2.8 mol of practical thiophenol per mol of V. The tubes were photolyzed in a 30–40° water bath by light from a 450-W Hanovia L lamp with Pyrex filter. After 80 min pmr showed complete disappearance of starting material in both samples. The pmr spectra were unchanged after another 75 min of photolysis. Both samples showed signals for II and VI, and there were no other appreciable peaks except for solvent and scavenger. In the unscavenged run the II/VI ratio was estimated at 1.1–1.2 on the basis of integration. For the scavenged run this ratio was 3.5–4 implying that 2.5/3.5–3/4 of II was the product of scavenging and that the cage effect was 40–45%.

(*S*)-**2-Methyl-3-phenylbutane** (**II**) **and** (*S*)-**2-methyl-3-phenyl-1-butene** (**VI**) were prepared from 400 mg of pure (*R,R*)-V in 4 ml of benzene, degassed, sealed, and irradiated for 3.5 hr at room temperature. The sample was opened and solvent was removed, and II and VI were bulb-to-bulb distilled under high vacuum. II and VI were separated by preparative vpc using $^3/_8$ in. × 8 ft 20% DEGS on Chromosorb P at 105°. Pmr (100 MHz, CCl_4): II, δ 7.25 (5 H, m, Ar H), 2.38 (1 H, p, J = 7.0 Hz, ArCH), 1.76 (1 H, octet, J = 7 Hz, $CH(CH_3)_2$), 1.27 (3 H, d, J = 7 Hz, Ar $CHCH_3$), 0.98 (3 H, d, J = 7 Hz, $CH(CH_3)CH_3$), 0.78 (3 H, d, J = 7 Hz, $CH(CH_3)CH_3$); VI, 7.20 (5 H, s, Ar H), 4.89 and 4.85 (2 H, d, $=CH_2$), 3.34 (1 H, q, J = 7 Hz, Ar CH), 1.56 (3 H, s, $CH_3C{=}$), 1.36 (3 H, d, J = 7 Hz, $ArCHCH_3$). See Table I for rotations.

Registry No.—(*S*)-(−)-II, 19643-73-3; (*R*)-(−)-IV, 33686-47-4; *meso*-V, 33686-48-5; *rac*-V, 33686-49-6; (*R,R*)-(+)-V, 33686-50-9; (*S*)-(+)-VI, 25145-46-4.

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[17] For details of this preparation see J. M. McBride, Thesis, Harvard University, 1967. Subsequent preparations by this method have given higher yields of IV as a by-product as did preparation by another method.[10]

The α-Methyl/Hydrogen Reactivity Ratio for the *anti*-7-Norbornenyl and 7-Norbornadienyl Systems

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The very large α-Me/H solvolytic rate ratio for the 7-norbornyl system (**4**/**1**) has been attributed to the "enormous demand on substituents for further stabilization" of the unusually strained 7-norbornyl cation.[2,3]

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(1) (a) NIH Postdoctoral Fellow, 1966–1968; address inquiries to Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. 15213. (b) Fellow of the French Centre National de la Recherche Scientifique, on leave from the University of Strasbourg, 1967–1968. (c) Deceased, Nov 23, 1969.

(2) (a) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967); (b) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

(3) It has been noted[4] that "steric ground state strain . . . in tertiary tosylates would enhance α-Me/H rate ratios" with the implication that the **4**/**1** tosylate rate ratio may be an inflated value. Comparison of the **4**-Cl/**2**-Cl ratio with the corresponding tosylate ratio (Table II of this paper) would indicate the inflation to be worth *ca.* $10^{1.9}$. On the other hand, the tosylate ratio will be deflated to the extent that solvent nucleophilicity (k_s)