Thermolyses of 3-Alkyl-4-phenyl-2-oxetanones and Related Compounds

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Thermolyses of cis- and trans-3-methyl-4-phenyl-2-oxetanones (1c and 1t), cis- and trans-3-isopropyl-4-phenyl-2-oxetanones (2c and 2t), and cis- and trans-3-tert-butyl-4-phenyl-2-oxetanones (3c and 3t) resulted in quantitative formation of the corresponding styrene which kept stereochemical uniformity. The strict stereo-specificity suggests the concerted nature of the fragmentation. The rates of reaction of these 2-oxetanones and related compounds, including 3,3-dimethyl-4-phenyl-2-oxetanone (4), 3,3-dimethyl-4,4-diphenyl-2-oxetanone (5), 4,4-dimethyl-3-phenyl-2-oxetanone (6), and cis- and trans-3,4-diphenyl-2-oxetanones (7c and 7t), in decane and/or dodecane were studied. The reactivity of 4-phenyl-2-oxetanone (8) was estimated from that of p-nitro derivative 9. The relative rates at 150 °C were 1c/2c/3c/1t/2t/3t/4/5/6/7c/7t/8, 1.0:0.31:0.028:11.4.3:2.1:0.29:6.9:3.8:(1.7):(13):(17). The least substituted 8 exhibited the highest reactivity. In 3,4-disubstituted derivatives, the trans isomer reacted more rapidly than the corresponding cis isomer without exception. For 1–3, it is shown that the bulkier the alkyl group, the slower the fragmentation. Since significant positive charge development has been previously shown to occur only at C-4, but not at C-3, the reactivity sequence cannot be attributed to the electronic effect of the alkyl group. On the other hand, if an assumption that the important factor is the increased steric strain at the concerted $2_s + 2_a$ transition state is accepted, the results can be explained reasonably. Indeed, log k_1 values of 1c, 2c, 3c, and 8 correlated quite linearly with the steric parameter E_s or v. The relative reactivities of 4–7 are also discussed.

Since the concerted nature may be anticipated in the decarboxylation of 2-oxetanones,[1] mechanistic studies of such reactions should be of great interest. Up to the present time there have been several papers describing the stereospecific fragmentation of certain 2-oxetanones,[2] but kinetic studies are rather deficient, only a limited number of works having appeared.[3] We have recently uncovered the substituent electronic effects at both the C-3 and C-4 positions,[3c] but our results themselves are still insufficient to account for certain well-documented behavior of 2-oxetanones. In particular, the observations that heavily substituted compounds, such as tetrasubstituted derivatives, are relatively stable[4] whereas those substituted by a smaller number of groups at times result in easy fragmentation[2a–c,3b,5,6] are hardly explained by the electronic effects.[3c] Because our previous results predict that the substitution of a hydrogen at C-4 by an electron-releasing group should *increase* the reactivity while any group at C-3 could not influence the reactivity, it is, therefore, highly desirable to carry out a systematic study which can provide a further clarification to the structure–reactivity relationship of 2-oxetanones. In this paper, we studied the thermal behavior of geometrically pure 3-alkyl-4-phenyl-2-oxetanones 1–3 and related compounds 4–9.

The scarcity of the kinetic data, in particular those of the 4-phenyl derivatives, should be, at least in part, due to the extreme sensitivity of such compounds toward acidic impurities in the reaction system. We have previously developed a method to overcome these difficulties.[3c]

Results

Substrates. 2-Oxetanones, including cis- and trans-3-methyl-4-phenyl- (1c and 1t), cis- and trans-3-isopropyl-4-phenyl- (2c and 2t), cis- and trans-3-tert-butyl-4-phenyl- (3c and 3t), 3,3-dimethyl-4-phenyl- (4), 3,3-dimethyl-4,4-diphenyl- (5), 4,4-dimethyl-3-phenyl- (6), and cis- and trans-3,4-diphenyl-2-oxetanones (7c and 7t), were prepared by the cyclization of the corresponding 3-hydroxypropionic acid according to the method developed by Adam, Baeza, and Liu.[2c] The geometrical isomers were separated at the

(1) S. Mageswaran and M. U. S. Sultanbawa, *J. Chem. Soc., Perkin Trans. 1*, 884 (1976). See also N. D. Epiotis, *J. Am. Chem. Soc.*, **94**, 1924 (1972).

(2) (a) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966); (b) O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **90**, 2333 (1968); (c) W. Adam, J. Baeza, and J.-C. Liu, *ibid.*, **94**, 2000 (1972); (d) U. Schöllkopf and I. Hoppe, *Angew Chem., Int. Ed. Engl.*, **14**, 765 (1975); (e) J. Mulzer, A. Pointner, A. Chucholowski, and G. Brüntrup, *J. Chem. Soc., Chem. Commun.*, **52** (1979). See also: (f) M. Tanabe and R. H. Peters, *J. Org. Chem.*, **36**, 2403 (1971); (g) J. A. Marshall and L. J. Karas, *J. Am. Chem. Soc.*, **100**, 3615 (1978). For N and S analogues, see: (h), L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Am. Chem. Soc.*, **92**, 1763 (1970); (i) F. Jung, N. K. Sharma, and T. Durst, *ibid.*, **95**, 3420 (1973); (j) T. Durst and B. P. Gimbarzevsky, *J. Chem. Soc., Chem. Commun.*, 724 (1975).

(3) (a) T. L. James and C. A. Wellington, *J. Am. Chem. Soc.*, **91**, 7743 (1969). (b) H. O. Krabbenhoft, *J. Org. Chem.*, **43**, 1305 (1978). (c) T. Imai and S. Nishida, *ibid.*, **44**, 3574 (1979). (d) Recently, we learned by a private communication that Dr. J. Mulzer and his co-workers are carrying out kinetic works that are similar to ours.

(4) 4,4-Dimethyl-3,3-diphenoxy-2-oxetanone has been reported to sublime at atmospheric pressure on heating with only partial decomposition [W. Adam and H.-H. Fick, *J. Org. Chem.*, **44**, 356 (1979); **43**, 4574 (1978)].

(5) (a) H. E. Zaugg, *Org. React.*, **8**, 305 (1954); (b) R. N. Lacey, *Adv. Org. Chem.*, **2**, 213 (1960); (c) H. Kröper in "Methoden der Organischen Chemie (Houben-Weyl)", 6/2, 4th ed., Georg Thieme, Stuttgart, 1963, p 511; (d) Y. Etienne and N. Fischer in "The Chemistry of Heterocyclic Compounds: Heterocyclic Compounds with Three- and Four-Membered Rings", Vol. 19, Part II, A. Weissberger, Ed., Interscience, New York, 1964, p 729; (e) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions", Interscience, New York, 1967, p 139; (f) W. T. Brady and A. D. Patel, *J. Org. Chem.*, **37**, 3536 (1972).

(6) The instability of 2-oxetanones of low molecular weight is also due to their tendency to form polyesters.[5a–d]
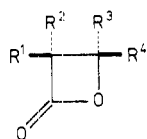
1c: R^1 = CH_3, R^2 = R^3 = H, R^4 = C_6H_5

1t: R^1 = CH_3, R^2 = R^4 = H, R^3 = C_6H_5

2c: R^1 = $CH(CH_3)_2$, R^2 = R^3 = H, R^4 = C_6H_5

2t: R^1 = $CH(CH_3)_2$, R^2 = R^4 = H, R^3 = C_6H_5

3c: R^1 = $C(CH_3)_3$, R^2 = R^3 = H, R^4 = C_6H_5

3t: R^1 = $C(CH_3)_3$, R^2 = R^4 = H, R^3 = C_6H_5

4: R^1 = R^2 = CH_3, R^3 = C_6H_5, R^4 = H

5: R^1 = R^2 = CH_3, R^3 = R^4 = C_6H_5

6: R^1 = C_6H_5, R^2 = H, R^3 = R^4 = CH_3

7c: R^1 = R^4 = C_6H_5, R^2 = R^3 = H

7t: R^1 = R^3 = C_6H_5, R^2 = R^4 = H

8: R^1 = R^2 = R^3 = H, R^4 = C_6H_5

9: R^1 = R^2 = R^3 = H, R^4 = p-$NO_2C_6H_4$

hydroxy acid stage. The assigned stereochemistry of 1–3 and 7 based on the NMR coupling constants[7] was consistent with that deduced from the consequence of the ring closure process.[2c] The coupling constant $(J_{3,4})$ of each compound was as follows: 1c, 6.7 Hz; 1t, 4.0 Hz; 2c, 6.5 Hz; 2t, 4.0 Hz; 3c, 6.9 Hz; 3t, 4.2 Hz; 7c, 6.8 Hz; 7t, 4.4 Hz. Since 7t was very unstable,[2b] only a brief purification was possible (see Experimental Section). 1t was also a labile compound, and the contamination of *trans*-1-phenylpropene in a small amount (ca. 3%) was unavoidable.[3c] All attempts to prepare 4-phenyl-2-oxetanone (8) had been fruitless.[8] In contrast, 4-(p-nitrophenyl)-2-oxetanone (9) could be obtained from 3-bromo-3-(p-nitrophenyl)-propionic acid with no trouble.[9]

Products. Under the standard conditions,[3c] the fragmentation of 1–3 was cleanly regiospecific and stereospecific. An emphasis should be laid upon the fact that 3c produced pure *cis*-3,3-dimethyl-1-phenyl-1-butene (*cis-β-tert*-butylstyrene).

In contrast to 1–3, 7c and 7t gave a mixture of *cis*- and *trans*-stilbene: cis/trans ratio of 76:24 from 7c and 4:96 from 7t at 150 °C and 88:12 from 7c and 2:98 from 7t at 171 °C.[10] Since the stilbenes were stable under the reaction conditions (in the presence of N,N,N',N'-tetramethylethylenediamine; TMEDA), the formation of isomeric stilbenes might be due to the prior epimerization of 7c to 7t, which could be catalyzed by TMEDA.[11] Indeed, in the absence of TMEDA, the cis/trans ratio in the product of 7c was 99.5:0.5 at 171 °C. A control experiment showed that *cis*-stilbene isomerized slowly to the trans isomer in the absence of TMEDA. Accordingly, it can be concluded that the fragmentation of 7 is essentially stereospecific as well.

Kinetics. The rate data obtained under the standard conditions are summarized in Table I.

Since 8 could not be obtained, its reactivity was estimated from that of p-nitro derivative 9 by assuming that

Table I. Kinetic Data for the Thermolysis of 2-Oxetanones[a]

2-oxe-tanone	temp, °C	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	rel rate (150 °C)
1c	120.0	0.315	32.3	−2.2	1.0
	135.0	1.50			
	150.0	6.29			
	165.1	24.8			
1t	110.0	1.62	29.4	−4.4	11
	120.0	4.34[b]			
	120.0	4.39[c]			
	130.0	11.6			
	140.0	28.6			
	150.0	(68.1)[d]			
2c	130.0	0.276	33.1	−2.7	0.31
	143.0	0.969			
	150.0	1.96			
	170.0	12.4			
2t	110.1	0.525	31.1	−2.1	4.3
	120.1	1.52			
	135.0	6.86			
	150.0	27.1			
3c	165.1	0.787[c]	34.5	−4.2	0.028
	175.1	1.64[c]			
	190.0	7.19[c]			
	205.0	21.6[c]			
	150.0	(0.175)[d]			
3t	120.0	0.710	31.5	−2.6	2.1
	135.1	3.18			
	150.0	13.0			
	160.0	32.4			
4	150.0	1.80			0.29
5	150.0	43.4			6.9
6	150.0	23.8			3.8
7c	150.0	(11)[d,e]			(1.7)[f]
7t	150.0	(79)[d]			(13)[f]
8	150.0	(110)[d]			(17)[f]
9	150.0	6.93			

[a] With a 2-oxetanone concentration of (7–9) × 10^{-3} mol/L in decane in the presence of an equimolar amount of TMEDA. The standard deviations in k_1, except for 9, were <3% (<2% in most cases). The k_1 for 9 showed a larger standard deviation (7%) because of the low solubility of 9, but no drifting was observed. [b] An average of three runs.[3c] [c] Dodecane was used as the solvent. [d] The figure was obtained by either extrapolation or estimation; see the text for 7c, 7t, and 8. [e] The apparent k_1 showed gradual upward drifting; the averaged k_1 was 1.5 × 10^{-4} s^{-1}; see the text. [f] The figure was less accurate than others.

the ρ value for 4-aryl-2-oxetanones was the same as that of the 4-aryl-3,3-dimethyl derivatives.[3c] For 7c and 7t, we needed some approximations, because the mutual epimerization took place during the thermolysis of these compounds. Since the extent of the epimerization observed in 7t was small (4% at 150 °C), k_{7t} was set equal to the apparent k_1. For k_{7c}, we considered the facts that the fragmentation was virtually stereospecific and that the decarboxylation of 7t was considerably faster than the epimerization of 7t to 7c. We can, therefore, assume that the ratios of the produced olefins (cis/trans ratio of 76:24 at 150 °C) give an approximate ratio for the fragmentation (k_{7c}) vs. epimerization $(k_{e,cis}[TMEDA])$.[12] Although the

(7) T. Sternhell, *Q. Rev., Chem. Soc.*, **23**, 236 (1969); T. J. Batterham, "NMR Spectra of Simple Heterocycles", E. C. Taylor and A. Weissberger, Eds., Wiley-Interscience, New York, 1973, p 369.

(8) 8 has been described as too reactive to be isolated in a pure form,[5a] although its successful preparation has been reported: T. B. Fomina, V. N. Artem'eva, Y. N. Sazanov, and M. M. Koton, *Dokl. Akad. Nauk SSSR*, **193**, 838 (1970); T. B. Fomina, V. N. Artem'eva, and Y. N. Sazanov, *Zh. Org. Khim.*, **7**, 2295 (1971).

(9) A. Basler, *Ber. Dtsch. Chem. Ges.*, **16**, 3001 (1883).

(10) The epimerization was less important at higher temperatures. This is reasonable because the epimerization is a bimolecular reaction whereas the fragmentation is a unimolecular reaction.

(11) Amines are known to epimerize 2-thiethanones: S. D. Carter and R. J. Stoodley, *J. Chem. Soc., Chem. Commun.*, 92 (1977).

(12) The k_{7c} showed a slight upward drifting (1.4 × 10^{-4} s^{-1} at 27% conversion whereas it was 1.6 × 10^{-4} s^{-1} at 76% conversion). Moreover, the cis/trans ratio of produced stilbenes became constant only after 20% conversion, a somewhat larger amount of *cis*-stilbene being formed at the early stage of the reaction. Accordingly, the reactivity index, which was determined by the analyses of the reaction after 20% conversion, was only given as a round number. The extinction coefficients of *cis*- and *trans*-stilbene at 285 nm (the wavelength at which the fragmentation of 7c was being followed) were 9400 and 25000, respectively.
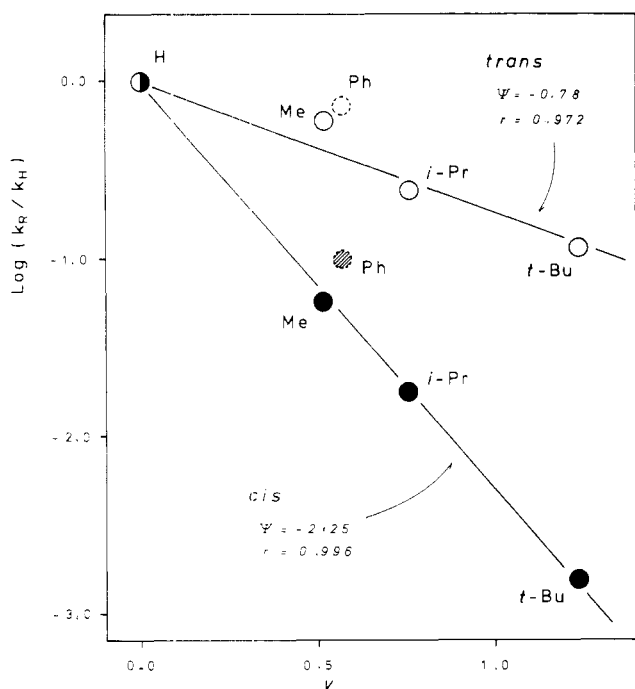
Figure 1. Plot of log k_1 vs. v for the thermolysis of 2-oxetanones. A plot of log k_1 vs. E_s also results in an equally good correlation.

figure is only in round numbers, it will suffice for the qualitative discussion given below. Since nearly stereospecific fragmentation was observed in the absence of TMEDA, the rate of **7c** was followed under such conditions, but the difficulties in obtaining reliable rate constants (driftings) arose again.

Discussion

As has been demonstrated in several cases,[2] the fragmentation of 3-alkyl-4-phenyl-2-oxetanones **1–3** was strictly stereospecific. The results are thus consistent with the anticipated concerted nature of the reaction.[1,13] The activation parameters (Table I) and the Hammett reaction constants[3c,14] were not contradictory to the conclusion.

From the reactivity sequence, it is clear that the least substituted **8** is the most reactive. In other words, it can be noted that the introduction of an alkyl group at C-3, either cis to the phenyl or trans to it, results in the reactivity decrease in 4-phenyl-2-oxetanones. The rate-retarding effect of a methyl trans to the phenyl can also be seen in the 3,3-dimethyl derivative **4**, which reacts more slowly than **1c** by a factor of 0.29. It should further be pointed out that the trans isomer reacts more rapidly than the corresponding cis isomer in all epimeric pairs and that the bulkier the alkyl group is, the slower the decarboxylation was (**1c/2c/3c**, 1.0:0.31:0.028, and **1t/2t/3t**, 11:4.3:2.1). Since the activation entropy differs only little from one compound to the next (Table I), the observed relative reactivities should be an outcome of the differences in activation energies.

For the effect of alkyl groups, one should consider the electronic and steric effects. The electronic effect, however, should not be important because the Hammett study indicates no charge being developed at the C-3.[3c] Accordingly, it is highly probable that the observed sequence of reactivities is primarily the result of steric effects. Indeed, a plot of log k_1 vs. E_s[15] (or v[16]) results in a good correlation, particularly in the cis isomers, suggesting that the major factor will be steric in origin (Figure 1). Now there will be three different steric interactions worthy of considerations, namely, (i) steric repulsions caused by eclipsing of the groups at C-3 and C-4 (due to a development of a partial double bond between the two carbons at the concerted transition state),[17,18] (ii) steric inhibition of resonance interaction between the phenyl and the partially developed double bond, and (iii) steric interactions other than the eclipsing effect on the $2_s + 2_a$ (or $2_s + 2_s + 2_s$) transition state.[13] If i were solely responsible for the reactivity sequence,[17] the magnitude of the rate reduction observed in the trans series seems to be too large for us. The same observation rules out a possibility that ii is predominating throughout. Although i and ii should be playing partial roles and i no doubt must be important in the cis series, we believe that iii is worthy of consideration because it can explain the results in a single term.

Before proceeding any further, it will be adequate to look at ketene–olefin cycloadditions, because the same type of steric interaction has been proposed to account for the fact that cis olefin reacts faster than trans olefin,[19] the result opposite to that of the 2-oxetanone fragmentation. The transition state **10c** is proposed to be more stable than **10t**,
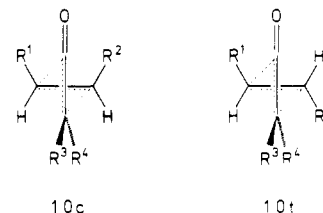
because severe steric destabilization should occur only in the interactions between the groups at an olefinic moiety and the terminal carbon of the ketene.[19] This happens to be so since the steric bulkiness of the terminal carbon of ketene is believed to be much larger than that of the carbonyl. In 2-oxetanone fragmentations, however, the two groups in question are oxygen and a carbonyl group. Since these groups may be similar in size,[20] no particular steric interaction can be predominating.[21] Now among the 2_s

(13) Either a $2_s + 2_a$ process (R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, Chapter 6) or a $2_s + 2_s + 2_s$ [R. Huisgen, L. A. Feiler, and G. Binsch, *Chem. Ber.*, 102, 3460 (1969); J. E. Baldwin and J. A. Kapecki, *J. Am. Chem. Soc.*, 92, 4868, 4874 (1970); M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, 10, 761 (1971)] may be suggested.

(14) The p value (−1.52)[3c] is similar to that reported for the ketene–styrene cycloaddition [p = −1.4: N. S. Isaacs and P. Stanbury, *J. Chem. Soc., Perkin Trans. 2*, 166 (1973)]. As to the effect of solvent polarity on the rates, a dependence in a medium degree may be anticipated, but the difficulties in removing the disturbance caused by the acid-catalyzed process did not allow the quantitative studies.

(15) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 556.

(16) M. Charton, *J. Am. Chem. Soc.*, 97, 1552 (1975).

(17) This is indeed proposed as the major factor for the thermal stability of tetrasubstituted β-sultines.[2i]

(18) The starting 2-oxetanones will most probably take a puckered conformation, although the parent 2-oxetanone is known to be flat: J. Bregman and S. H. Bauer, *J. Am. Chem. Soc.*, 77, 1955 (1955); J. R. Durig and A. C. Morrissey, *J. Mol. Struct.*, 2, 377 (1968); L. M. Boggia, P. G. Favero, and O. M. Sorarrain, *Chem. Phys. Lett.*, 12, 382 (1971); D. Coffey, Jr., and M. V. Hershberger, *J. Mol. Spectrosc.*, 59, 28 (1976). In 1–3 and 7, the $J_{3,4}$ showed only small changes from one compound to the next in both cis and trans series, but each compound may have a different degree of puckering. It is pointed out that the coupling constants can be influenced by several factors other than dihedral angle modifications: H. Booth, *Prog. Nucl. Magn. Reson. Spectrosc.*, 5, 160 (1969).

(19) T. DoMinh and O. P. Strausz, *J. Am. Chem. Soc.*, 92, 1766 (1970); R. Huisgen and H. Mayr, *Tetrahedron Lett.*, 2965, 2969 (1975); ref 14.

(20) The group contribution to the van der Waals volume of a molecule is 5.2 cm³/mol for ether oxygen and 5.0 cm³/mol for an sp² carbon atom [A. Bondi, *J. Phys. Chem.*, 68, 441 (1964)]. The same conclusion can be obtained from either A values [E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, 4, 761 (1965)] or E_s values [S. H. Unger and C. Hansch, *Prog. Phys. Org. Chem.*, 12, 91 (1976)].

+ 2_a transition states **11a**, **11b**, **12a**, and **12b**, we can see
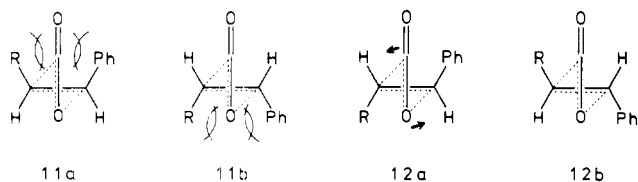
that the trans-derived **12a** can escape from the steric interactions by deforming the geometry slightly.[22] On the other hand, the transition states **11a** and **11b** derived from the cis isomer can have no such way to reduce the steric destabilization. Accordingly, the cis isomer reacted more slowly than the corresponding trans isomer. The increased steric bulk from methyl to *tert*-butyl naturally results in a rather sharp decrease of the reactivity in both cis and trans isomers.

In contrast to **4**, **5** exhibited somewhat higher reactivity than **1c** (**1c/5**, 1.0:6.9). The two phenyl groups at C-4 provide significant electronic stabilization of the transition state for **5**, but **5** was still less reactive than **8**.[23] The steric destabilization seems to counterbalance the electronic stabilization. 3,4-Diphenyl derivatives **7c** and **7t** deserve some comments, because they reacted more rapidly than predicted from the steric bulk of such a group; the points for **7c** and **7t** deviate above the regression lines in Figure 1. The deviation may be explained by an assumption that a small amount of stabilization can be provided by resonance interactions between the phenyl and the partially developed double bond in the transition state. It should also be noted that **6** exhibited somewhat high reactivity (**1c/4/6**, 1.0:0.29:3.8) although we can anticipate similar steric effects for **4** and **6**. This may be due to an efficient stabilization of the transition state by the two methyl groups in **6**.[24] The phenyl group at C-3 in the same compound will also contribute a little to the rate increase.

The transition state of the 2-oxetanone fragmentation is unique in nature. Partial breakages and formations of the bond may occur to a certain extent at all positions, but the charge development takes place unevenly, only at C-4 and oxygen.[3c] A similar case has been discussed by Egger[25] in the thermolysis of 3-ethoxycyclobutanone, and a quasi-zwitterion transition state is proposed. If we take into account the fact that the two neutral species, styrene and carbon dioxide, are produced in the fragmentation, a more even quadrupolar-type transition state seems to be more likely. The HOMO-LUMO interactions[26,27] may provide

an explanation for the uneven charge development, since an HOMO of styrene has a larger orbital coefficient at the β position than at the α,[26c] whereas the central atom of carbon dioxide has the largest coefficient in its LUMO.[28] A possibility that such an uneven charge development during the fragmentation may lead to the formation of a charge-transfer complex as an incipient product will perhaps be postulated.

In conclusion, it is demonstrated that, in a series of 4-phenyl-2-oxetanones, the least substituted **8** is the most reactive. A substitution of a hydrogen at C-3 by an alkyl group inevitably results in a reactivity decrease, which is most probably attributed to the steric destabilization of the concerted $2_s + 2_a$ transition state. The eclipsing effect will also be important in the cis isomers. The work was effects discussed in the present study may explain the high thermal stabilities of certain 2-oxetanones.[4-6]

Experimental Section

UV spectra were recorded on a Cary Model 17 spectrophotometer. IR spectra were taken on a Hitachi Model 215 grating spectrophotometer. NMR spectra were obtained with a JEOL PS-100 spectrometer; the chemical shifts are given in parts per million from tetramethylsilane. GC work was done on a Hitachi 063 gas chromatograph. High-pressure LC analysis was carried out with a Hitachi Model 635 liquid chromatograph. Microanalyses were done by the Microanalytical Laboratory, Faculty of Pharmaceutical Science, Hokkaido University. Melting points and boiling points are uncorrected.

3-Hydroxypropionic Acids. A modified procedure of that of Adam, Baeza, and Liu[2c] was employed for the preparation of various 3-hydroxypropionic acids. Separations of the geometrical isomers were accomplished by column chromatography (silica gel with a mixture of hexane, ether, and acetic acid in a 50:50:2 or 70:30:2 ratio as the eluent), and geometrically pure compounds were isolated in 15–30% yield. For example, the reaction of lithium 2-lithiopropionate with benzaldehyde gave a 1:1 mixture of *erythro*- and *threo*-3-hydroxy-2-methyl-3-phenylpropionic acid in 97% yield. After the chromatographic separation and recrystallization, the pure threo isomer, mp 96–98 °C (lit. mp 92–94,[29] 96.5–97.5 °C[30]), and the pure erythro isomer, mp 65–68 °C (lit.[29] mp 65–66 °C), were isolated in 21 and 17% yield, respectively. *threo*-3-Hydroxy-2-isopropyl-3-phenylpropionic acid exhibited a double melting point, mp 124–126 and 148–150 °C (lit.[29] mp 127–129 °C); the erythro isomer had a melting point of 157–158 °C (lit.[29] mp 153 °C). *threo*-2-*tert*-Butyl-3-hydroxy-3-phenylpropionic acid was contaminated by impurities other than erythro isomer which were difficult to remove, and hence purification of the sample was carried out as for **3t**. The crude material melted at 117–124 °C: NMR (acetone-d_6) δ 1.03 (s, 9 H), 2.64 (d, J = 5.0 Hz, 1 H), 5.02 (d, J = 5.0 Hz, 1 H), 7.3 (m, 5 H). The erythro isomer was purified with no trouble: mp 188–189 °C; NMR (acetone-d_6) δ 1.21 (s, 9 H), 2.65 (d, J = 10.3 Hz, 1 H), 4.96 (d, J = 10.3 Hz, 1 H), 7.3 (m, 5 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.07; H, 8.26. 3-Hydroxy-2,2-dimethyl-3-phenylpropionic acid melted at 134–136 °C (lit. mp 134.5–135.5,[2c] 134 °C[31]) and 3-hydroxy-3-methyl-2-phenylbutyric acid at 92–94 °C (lit. mp 91–93,[32] 91–92,[33] 93–94 °C[34]). *threo*-3-Hydroxy-2,3-diphenylpropionic acid, mp 143–144.5 °C (lit. mp 142–143,[35] 142–143.5 °C[36]), and its erythro isomer, mp 176–177.5

(21) In the reaction of *p*-toluenesulfonyl isocyanate with olefins, it has been noted that the cis olefin reacts several times faster than the trans isomer: F. Effenberger, G. Prossel, and P. Fischer, *Chem. Ber.*, 104, 2002 (1971). The results are discussed in terms of steric effects similar to those argued in the ketene-olefin cycloaddition, but we can explain them by assuming that the cis olefin is more highly strained and hence reacts faster than the trans isomer.

(22) The $2_s + 2_s + 2_a$ transition state will take a diagonal conformation (see ref 13 and 19). The same argument can be applied for such a transition state.

(23) The magnitude in bond stretchings at the transition state may differ from one compound to the next. Therefore, both the electronic and steric effects will influence the reactivity but not exactly to the same extent.

(24) The σ^+ value for methyl is known to be significantly large: H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80, 4979 (1958). Accordingly, the stabilization of the transition state provided by the two methyl groups in **6** may be larger than that given by a phenyl in **4**. For the phenyl case, see also H. C. Brown, Y. Okamoto, and T. Inukai, *J. Am. Chem. Soc.*, 80, 4964 (1958).

(25) K. W. Egger, *J. Am. Chem. Soc.*, 95, 1745 (1973).

(26) (a) K. Fukui, *Acc. Chem. Res.*, 4, 57 (1971); (b) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, 13, 751 (1974); (c) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Interscience, New York, 1976; (d) K. N. Houk in "Pericyclic Reactions", Vol. II, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, Chapter 4.

(27) For a consideration of ketene-olefin cycloadditions, see ref 14 and 19.

(28) C. P. Courtoy, *Ann. Soc. Sci. Bruxelles, Ser. 1*, 73, 5 (1959).

(29) J. Canceill, J. Gabard, and J. Jacques, *Bull. Soc. Chim. Fr.*, 2653 (1966).

(30) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, 76, 2291 (1954).

(31) R. Fitting and H. W. Jayme, *Justus Liebigs Ann. Chem.*, 216, 118 (1877).

(32) F. F. Blicke and H. Raffelson, *J. Am. Chem. Soc.*, 74, 1730 (1952).

(33) H. L. Cohen and G. F. Wright, *J. Org. Chem.*, 18, 432 (1953).

(34) A. W. Weston and R. W. DeNet, *J. Am. Chem. Soc.*, 73, 4221 (1951).

°C (lit. mp 176–177,[35] 177–178 °C[36]), were prepared in the same manner.

2-Oxetanones. Most of the 2-oxetanones were prepared from the corresponding 3-hydroxypropionic acid.[2c] Although 3-alkyl-4-phenyl-2-oxetanones have not been described in the literature, 4–7 are known: 4,[3c] mp 25–26.5 °C (lit.[2c] a liquid); 5, mp 100–101.5 °C (lit.[2c] mp 101–102 °C); 6,[3c] mp 53–54 °C (lit.[2d] no details given); 7c, mp 120–120.5 °C (lit.[2b] mp, 120–121 °C). 7t was too unstable to be purified by our methods. The reaction of *threo*-3-hydroxy-2,3-diphenylpropionic acid with 1.25 equiv of benzenesulfonyl chloride in pyridine[2c] resulted in the formation of a faintly yellow liquid, which showed characteristic IR bands at 1830, 1760, and 1605 cm⁻¹. The NMR spectrum of this liquid was closely similar to that reported by Chapman and Adams[2b] for 7t: NMR (CCl₄) δ 4.60 (d, J = 4.4 Hz, 1 H), 5.35 (d, J = 4.4 Hz, 1 H), 7.30 (br s, 5 H), 7.37 (br s, 5 H). When this crude oil was dissolved in chloroform or a pentane–ether mixture, a white solid deposited, and it was no longer soluble in the solvents. The solid showed no band at 1830 cm⁻¹ but a broad band at 1605 cm⁻¹ in the IR region. Florisil column chromatography also resulted in the formation of a white solid residue. Distillation under reduced pressure (<10⁻⁴ mm) gave stilbene as the distillate. After these experiments, we realized that the purest sample of 7t was indeed the crude oil obtained in the cyclization reaction. Accordingly, we carried out kinetic measurements and product analysis of 7t with a sample treated in the following manner. The crude product, after evaporation of the solvent under reduced pressure, was dripped down into a flask along a clean glass rod to remove the white solid and a trace amount of pyridine (by evaporation). The resultant viscous liquid was diluted with decane for use in the experiments. The amount of 7t dissolved in the solution was calculated from the weight of the crude oil and the increased weight of the glass rod. The UV analysis of the resultant solution indicated that stilbene was practically absent. Satisfactory results in both kinetics and product analysis were obtained in this way.

3-Alkyl-4-phenyl-2-oxetanones 1–3 gave the following data. 1t:[3c] mp 26–29 °C. 1c: bp 115–117 °C (1.5 mm); IR (thin film) 1830 cm⁻¹; NMR (CCl₄) δ 0.91 (d, J = 8.0 Hz, 3 H), 3.99 (p with further splittings, $J \approx 7.3$ Hz, 1 H), 5.56 (d, J = 6.7 Hz, 1 H), 7.36 (m, 5 H). Anal. Calcd for C₁₀H₁₀O₂: C, 74.05; H, 6.22. Found: C, 74.09; H, 6.25. 2t: mp 29.5–30.0 °C; IR (KBr) 1825 cm⁻¹; NMR (CCl₄) δ 1.08 (d, J = 6.5 Hz, 3 H), 1.13 (d, J = 6.5 Hz, 3 H), 1.92–2.48 (m, 1 H), 3.19 (dd, J = 8.7 and 4.0 Hz, 1 H), 5.14 (d, J = 4.0 Hz, 1 H), 7.32 (s, 5 H). Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.71; H, 7.44. 2c: mp 46.5–47.5 °C; IR (KBr) 1810, 1805 cm⁻¹; NMR (CCl₄) δ 0.53 (d, J = 6.5 Hz, 3 H), 1.05 (d, J = 6.5 Hz, 3 H), 1.47–2.00 (m, 1 H), 3.50 (dd, J = 10.8 and 6.5 Hz, 1 H), 5.48 (d, J = 6.5 Hz, 1 H), 7.33 (s, 5 H). Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.82; H, 7.42. 3t: mp 37.5–38.0 °C; IR (KBr) 1810 cm⁻¹; NMR (CCl₄) δ 1.12 (s, 9 H), 3.24 (d, J = 4.2 Hz, 1 H), 5.19 (d, J = 4.2 Hz, 1 H), 7.32 (br s, 5 H). Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.89. Found: C, 76.43; H, 8.05. 3c: mp 85.0–85.7 °C; IR (KBr) 1810 cm⁻¹; NMR (CCl₄) δ 0.84 (s, 9 H), 3.77 (d, J = 7 Hz, 1 H), 5.56 (d, J = 7 Hz, 1 H), 7.34 (br s, 5 H). Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.89. Found: C, 76.34; H, 7.96.

All attempts to prepare 8 had been fruitless.[8] The methods tried included (i) a cyclization of 3-hydroxy-3-phenylpropionic acid by the same method as above,[2c] (ii) the reaction of the benzenethiol ester of the same acid with Hg(OSO₂CH₃)₂,[37] and (iii) a cycloaddition of ketene with benzaldehyde in the presence of BF₃,[8] ZnCl₂, or sodium acetate.[5a] 9 was prepared from 3-bromo-3-(*p*-nitrophenyl)propionic acid [mp 169–171 °C (lit.[9] mp 170–172 °C)] by following the procedures described in the literature:[9] mp 90.0–91.5 °C (lit.[9] mp 91.9 °C).

Thermolysis Products. A solution of 2-oxetanone in decane [(3.4–3.9) × 10⁻⁴ mol/L, except for 9] was prepared, and an equimolar amount of TMEDA was added to it. After being

degassed,[38] the solution was sealed in a base-treated glass tube and heated at 170 °C for 10 half-lives, except for 3c, which was allowed to react only for 106 h (6 half-lives, 99% conversion). The resultant mixture was first examined by high-pressure LC [Hitachi no. 3040 column, hexane–ether (9:1) as the eluent, UV detector at 220 nm] for the extent of 2-oxetanone consumption, because most of the 2-oxetanones decomposed under the GC conditions. The analysis indicated the conversion as being quantitative in all cases. The thermolyzed solution was then analyzed by GC (PEG 20M, 20% on Celite 545) for the products. The amount of olefin produced was quantitative without exception.

All the olefins are known compounds, and hence they were characterized by comparison with authentic samples prepared either by the dehydration of the corresponding alcohol or by the Wittig reaction. The olefins thus confirmed by their production were *cis*- and *trans*-1-phenylpropenes,[39–42] *cis*- and *trans*-3-methyl-1-phenyl-1-butenes,[39] *cis*- and *trans*-3,3-dimethyl-1-phenyl-1-butenes,[39] 2-methyl-1-phenylpropene,[40,43] 2-methyl-1,1-diphenylpropene,[44] *cis*-stilbene,[45] *trans*-stilbene,[45–47] and *p*-nitrostyrene.[48] The last olefin [mp 26–27 °C (lit.[9,48] mp 29 °C)] had a tendency to polymerize in a concentrated solution, but the presently applied conditions for 9 (1.1 × 10⁻³ mol/L in the presence of TMEDA) allowed us to observe the quantitative formation of the styrene.

The reaction time and cis/trans ratio of the produced olefins were as follows: 1c, 5 h, 100/0; 1t, 35 min, 0.9/99.1; 2c, 15.7 h, 100/0; 2t, 1.3 h, 0/100; 3c, 106 h, 100/0; 3t, 2.3 h, 0/100. A small amount of cis olefin in the product 1t was due to the contamination of 1c (ca. 1% by high-pressure LC analysis) in the sample of 1t used for the product analysis. 7c and 7t produced a mixture of *cis*- and *trans*-stilbenes; see the text for the results. Control experiments indicated that *cis*-stilbene isomerized to the trans isomer to a minor extent (cis/trans, 99.1:0.9, after 2.5 h at 171 °C) in the absence of TMEDA, but no isomerization was observed in the presence of TMEDA. The thermolyses of 4, 5, and 6 were also strictly regiospecific to give the corresponding styrene derivative in quantitative yield.

Equilibration of Styrenes. An equilibrated mixture of styrenes was prepared by heating geometrically pure samples in decane in the presence of a small amount of iodine under an argon atmosphere.[49] At 171 °C, the cis/trans composition reached from both geometrical isomers was as follows: 1-phenylpropene, 8.3:91.7; 3-methyl-1-phenyl-1-butene, 2.8:97.2; 3,3-dimethyl-1-phenyl-1-butene, <0.1/>99.9 (the cis isomer being undetectable by GC); stilbene, 1.7:98.3.

Kinetic Measurements. The standard procedures have been described previously.[3c] The wavelengths used for the kinetic studies were 250 nm for 1t, 240 nm for 1c, 251 nm for 2t, 241 nm for 2c, 251 nm for 3t, 236 nm for 3c, 244 nm for 4 and 6, 243 nm for 5, 295 nm for 7t, 285 nm for 7c,[12] and 290 nm for 9. Because of the low solubility in decane, the kinetic measurements of 9 were carried out under dilute conditions (1.1 × 10⁻³ mol/L). The rate constants thus determined showed somewhat large deviations (the standard deviation being ca. 7%), but no drifting in k_1 was observed. In all other cases, the standard deviation was less than

(35) R. A. Auerbach and C. A. Kingsbury, *Tetrahedron*, 27, 2069, (1971).

(36) H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, 79, 1920 (1957).

(37) S. Masamune, Y. Hayase, W. K. Chan, and R. L. Sobczak, *J. Am. Chem. Soc.*, 98, 7874 (1976).

(38) Exclusion of oxygen was required because the produced olefin was oxidized under nondegassed conditions.

(39) K. Yasufuku, S. Hirose, S. Nozakura, and S. Murahashi, *Bull. Chem. Soc. Jpn.*, 40, 2139 (1967).

(40) H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, 18, 1759 (1965).

(41) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, 85, 3645 (1963).

(42) R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 75, 4094 (1953).

(43) C. E. Boord, A. L. Henne, K. W. Greenlee, W. L. Perilstein, and J. M. Derfer, *Ind. Eng. Chem.*, 41, 609 (1949); M. G. Voronkov, A. S. Broun, and G. B. Karpenko, *Zh. Obshch. Khim.*, 19, 1927, 1934 (1949).

(44) P. Sabatier and M. Murat, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 156, 1433 (1913).

(45) D. S. Blackman and P. H. Plesch, *J. Chem. Soc.*, 2188 (1952).

(46) C. F. Duin, *Recl. Trav. Chim. Pays-Bas*, 45, 345 (1926).

(47) A. Smakula and A. Wassermann, *Z. Phys. Chem., Abt. A*, 155, 353 (1931).

(48) M. Pestemer, T. Langer, and F. Manchen, *Monatsh. Chem.*, 68, 326 (1936).

(49) For the smooth equilibration of these styrene derivatives, exclusion of air was required.

3% (less than 2% in most cases). All results are summarized in Table I.

In the absence of TMEDA, **6** as well as **7c** gave somewhat larger rate constants than those obtained in the presence of TMEDA. Driftings in k_1 were also observed. For the evaluation of k_{7c}, it was assumed that the apparent k_1 was a sum of the two competing reactions, the fragmentation (k_{7c}) and the epimerization $k_{e,cis}$· [TMEDA]). See the text for the estimation procedures.

Registry No. **1c**, 73378-17-3; **1t**, 71155-82-3; **2c**, 73378-18-4; **2t**, 73378-19-5; **3c**, 73378-20-8; **3t**, 73378-21-9; **4**, 35947-70-7; **5**, 35947-66-1; **6**, 57015-11-9; **7c**, 16141-47-2; **7t**, 20432-17-1; **8**, 4287-98-3; **9**, 35202-08-5; *erythro*-3-hydroxy-2-methyl-3-phenylpropionic acid, 14366-86-0; *threo*-3-hydroxy-2-methyl-3-phenylpropionic acid, 14366-87-1; *threo*-3-hydroxy-2-isopropyl-3-phenylpropionic acid, 14664-78-9; *erythro*-3-hydroxy-2-isopropyl-3-phenylpropionic acid, 14929-06-7; *threo*-2-*tert*-butyl-3-hydroxy-3-phenylpropionic acid, 58113-93-2; *erythro*-2-*tert*-butyl-3-hydroxy-3-phenylpropionic acid, 58113-94-3; 3-hydroxy-2,2-dimethyl-3-phenylpropionic acid, 23985-59-3; 3-hydroxy-3-methyl-2-phenylbutyric acid, 6343-61-9; *threo*-3-hydroxy-2,3-diphenylpropionic acid, 4603-32-1; *erythro*-3-hydroxy-2,3-diphenylpropionic acid, 4603-33-2; 3-bromo-3-(*p*-nitrophenyl)-propionic acid, 57999-52-7; 2,2-dimethyl-3,3-diphenyl-3-hydroxypropionic acid, 27925-29-7.

Arylation and Alkylation of Olefins by Arylamines or Hydrazines via Carbon–Nitrogen Bond Cleavage in the Presence of Palladium(II) Salts

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Arylamines (ArNH₂) have been found to function as arylating agents by way of C–N bond cleavage to give aryl-substituted olefins when treated with palladium salts and acetic acid. The reactivity of various amines and olefins has been investigated. Hydrazines such as phenylhydrazine and methylhydrazine are also able to act as arylating and alkylating agents, respectively. The addition of *tert*-butyl nitrite greatly increases the yields.

Aromatic substitution of olefins by palladium salts is a very convenient method for preparing aromatic-substituted olefins.[1] In subsequent related studies, we tried to react styrene with phenyl azide in the hope of obtaining nitrogen-containing products such as aminostilbenes and triazolines. However, no significant amounts of such products were obtained; instead (*E*)-stilbene was obtained in 2% yield together with (*E,E*)-1,4-diphenylbutadiene (4%) and acetanilide (29%). This suggested to us that aniline was formed from the decomposition of phenyl azide and that the aniline formed reacted with styrene to give (*E*)-stilbene via the C–N bond cleavage. We have found that various primary arylamines such as aniline and toluidine and also some phenyl- or methylhydrazines undergo the C–N bond cleavage and that the resulting organic moiety can be transferred to olefins to give substituted olefins.

In this paper we describe the results of reactions of amines with olefins in the presence of palladium salts.[2]
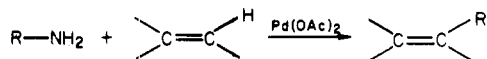
Results

A mixture of equimolar amounts of palladium acetate, aniline, and styrene in dioxane–acetic acid was heated at reflux for 8 h in air to give a 19% yield of (*E*)-stilbene together with (*E,E*)-1,4-diphenylbutadiene (11%), acet-

Table I. Reactions of Amines with Styrene

amine	product	yield, %[a] condn A[b]	condn B[c]
aniline	(*E*)-stilbene	19[d]	52
p-toluidine	(*E*)-*p*-methyl-stilbene	28[e]	74
p-anisidine	(*E*)-*p*-methoxy-stilbene	30[e]	62
p-nitroaniline	(*E*)-*p*-nitro-stilbene	17[e]	51
p-chloroaniline	(*E*)-*p*-chloro-stilbene	40[e]	
α-naphthylamine	(*E*)-α-styryl-naphthalene		48
β-naphthylamine	(*E*)-β-styryl-naphthalene		38
phenylhydrazine	(*E*)-stilbene	29	30
methylhydrazine	(*E*)-β-methyl-styrene	4	9
hydrazobenzene	(*E*)-stilbene	1	

[a] Based on the starting amine by VPC. [b] Reactions were carried out with amine, styrene, and Pd(OAc)₂ (1 mmol each), dioxane (11 mL), and acetic acid (2.2 mL) under reflux with stirring for 8 h. [c] Reactions were carried out with amine, styrene, Pd(OAc)₂, and *tert*-butyl nitrite (1 mmol each) and acetonitrile (10 mL) at 60 °C with stirring for 8 h. [d] Acetanilide (65%), 1,4-diphenyl-butadiene (11%), and biphenyl (trace) also were formed. [e] Considerable amounts of the corresponding acetanilide derivatives were formed via condensation of anilines and acetic acid.

anilide (65%), biphenyl (trace), (*E*)-*p*-aminostilbene (trace), ammonia, and metallic palladium. Of particular interest is that a considerable amount of (*E*)-stilbene is formed while essentially no aminostilbene, the usual aro-

(1) (a) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, **91**, 7166 (1969); (b) I. Moritani and Y. Fujiwara, *Synthesis*, **524** (1973); (c) Y. Fujiwara, R. Asano, I. Moritani, and S. Teranishi, *J. Org. Chem.*, **41**, 1681 (1976); (d) O. Maruyama, M. Yoshidomi, Y. Fujiwara, and H. Taniguchi, *Chem. Lett.*, 1229 (1979).

(2) A preliminary account of a portion of this study has been published: F. Akiyama, S. Teranishi, Y. Fujiwara, and H. Taniguchi, *J. Organomet. Chem.*, **140**, C7 (1977).