heptane (2:3) mixture gave **12**: mp 195–196.5 °C dec; 95 mg, 44%. The mother liquor of the recrystallization was concentrated, and additional **12** (13 mg) was collected. The remaining solution was evaporated, and the residue was recrystallized from a mixture of dichloromethane–cyclohexane to give **13**: mp 175–178 °C dec; 22 mg, 10%. In a repeated run, **12** and **13** were isolated in 72% and 9% yield, respectively.

Thermal Stability of 12 and 13. Purified **12** (22 mg) and diphenyl ether (an internal standard) were dissolved in either acetonitrile, 1,2-dichloroethane, or benzene, and the isomerization of **12** was examined by HPLC analysis (μ-Bondapack C18, methanol–water, 3:1, UV detector at 240 nm; ε at 240 nm being **12**, 1070; **13**, 6270; **6**, 13000). In acetonitrile at 80 °C, the amounts of **12:13:6** were 47:18:11 after 4.2 h and 31:29:9 after 8.3 h. When 1,1-dicyclopropylethylene (8 mg) was added to the starting mixture to trap the regenerated TCNE, the amounts of **12:13:6** were 25:1:58 after 4.2 h and 20:2:61 after 8.3 h. Apparently, the reverse process to regenerate **6** and TCNE took place in a reasonable rate. Even in 1,2-dichloroethane, the amounts of **12:13:6** after 8 h at 80 °C were 87:8:5. In benzene, however, the isomerization was practically not observed. At room temperature, the isomerization was found to be very slow in all three solvents examined; less than 2% after 15 h in acetonitrile. In contrast to **12**, **13** was stable in either acetonitrile or 1,2-dichloroethane at 80 °C.

The HPLC-determined ratio of **12:13** in the reaction of **6** with TCNE at room temperature in these three solvents was as follows: in acetonitrile 96:4, in 1,2-dichloroethane 86:14, and in benzene 60:40 (52:48 at 80 °C)[10] after 14–16 h.

Reaction of 7 with TCNE. A blue-violet solution obtained by mixing **7** (142 mg, 0.55 mmol) and TCNE (67 mg, 0.52 mmol) in 1,2-dichloroethane (13 mL) turned brown after 12 h at room temperature. Since HPLC analysis indicated that the consumption of **7** was 93%, the solution was concentrated. From the concentrated solution, **14** (73 mg, 37% yield) was separated as crystals and recrystallized from benzene. **14**: mp 241.5–242.5 °C dec; IR (KBr) 3090, 3070, 3020, 2940, 2860, 2250, 1660, 1450, 970, 950, 770, 740, 730 cm^{-1}; UV max (acetonitrile) 274 nm (log ε 4.05), 284 (3.99); ^1H NMR (100 MHz, acetone-d_6) δ 0.44–0.72 (m, 2 H), 0.72–1.00 (m, 2 H), 1.52–1.82 (m, 1 H), 2.73–3.27 (m, 2 H), 4.30–4.68 (m, 1 H), 5.62–6.16 (m, 2 H), 7.30–7.80 (m, 4 H), 7.80–8.22 (m, 4 H); mass spectrum (70 eV) *m/z* (rel intensity) 386 (M^+, 16), 258 (20), 191 (12), 178 (100), 93 (22). Anal. ($C_{26}H_{18}N_4$) C, H, N.

Reaction of 8 with TCNE. A blue solution obtained by mixing **8** (76 mg, 0.20 mmol) and TCNE (26 mg, 0.20 mmol) in dichloromethane (10 mL) turned slightly blue after 6 h. Since this color persisted for additional hours, 5 mg of TCNE was added to the solution, and the resultant mixture was kept standing for 50 h. The solvent was removed, and the residue was placed on the top of a florisil column (2 g). Elution of the column with dichloromethane gave a solid (97 mg), which was recrystallized from benzene and then from a 1:1 mixture of ethyl acetate and heptane to give **16** (69 mg, 68% yield): mp 322–323 °C dec; IR (KBr) 3100, 3080, 3020, 2250, 1635, 1480, 1450, 1430, 1030, 1020, 930, 745, 730 cm^{-1}; UV max (acetonitrile) 201 nm (log ε 4.51), 208 (4.51), 228^{sh} (4.33), 262 (4.24), 272 (4.24), 281^{sh} (4.14); ^1H NMR (100 MHz, $CDCl_3$) δ −1.02 to −0.85 (m, 1 H), −0.40 to 0.69 (m, 11 H), 0.79–1.25 (m, 7 H), 1.80–2.01 (m, 1 H), 4.03 (d, 1 H, *J* = 10.3 Hz), 5.06 (d, 1 H, *J* = 10.3 Hz), 7.28–7.57 (m, 4 H), 7.65–7.76 (m, 3 H), 8.04–8.17 (m, 1 H); mass spectrum (70 eV) *m/z* (rel intensity) 506 (M^+, 0.7), 278 (35), 134 (100). Anal. ($C_{35}H_{30}N_4$) C, H, N.

Acknowledgment. The present research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (No. 60470020) to which we are very grateful.

Radical Addition to the Carbonyl Carbon Promoted by Aqueous Titanium Trichloride: Stereoselective Synthesis of α,β-Dihydroxy Ketones

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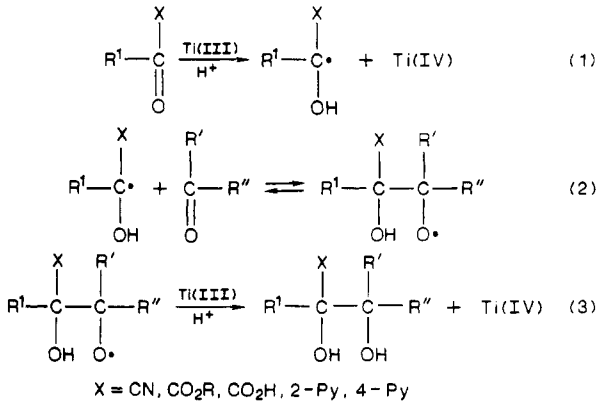
Ketyl radicals, formed by chemoselective Ti(III) reduction of α,β-dicarbonyl compounds, add to the carbonyl carbon of aldehydes under mild conditions to afford α,β-dihydroxy ketones in good to excellent yields. Simple diastereoselectivity strongly depends on the bulk of groups bonded to both the ketyl radical and the aldehydic function. The relative configuration of two of the keto diols was established by single-crystal X-ray diffractometry.

During our investigation of new synthetic reactions promoted by aqueous Ti(III) ion, we reported that carbon-centered radicals RĊ(X)OH, generated by reduction of the corresponding carbonyl compounds (eq 1), add to the carbonyl carbon of aldehydes and ketones (eq 2) to afford α,β-dihydroxy nitriles (X = CN),[1,2] α,β-dihydroxy esters or acids (X = CO_2R or CO_2H),[2,3] pyridyl diols (X = 2-Py or 4-Py),[4] and allylpinacols (eq 3).[5]

Radical addition to carbonyl carbon (eq 2) is not considered a useful reaction in σ carbon–carbon bond formation because the intermediate alkoxy radical undergoes fast β-bond cleavage.[6,7] Nevertheless, under our reaction conditions,[1-5] aldehydes and ketones can be used as intermolecular radical traps because rapid reduction of the intermediate alkoxy radicals by Ti(III) ion (eq 3) makes the addition step (eq 2) practically irreversible, leading to the formation of a new carbon–carbon bond in synthetically useful yields. Besides, the presence of metal ions, which restrict the number of possible transition states by



(1) Clerici, A.; Porta, O.; Riva, M. *Tetrahedron Lett.* **1981**, *22*, 1043.
(2) Clerici, A.; Porta, O. *J. Org. Chem.* **1982**, *47*, 2852.
(3) Clerici, A.; Porta, O.; Zago, P. *Tetrahedron* **1986**, *42*, 561.
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(5) Clerici, A.; Porta, O. *J. Org. Chem.* **1983**, *48*, 1690.
(6) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986; pp 14, 109.
(7) (a) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69. (b) Kochi, J. K. *Free Radicals*; Wiley Interscience: New York, 1973; Vol 2, p 683.

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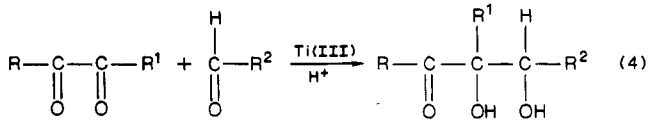
Table I. Ti(III)-Mediated Reduction of α,β-Dicarbonyl Compounds[a]

RCOCOR[1] (1)	R	R[1]	products and yields[b] (%)	
1a	C_6H_5	C_6H_5	$C_6H_5COCHOHC_6H_5$ (quant)	
1b	C_6H_5	H	$(C_6H_5COCHOH-)_2$ (60)	$C_6H_5COCH_2OH$ (30)
1c	C_6H_5	CH_3	$C_6H_5COCHOHCH_3$ (30)	$C_6H_5CHOHCOCH_3$ (63)
			$C_6H_5COCHOHCH_3$ (8)[c]	$C_6H_5CHOHCOCH_3$ (42)[c]

[a] Molar ratio 1:$TiCl_3$ = 1:2. [b] ^1H NMR yields are based on 1; the difference from 100% is unreacted 1. [c] Molar ratio 1c:$TiCl_3$ = 1:1.

complexation to the reactants,[8] enhances the diastereoselectivity of these reactions.

We now report a facile synthesis of α,β-dihydroxy ketones **3** starting from α,β-dicarbonyl compounds **1**, aldehydes **2**, and aqueous $TiCl_3$ (eq 4). High yields and good stereochemical control were achieved.



(4)

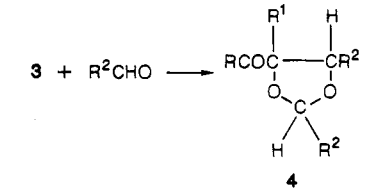
1a, R = R[1] = C_6H_5; **1b**, R = C_6H_5, R[1] = H; **1c**, R = CH_3, R[1] = C_6H_5

Results and Discussion

Reduction of α,β-Dicarbonyl Compounds 1. To test the reactivity of **1** toward Ti(III) ion, compounds **1a–c** (10 mmol) were allowed to react with 20 mmol of a 15% aqueous $TiCl_3$ solution in acetic acid, acetone, or methanol (Table I). Benzil (**1a**) and 1-phenyl-1,2-propanedione (**1c**) were reduced to the corresponding α-hydroxy ketones, probably through disproportionation of the intermediate ketyl radicals;[8,9] phenylglyoxal (**1b**) afforded the dimer 1,4-diphenyl-2,3-dihydroxy-1,4-butanedione (60%) and α-hydroxyacetophenone (30%). From the data in Table I it emerges that these reductions are chemoselective: reduction of **1b** occurs solely at the aldehydic function, while in the reduction of **1c** the benzoyl group is more reactive than the acetyl group. Therefore, the ease of reduction by this method with compounds bearing multiple carbonyl groups should decrease in the order aldehydes > aromatic ketones > aliphatic ketones.

Reduction of α,β-Dicarbonyl Compounds in the Presence of an Aldehyde. When the reduction of **1a–c** was performed under the same conditions with an aldehyde **2** (10 mmol) in the reaction mixture, formation of the products of Table I was suppressed,[10] and α,β-dihydroxy ketones **3** were formed in good to excellent yields (Table II). Dihydroxy ketones **3** are generally stable and crystalline and were obtained as diastereomeric mixtures with a syn/anti ratio that depended on the steric bulk of both R^1 and R^2. In many experiments the major isomer crystallized directly from the reaction mixture or was easily separated by chromatography and crystallization.

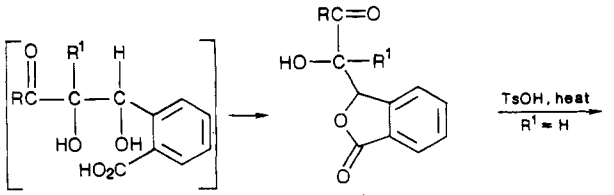
The ratio of the reagents and the reaction temperature were critical to ensure a high yield of **3**: a molar ratio of aldehyde to dicarbonyl compound greater than 1 and/or a reaction temperature above 0 °C favor the formation of cyclic acetals **4** (eq 5).[11] With aromatic aldehydes bearing an electron-donating substituent (2-CH_3 or 2-CH_3O), formation of **4** occurs even at 0 °C.[12]



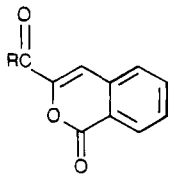
(5)

4

The functional groups cyano, hydroxy, methoxy, carboxy, and chloromethyl were tolerated under these conditions and did not interfere with carbonyl addition. However, in the reactions of **1a–c** with 2-carboxybenzaldehyde (entries j, t, and z), compounds **3** were lactonized to phthalidyl derivatives **5** under the reaction conditions, indicating a preexisting interaction between the metal ion and both the hydroxy and carboxy groups.[3,13] When **5t** was refluxed with *p*-toluenesulfonic acid in benzene, 3-benzoylisocoumarin (**6t**) was obtained in quantitative yield.

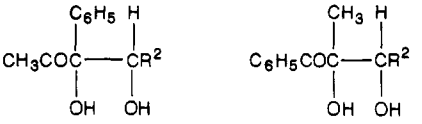


5j: R = R[1] = C_6H_5
5t: R = C_6H_5; R[1] = H
5z: R = CH_3; R[1] = C_6H_5
5z′: R = C_6H_5; R[1] = CH_3



6t: R = C_6H_5

From Table I it appears that the reduction of **1c** occurs at both the benzoyl and acetyl groups. One might expect that in the presence of a trapping aldehyde the two isomeric ketyl radicals would afford two different keto diols **3**, and these were observed in the reaction of **1c** with acetaldehyde: both **3v** and **3v′** were formed, each as a mixture of two diastereomers. However, when **1c** was reduced in the presence of benzaldehyde, only **3w** with relative syn configuration was obtained.



3v: $R^2 = CH_3$
3w: $R^2 = C_6H_5$

3v′: $R^2 = CH_3$

Furthermore, in a competition experiment, **1c** (10 mmol) reacted with a 1:1 mixture of acetaldehyde and benzaldehyde (10 mmol) in the presence of a 15% aqueous $TiCl_3$ solution to afford only the benzaldehyde adduct **3w**

(8) Clerici, A.; Porta, O. *J. Org. Chem.* **1987**, *52*, 5099.
(9) Data from the literature suggest that the ketyl radical from benzil disproportionates rather than dimerize due to steric factors: Beckett, A.; Osborne, A. D.; Porter, G. *Trans Faraday Soc.* **1964**, *60*, 873. Other authors suggest that the dimer is very unstable both thermally and in solution: Bumbury, D. L.; Wang, C. T. *Can. J. Chem.* **1968**, *46*, 1473.
(10) Radical addition to R^2CHO is faster and/or less reversible than its dimerization or disproportionation (see ref 1–5).
(11) Clerici, A.; Porta, O. *Synth. Commun.* **1988**, *18*, 2281.
(12) According to the mechanism proposed for the formation of **4** (see ref 10) an electron donor substituent, increasing the nucleophilicity of the aldehydic carbonyl oxygen, favors the formation of the Lewis acid complexed carbonyl substrate and, hence, the formation of **4**.
(13) (a) Reetz, M. T.; Steinbach, R.; Westermann, J.; Urz, R.; Wenderoth, B.; Peter, R. *Angew. Chem. Suppl.* **1982**, 257. (b) Seebach, D.; Weidmann, B.; Widler, L. *Modern Synthetic Methods*; Scheffold, Ed.; Wiley Interscience: New York, 1983; Vol 3.

Table II. Isolated Product Yields in the Ti(III)-Mediated Reaction

$C_6H_5COCOR^1$ (1a–c) + R^2CHO (2) → $RCOC(R^1)OHCH(R^2)OH$ (3)

entry	R^1	R^2	3, %	isomer ratio[a] syn:anti	other products (%)
a	C_6H_5	H	100	–	–
b	C_6H_5	CH_3	97	60:40	$C_6H_5COCHOHC_6H_5$ (tr)
c	C_6H_5	$ClCH_2$	86	63:37	$C_6H_5COCHOHC_6H_5$ (15)
d	C_6H_5	C_2H_5	90	63:37	$C_6H_5COCHOHC_6H_5$ (4)
e	C_6H_5	i-C_3H_7	57	82:18	$C_6H_5COCHOHC_6H_5$ (40)
f	C_6H_5	$C_6H_5CH_2$	87	80:20	$C_6H_5COCHOHC_6H_5$ (10)
g	C_6H_5	$C_6H_5(CH_2)_2$	84	>99:1	$C_6H_5COCHOHC_6H_5$ (13)
h	C_6H_5	C_6H_5	100	>99:1	–
i	C_6H_5	p-NCC_6H_4	98	>99:1	–
j	C_6H_5	o-$HO_2CC_6H_4$	90[b]	>99:1	–
k	H	CH_3	68 (73)[c]	50:50	$C_6H_5COCH_2OH$ (16), $(C_6H_5COCHOH)_2$ (11)
l	H	i-C_3H_7	30 (35)	40:60	$C_6H_5COCH_2OH$ (32), $(C_6H_5COCHOH)_2$ (16)
m	H	$C_6H_5CH_2$	69 (74)	50:50	$C_6H_5COCH_2OH$ (19), $(C_6H_5COCHOH)_2$ (7)
n	H	$C_6H_5(CH_2)_2$	58 (65)	29:71	$C_6H_5COCH_2OH$ (22), $(C_6H_5COCHOH)_2$ (13)
o	H	C_6H_5	80 (90)	50:50	$C_6H_5COCH_2OH$ (7), $(C_6H_5COCHOH)_2$ (3)
p	H	p-NCC_6H_4	80 (90)	50:50	$C_6H_5COCH_2OH$ (7), $(C_6H_5COCHOH)_2$ (3)
q	H	o-$CH_3C_6H_4$	70 (86)	32:68	$C_6H_5COCH_2OH$ (10), $(C_6H_5COCHOH)_2$ (4)
r	H	o-$CH_3OC_6H_4$	86 (96)	28:72	$C_6H_5COCH_2OH$ (tr), $(C_6H_5COCHOH)_2$ (tr)
s	H	o-HOC_6H_4	73 (80)	1:99	$C_6H_5COCH_2OH$ (12), $(C_6H_5COCHOH)_2$ (8)
t	H	o-$HO_2CC_6H_4$	71[b] (75)	1:99	$C_6H_5COCH_2OH$ (15), $(C_6H_5COCHOH)_2$ (10)
u	H	2-furyl	69 (76)	38:62	$C_6H_5COCH_2OH$ (16), $(C_6H_5COCHOH)_2$ (8)
v	CH_3	CH_3	**3v** (53) **3v′** 64 (16)	60:40 60:40	$C_6H_5COCHOHCH_3$ (tr), $C_6H_5CHOHCOCH_3$ (26)
w	CH_3	C_6H_5	**3w** 93 (98)	>99:1	–
z	CH_3	o-$HO_2CC_6H_4$	**5z** 46 (50) **5z′** 27 (33)	>99:1 60:40	$C_6H_5COCHOHCH_3$ (tr), $C_6H_5CHOHCOCH_3$ (17)

[a] Isomer ratios were determined by ^1H NMR analysis of the crude reaction product. [b] Isolated as the lactone. [c] Numbers in parentheses are yields determined by ^1H NMR analysis of the crude product.

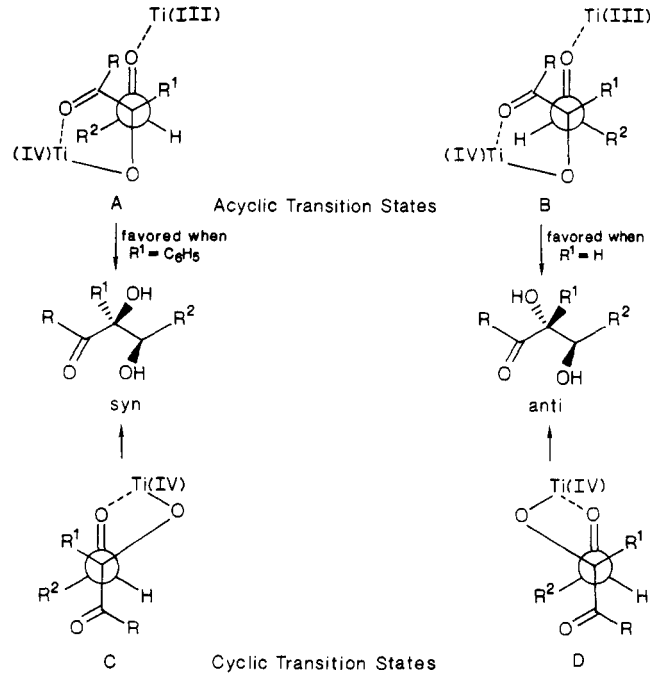
in 90% yield. The higher reactivity of benzaldehyde with respect to acetaldehyde and the higher reduction rate[14] of the benzoyl group with respect to the acetyl group in **1c** would explain the selectivity observed for entry w.

As shown in Table II (entries a–g and k–n), yields of **3** decrease with increase in the steric bulk of R^2 in a series of aliphatic aldehydes, to the point that none of **1a–c** reacts with 2,2-dimethylpropionaldehyde (R^2 = t-C_4H_9). Yields of **3** are high with aromatic aldehydes and, although the phenyl group is considered larger than most alkyl groups, benzaldehyde is by far more reactive than acetaldehyde. It is worth noting that radicals from **1a** and **1b** selectively add to benzaldehyde in the presence of acetaldehyde, affording adducts **3h** and **3o**, respectively.

Thus the present results indicate that the intermediate radicals from the dicarbonyl substrate are highly sensitive to electronic effects, while steric factors intervene only when electronic differences are negligible.

Finally, unlike the radicals of eq 1–3,[1-5] which add in to both acetaldehyde and acetone almost quantitatively,[15] radicals derived from **1a–c** do not react with ketones (acetone may be conveniently used as a cosolvent in these reactions). We believe that the different reactivity of the two radical types is to be ascribed to their intrinsic stabilization.[16] Radicals from α,β-dicarbonyl compounds **1a–c** are more stabilized than radicals of eq 1–3, and a greater stabilization is associated with both lower reactivity and higher selectivity of the species involved.

Scheme I



Stereochemistry and Configurational Assignments. The reaction of benzil with aldehydes becomes more stereoselective with increasing bulk of R^2 (Table II), to the point that only a single stereoisomer is detectable when R^2 is phenylethyl, phenyl, or aryl (entries g–j). A similar trend is observed when the radical involved in the addition to aldehydes is $C_6H_5\dot{C}OHCOCH_3$ (cf. entries v, w, z with entries b, h, j, respectively).

The relative stereochemistries of the diastereomers formed in two representative examples (entries j and w)

(14) The half-wave potentials indicate the comparatively greater influence of the phenyl group as opposed to the methyl group on the ease of reduction of α,β-dicarbonyl compounds. Progressively more negative potentials are demonstrated in the series: benzil (–0.53 V), acetylbenzoyl (–0.60 V), and diacetyl (–0.74 V), $E_{1/2}$ (V) vs Hg pool. Rogers, W.; Kipnes, S. M. *Anal. Chem.* **1955**, *27*, 1916.

(15) However, competitive experiments have shown that, with the radicals of eq 1–3, acetaldehyde is by far more reactive than acetone. Clerici, A.; Porta, O., unpublished results.

(16) While radicals of eq 1–3 possess only thermodynamic stabilization (Kort, H. G.; Sustmann, R.; Merenyi, R.; Viehe, H. G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 67) radicals formed by reduction of **1a–c**, owing to steric factors, also have kinetic stabilization (Marujama, K.; Katagiri, T. *J. Am. Chem. Soc.* **1986**, *108*, 6263.

were determined by single-crystal X-ray diffractometry, and both **5j**[17] and **3w**[18] were found to have simple syn diastereoselectivity[19] (Masamune nomenclature[20]). By analogy with **5j** and **3w**, assuming an analogous topology in the transition state, the prevailing or single diastereomer in compounds **3b–i**, **3v**, and **5z** should have syn relative configuration. The sense of diastereoselectivity found is in accord with an acyclic transition state A (Scheme I) in which the phenyl group ($R^1 = C_6H_5$) attached to the incoming ketyl radical avoids steric interaction with the R^2 group bound to the aldehydic function.

Our experiments show that the syn/anti ratio increases with increasing bulk of R^2. Accordingly, transition state B, which leads to anti configuration, is progressively more destabilized with respect to A as R^2 is made bulkier, because of the C_6H_5–R^2 interaction. It follows that the more demanding steric interaction involves C_6H_5 and R^2, rather than R^2 and the RCO group held in a rigid position by intramolecular complexation[21] with Ti(III) ion.[22] Presumably, preexisting Ti chelation with the attacking radical does not permit a cyclic transition state with intermolecular Ti bridging between the reactants. If the determining factor for the stereochemistry was the Ti-bridged conformer C rather than steric control (conformer A), the syn/anti ratio should decrease with increasing bulk of R^2[21] because of the importance of the C_6H_5–R^2 interaction in C.

Replacing the phenyl group with a hydrogen atom at the radical center ($R^1 = H$) makes the reaction stereorandom in some cases (entries k, m, o, and p) or reverses simple diastereoselectivity (entries l, n, and q–u); the major isomer **3n** is reported to have relative anti configuration.[23,24] Yet an acyclic transition state holds since the more demanding steric interaction would now involve R^2 and the five-membered Ti-chelated ring[22] of the incoming radical, destabilizing transition state A with respect to B. When two sites of potential Ti complexation are available in the aldehyde (entries s and t),[25] the "effective bulk" of R^2 makes the reaction completely diastereoselective.

Experimental Section

General Methods. All starting materials were commercially available research grade chemicals and used as received. The $TiCl_3$ solution (15% w/v, C. Erba) was standardized against 0.1 N Ce(IV) solution. ^1H NMR spectra were recorded on a 90-MHz Varian Model EM-390 and a 250-MHz Brucker Model AC-250 instrument with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a Varian Model XL 100 spectrometer. IR spectra were recorded on a Perkin-Elmer Model E 177 instrument. Mass spectra were determined on a Hitachi-Perkin-Elmer Model RMU 6D spectrometer at 70 eV. Melting points were taken on a Köfler apparatus (uncorrected). All new compounds gave satisfactory elemental analyses. Column and thin-layer chromatography were carried out by using Merck silica gel 60 (0.06–0.24 mm) and Merck kieselgel GF-254 (2 mm) plates, respectively.

General Procedure. To a well stirred solution of the substrate (**1a–c**, 10 mmol) and aldehyde **2** (10 mmol) under N_2 in acetone (25 mL) at 0 °C was added a 15% aqueous $TiCl_3$ solution (20 mmol, 20 mL) at once. The reaction mixture was allowed to stir at 0 °C for 1 h until its blue color was nearly dissipated. The crude mixture was then extracted with ethyl acetate (3 × 100 mL), and the combined extracts were washed with water, dried over anhydrous Na_2SO_4, and reduced in vacuo to leave in most examples a solid which was recrystallized or chromatographed on a silica gel column (50 × 2.5 cm) with the appropriate eluant. Reduction of **1a–c** (Table I) was performed under the above experimental conditions, omitting the aldehyde **2**. Yields in parentheses and isomer ratios of **3** in Tables I and II were determined by ^1H NMR spectroscopy on an aliquot of the crude reaction mixture. Data not in parentheses are isolated yields based on the starting **1a–c**.

Spectroscopic Data. All compounds of Tables I and II were isolated, and their structural assignments were deduced from the following data.

Benzoin. In the reduction of **1a**, benzoin precipitated directly from the reaction mixture in quantitative yield and was identified by comparison with an authentic sample.

1,4-Diphenyl-2,3-dihydroxybutane-1,4-dione was obtained as a diastereomeric mixture meso/*dl*, 1:1) in the reduction of **1b**. The two isomers were separated by fractional recrystallization from ethanol; *dl* isomer (prisms): mp 120–1 °C (lit.[26] mp 119 °C); ^1H NMR ($CDCl_3$) δ 4.0 (2 H, 2 OH, d, J = 7.3 Hz, D_2O exch), 5.35 (2 H, 2 CH, d, J = 7.3 Hz, s after D_2O exch), 7.3–8.2 (10 H, Ph H, m). Meso isomer (needles): mp 127–9 °C (lit.[26] mp 128 °C); ^1H NMR ($CDCl_3$) δ 3.9 (2 H, 2 OH, s, D_2O exch), 5.39 (2 H, 2 CH, s), 7.3–8.2 (10 H, Ph H, m).

α-Hydroxyacetophenone was obtained in 30% yield in the reduction of **1c** and identified by comparison with an authentic sample, mp 85 °C (lit.[27] mp 86–87 °C).

1-Hydroxy-1-phenylpropan-2-one was obtained as major product (63% yield) in the reduction of **1c** (liquid, bp_{12} 124–5 °C):[28] ^1H NMR ($CDCl_3$) δ 2.05 (3 H, CH_3, s), 4.5 (1 H, OH, s, D_2O exch), 5.05 (1 H, CH, s), 7.2–7.6 (5 H, Ph H, m).

2-Hydroxy-1-phenylpropan-1-one was obtained as minor product (30% yield) in the reduction of **1c** (liquid, bp_{11} 120 °C):[29] ^1H NMR ($CDCl_3$) δ 1.4 (3 H, CH_3, d), 4.4 (1 H, OH, s, D_2O exch), 5.15 (1 H, CH, q), 7.3 (3 H, Ph H, m), 8 (2 H, Ph H, m).

2,3-Dihydroxy-1,2-diphenylpropan-1-one (3a). After recrystallization of the crude reaction mixture from hexane/ethyl acetate (1:1) at 0 °C, 2.4 g (99% yield) of **3a** was obtained: mp 86 °C (lit.[30] mp 85–6 °C); ^1H NMR ($CDCl_3$) δ 3.1 (1 H, OH, s, D_2O exch), 3.58 (1 H, CH, d, J = 12 Hz), 4.48 (1 H, CH, d, J = 12 Hz), 4.7 (1 H, OH, s, D_2O exch), 7.1–7.6 (8 H, Ph H, m), 7.9 (2 H, Ph H, m); IR (Nujol) ν_{max} 3500, 3340 (OH), 1670 (CO) cm^{-1}; MS m/e 242 ($M^{\cdot+}$), 241, 137 (M – PhCO, base peak), 119, 105, 77.

2,3-Dihydroxy-1,2-diphenylbutan-1-one (3b). See ref 10.

4-Chloro-2,3-dihydroxy-1,2-diphenylbutan-1-one (3c). The major isomer precipitated directly from the reaction mixture; the solid was filtered off (1.6 g, 55%) and recrystallized from ethyl acetate/chloroform (8:2): mp 163–5 °C (needles); ^1H NMR ($CDCl_3$ + DMSO) δ 3.5 (1 H, CHCl, dd, J = 12, 10 Hz), 3.85 (1 H, CHCl, dd, J = 12, 2.5 Hz), 4.3 (2 H, 2 OH, D_2O exch), 4.57 (1 H, *CH*OH, dd, J = 10, 2.5 Hz), 7.2–7.6 (8 H, Ph H, m), 8 (2 H, Ph H, m); IR (Nujol) ν_{max} 3440, 3400 (OH), 1655 (CO) cm^{-1}; MS m/e 211 ($PhCOCOHPh^+$), 187–185 (M – PhCO), 169–167 (M – PhCO – H_2O), 105 (base peak), 77, 51. The minor isomer (0.9 g, 31%) was extracted from the mother liquor of the above filtration with ethyl acetate (thick oil): ^1H NMR ($CDCl_3$) δ 3.16 (1 H, CHCl, dd, J = 12, 3 Hz), 3.5 (1 H, CHCl, dd, J = 12, 10 Hz), 4.3 (2 H, 2 OH, s, D_2O exch), 4.9 (1 H, *CH*OH, dd, J = 10, 3 Hz), 7.2–7.8 (8 H, Ph H, m), 7.9 (2 H, Ph H, m).

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(24) By analogy with the products of entry n, the anti relative configuration was assigned to the prevailing diastereomer in compounds **3k–u** (Table II).
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2,3-Dihydroxy-1,2-diphenylpentan-1-one (3d). See ref 10.

2,3-Dihydroxy-1,2,4-triphenylbutan-1-one (3f). The two isomers precipitated from the reaction mixture (2.9 g, 87%). ^{1}H NMR analysis of the crude solid revealed the presence of two isomers in the ratio 80:20. Major isomer: ^{1}H NMR ($CDCl_3$) δ 2.3 (1 H, CHPh, dd, J = 14.5, 2 Hz), 2.6 (1 H, CHPh, dd, J = 14.5, 11 Hz), 4.35 (2 H, 2 OH, s, D_2O exch), 4.85 (1 H, C*H*OH, dd, J = 11, 2 Hz), 7–7.5 (13 H, Ph H, m), 7.9 (2 H, Ph H, m). IR (Nujol) ν_{max} 3480 (OH), 1670 (CO) cm^{-1}. Minor isomer: ^{1}H NMR ($CDCl_3$) δ 2.73 (1 H, CHPh, dd, J = 14, 10 Hz), 2.83 (1 H, CHPh, dd, J = 14, 3 Hz), 4.3 (2 H, 2 OH, s, D_2O exch), 4.65 (1 H, C*H*OH, dd, J = 10, 3 Hz), 7–7.5 (13 H, Ph H, m), 7.9 (2 H, Ph H, m). The major isomer crystallized out by dissolving the crude solid in ether/hexane (1:1), mp 133–6 °C, upon recrystallization from ethyl acetate.

2,3-Dihydroxy-1,2-diphenyl-4-methylpentan-1-one (3e). After workup, the crude reaction mixture was chromatographed on a silica gel column. Elution with hexane/ethyl acetate (4:1) afforded in the order: **3e** (major isomer, 1.35 g, 47%), **3e** (minor isomer, 0.3 g, 10%), benzoin (0.8 g, 40%). The major isomer **3e** recrystallized from petroleum ether/ether (4:1): mp 142–3 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (3 H, CH_3, d, J = 10 Hz), 0.95 (3 H, CH_3, d, J = 10 Hz), 1.3 (1 H, CH, m), 2.5 (1 H, OH, d, J = 6 Hz, D_2O exch), 4.1 (1 H, OH, s, D_2O exch), 4.65 (1 H, CH, dd, J = 6, 2.4 Hz, after D_2O exch d, J = 2.4 Hz), 7.2–7.6 (8 H, Ph H, m), 7.9 (2 H, Ph H, m); IR (Nujol) ν_{max} 3500, 3400 (OH), 1670 (CO) cm^{-1}. The minor isomer **3e** was slightly contaminated with benzoin: mp 110–7 °C (from petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.9 (3 H, CH_3, d, J = 9 Hz), 0.9 (3 H, CH_3, d, J = 5 Hz), 1.75 (1 H, CH, m), 2.5 (1 H, OH, s, D_2O exch), 4.2 (1 H, OH, s, D_2O exch), 4.5 (1 H, CH, d, J = 2.4 Hz), 7.2–7.6 (8 H, Ph H, m), 8 (2 H, Ph H, m).

2,3-Dihydroxy-1,2,5-triphenylpentan-1-one (3g). The only isomer formed precipitated directly from the reaction mixture. After filtration 3 g (84%) of pure **3g** was recovered. The solid recrystallized from ethyl acetate and melted at 158–61 °C: ^{1}H NMR ($CDCl_3$) δ 1.35 (1 H, CH_2, m), 1.8 (1 H, CH_2, m), 2.5 (1 H, CHPh, m), 2.8 (1 H, CHPh, m), 2.9 (1 H, OH, s broad, D_2O exch), 4.18 (1 H, OH, s, D_2O exch), 4.62 (1 H, CH, dd, J = 3, 10 Hz), 7–7.5 (13 H, Ph H, m), 8 (2 H, Ph H, m); IR (Nujol) ν_{max} 3520, 3370 (OH), 1650 (CO) cm^{-1}; MS m/e 241 (M – PhCO), 223 (M – PhCO– H_2O), 212, 134, 107, 105 (base peak), 91, 79, 77, 51.

2,3-Dihydroxy-1,2,3-triphenylpropan-1-one (3h). The only isomer formed precipitated directly from the reaction mixture. After filtration 3.15 g (99%) of **3h** was recovered as fine needles: mp 120–2 °C dec; ^{1}H NMR (DMSO) δ 5.6 (1 H, CH, d, J = 4.5 Hz, after D_2O exch s), 5.8 (1 H, OH, d, J = 4.5 Hz, D_2O exch), 6.3 (1 H, OH, s, D_2O exch), 7–7.5 (13 H, Ph H, m), 7.9 (2 H, Ph H, m); IR (Nujol) ν_{max} 3440, 3260 (OH), 1670 (CO) cm^{-1}.

2,3-Dihydroxy-1,2-diphenyl-3-(4-cyanophenyl)propan-1-one (3i). The only isomer formed precipitated directly from the reaction mixture. After filtration 3.4 g (98%) of pure **3i** was recovered as white powder: mp 127–8 °C dec; ^{1}H NMR (DMSO) δ 5.65 (1 H, CH, d, J = 4.5 Hz, s after D_2O exch), 6.05 (1 H, OH, d, J = 4.5 Hz, D_2O exch), 6.6 (1 H, OH, s, D_2O exch), 7.0–8.0 (14 H, Ph H, m); IR (Nujol) ν_{max} 3450, 3260 (OH), 2220 (CN), 1665 (CO) cm^{-1}; MS m/e 211 (PhCOCH(OH)Ph$^+$), 131, 130, 107, 105, 102, 77, 51.

2-Hydroxy-2-phenyl-2-phthalidylacetophenone (5j). The only isomer formed precipitated directly from the reaction mixture. After filtration 3.1 g (90%) of pure **5j** was recovered and recrystallized from methanol, mp 210–2 °C; **5j** was shown to have syn relative configuration by single crystal X-ray diffractometry: ^{1}H NMR ($CDCl_3$) δ 5.85 (1 H, Ph H, d),[31] 6.6 (1 H, CH, s), 7.0 (1 H, OH, s, D_2O exch), 7.2–7.6 (8 H, Ph H, m), 7.6–7.9 (3 H, Ph H, m), 8.1–8.2 (2 H, Ph H, m); IR (Nujol) ν_{max} 3350 (OH), 1760 (CO, lactone), 1680 (CO) cm^{-1}; MS m/e 344 (M$^{\cdot+}$), 239 (M – PhCO), 222, 194, 134, 133, 105 (base peak), 77.

2,3-Dihydroxy-1-phenylbutan-1-one (3k). After usual workup, 1.7 g of a residue was obtained as a thick oil. ^{1}H NMR analysis of the crude mixture revealed the presence of two isomers **3k** in 1:1 ratio. Upon purification on a silica gel column with hexane/ethyl acetate (4:1) as eluant, the isomer eluted first (0.6 g, 33%) melted at 79–80 °C (recrystallized from ether): ^{1}H NMR ($CDCl_3$) δ 1.35 (3 H, CH_3, d, J = 6 Hz), 2.5–3.5 (2 H, 2 OH, s broad, D_2O exch), 4.12 (1 H, CH, qd, J = 6, 2.4 Hz), 4.9 (1 H, CH, d, J = 2.4 Hz), 7.5 (3 H, Ph H, m), 7.9 (2 H, Ph H, m); IR (Nujol) ν_{max} 3350 (OH), 1690 (CO) cm^{-1}. MS m/e 180 (M$^{\cdot+}$), 162 (M – H_2O), 136 (M – CH_3CO), 123, 105 (base peak), 77, 58, 51. The isomer eluted second (0.65 g, 35%) was a thick oil: ^{1}H NMR ($CDCl_3$) δ 0.95 (3 H, CH_3, d, J = 6 Hz), 3.5 (2 H, 2 OH, s broad, D_2O exch), 4.2 (1 H, CH, qd, J = 6, 3.4 Hz), 5.25 (1 H, CH, d, J = 3.4 Hz), 7.5 (3 H, Ph H, m), 8 (2 H, Ph H, m); IR (film) ν_{max} 3360 (OH), 1690 (CO) cm^{-1}.

2,3-Dihydroxy-1-phenyl-4-methylpentan-1-one (3l). After workup, elution of the crude mixture (1.7 g) on a silica gel column with hexane/ethyl acetate (4:1) afforded a mixture of two isomers **3l** (0.62 g, 30%) in the ratio 60:40. Separation of the isomeric mixture was not achieved: ^{1}H NMR ($CDCl_3$) (mixture of two isomers) δ 0.8–1.2 (6 H, 2 CH_3, 4 d), 1.8–2.1 (1 H, CH, m), 3.5–3.7 (1 H, CH, m), 3.5 (1 H, 1 OH, s broad, D_2O exch), 4.0 (1 H, 1 OH, s broad, D_2O exch), 5.2 (1 H, CH, m), 7.5 (3 H, Ph H, m), 8 (2 H, Ph H, m); IR (Nujol) ν_{max} 3400 (OH), 1680 (CO) cm^{-1}.

2,3-Dihydroxy-1,4-diphenylbutan-1-one (3m). After usual workup, the crude mixture (2.56 g) was eluted from a silica gel column with hexane/ethyl acetate (4:1). The phase that moved first corresponded to the isomer which, upon recrystallization from hexane/ether (7:3), melted at 102–4 °C (0.9 g, 35%): ^{1}H NMR ($CDCl_3$) δ 2.2 (1 H, OH, s broad, D_2O exch), 3.05 (2 H, CH_2, d, J = 7.5 Hz), 4.15 (1 H, CH, dt, J = 7.5, 1.3 Hz), 4.2 (1 H, OH, s broad, D_2O exch), 4.95 (1 H, CH, d, J = 1.3 Hz), 7.2–7.8 (10 H, Ph H, m); IR (Nujol) ν_{max} 3500 and 3250 (OH), 1680 (CO) cm^{-1}. After recrystallization from hexane/ethyl acetate (4:1), the less mobile isomer melted at 116–8 °C: ^{1}H NMR ($CDCl_3$) δ 2.4 (1 H, OH, s broad, D_2O exch), 2.66 (1 H, CH_2, dd, J = 14, 5.4 Hz), 2.75 (1 H, CH_2, dd, J = 14, 7.2 Hz), 4.2 (1 H, CH, ddd, J = 4.2, 5.4, 7.2 Hz), 4.5 (1 H, OH, s, D_2O exch), 5.25 (1 H, CH, d, J = 4.2 Hz), 7.2–7.9 (10 H, Ph H, m); IR (Nujol) ν_{max} 3420 and 3300 (OH), 1680 (CO) cm^{-1}; MS m/e 256 (M$^{\cdot+}$), 238 (M – H_2O), 209, 165, 136, 105 (base peak), 91, 77, 65, 58, 51.

2,3-Dihydroxy-1,5-diphenylpentan-1-one (3n). After workup, 2.7 g of the residue was recovered. ^{1}H NMR analysis revealed the presence of two isomers in 71:29 ratio. Elution of the crude residue with hexane/ethyl acetate (4:1) on a silica gel column afforded in the order: α-hydroxyacetophenone (0.2 g, 17%), the minor isomer (0.45 g, 17%), and the major isomer (1.1 g, 41%). The major isomer was recrystallized from hexane/ether (1:1): mp 91–3 °C (lit.[23] mp 91 °C). According to ref 23, this is the stereomer with anti configuration: ^{1}H NMR ($CDCl_3$) δ 1.3–2 (2 H, CH_2, m), 2.3–3 (2 H, CH_2, m), 3.9 (1 H, CH, dt, J = 9, 4 Hz), 3.8–4 (2 H, 2 OH, s broad, D_2O exch), 5.2 (1 H, CH, d, J = 4 Hz), 7–8 (10 H, Ph H, m); IR (Nujol) ν_{max} 3400 (OH), 1660 (CO) cm^{-1}. Minor isomer (syn configuration) was a thick oil: ^{1}H NMR ($CDCl_3$) δ 1.9–2.2 (2 H, CH_2, m), 2.7–3 (2 H, CH_2, m), 3.7–4 (2 H, 2 OH, s broad, D_2O exch), 3.95 (1 H, CH, dt, J = 1.5, 7.2 Hz), 4.95 (1 H, CH, d, J = 1.5 Hz), 7.2–8 (10 H, Ph H, m).

2,3-Dihydroxy-1,3-diphenylpropan-1-one (3o). After usual workup, 2.5 g of solid residue was obtained. The solid was dissolved in hexane/ethyl acetate (7:3) and stored at 0 °C for several days. The stereomer **3o** (0.90 g, 40%) with syn configuration crystallized out as fine needles: mp 110 °C (lit.[32] mp 117–9 °C); ^{1}H NMR ($CDCl_3$) δ 3.0 (1 H, OH, s broad, D_2O exch), 4.0 (1 H, OH, s broad, D_2O exch), 4.92 (1 H, CH, AB system, J = 3.3 Hz), 5.22 (1 H, CH, AB system, J = 3.3 Hz), 7.2–7.6 (8 H, Ph H, m), 7.9 (2 H, Ph H, m); IR (Nujol) ν_{max} 3470 (OH), 1690 (CO) cm^{-1}. The mother liquors of the above crystallization, evaporated to a small volume, were chromatographed on a silica gel plate and developed in hexane/chloroform/ether (5:1:4). The main band afforded, upon evaporation of the solvents, the isomer **3o** with anti configuration[33] (thick oil): ^{1}H NMR ($CDCl_3$) δ 2.0–3.0 (1 H, OH, s broad, D_2O exch), 5.08 (1 H, CH, AB system, J = 4 Hz), 5.41 (1 H, CH, AB system, J = 4 Hz), 7.2–7.6 (8 H, Ph H, m), 7.9 (2 H, Ph H, m).

(31) As confirmed by ^{13}C NMR data, the proton at 5.85 ppm is the proton at position 4 of the isobenzofuran-1-one ring. The high field at which it was found indicates that the proton lies within the shielding cone of one of the two phenyl rings present in the molecule. A further confirmation is given by the X-ray structure of **5j** (see ref 17).

(32) Reichel, L.; Doring, H. W. *Liebigs Ann. Chem.* **1957**, *606*, 137.

(33) *Chem. Abstr.* **1961**, *55*, 4422.

2,3-Dihydroxy-1-phenyl-3-(4-cyanophenyl)propan-1-one (3p). After workup, 2.7 g of solid residue was obtained. When the residue was dissolved in chloroform, the higher melting point isomer crystallized out (1.1 g, 41%) as fine needles: mp 142–5 °C; ^{1}H NMR ($CDCl_3$ + DMSO) δ 4.5 (2 H, 2 OH, broad, D_2O exch), 5.1 (1 H, CH, AB system, J = 2.7 Hz), 5.2 (1 H, CH, AB system, J = 2.7 Hz), 7.6 (7 H, Ph H, m), 8.0 (2 H, Ph H, m); IR (Nujol) ν_{max} 3350 (OH), 2220 (CN), 1690 (CO) cm^{-1}; MS m/e 136, 131, 130, 105 (base peak), 102, 77, 51. The mother liquors of the above crystallization, stored for a few days at 0 °C, afforded the lower melting isomer (1 g, 39%): mp 124–5 °C; ^{1}H NMR ($CDCl_3$) δ 3.4 (2 H, 2 OH, s broad, D_2O exch), 5.1 (1 H, CH, AB system, J = 5.7 Hz), 5.2 (1 H, CH, AB system, J = 5.7 Hz), 7.6 (7 H, Ph H, m), 8.0 (2 H, Ph H, m); IR (Nujol) ν_{max} 3500, 3360 (OH), 2220 (CN), 1690 (CO) cm^{-1}.

2,3-Dihydroxy-1-phenyl-3-(2-methylphenyl)propan-1-one (3q). A thick oil (2.5 g) was obtained after workup. The crude oil was chromatographed on a silica gel column with hexane/ethyl acetate (4:1). The main fraction (1.8 g, 70%) was a mixture of the two isomers **3q** and was further chromatographed on a silica gel plate (hexane/ethyl acetate, 9:1). The band that moved first was enriched in the minor isomer, but complete resolution of this isomeric mixture was unsuccessful. Minor isomer: ^{1}H NMR ($CDCl_3$) δ 2.25 (3 H, CH_3, s), 3.7–4 (2 H, 2 OH, s broad, D_2O exch), 5.06 (1 H, CH, AB system, J = 4.2 Hz), 5.15 (1 H, CH, AB system, J = 4.2 Hz), 7–8 (9 H, Ph H, m). Major isomer: ^{1}H NMR ($CDCl_3$) δ 2.20 (3 H, CH_3, s), 3.7–4.0 (2 H, 2 OH, s broad, D_2O exch), 5.3 (1 H, CH, AB system, J = 5 Hz), 5.32 (1 H, CH, AB system, J = 5 Hz), 7.8 (9 H, Ph H, m).

2,4-Bis(2-methylphenyl)-5-benzoyl-1,3-dioxolane (4q). When a slight excess of *o*-tolualdehyde was used, formation of **4q** occurred even at 0 °C. With a 1:1.5 molar ratio of phenylglyoxal/aldehyde, formation of **4q** occurred in 30% yield together with 65% yield of **3q**. By ^{1}H NMR analysis, **4q** was shown to be a mixture of two isomers only, instead of four. Upon dilution of the crude residue on a silica gel column with hexane/ethyl acetate (4:1), the first eluted fraction (0.6 g, 17%) was the major isomer **4q** (oil): ^{1}H NMR ($CDCl_3$) δ 2.2 (3 H, CH_3, s), 2.4 (3 H, CH_3, s), 5.2 (1 H, CH, AB system, J = 6 Hz), 5.75 (1 H, CH, AB system, J = 6 Hz), 6.28 (1 H, CH, s), 7–8 (13 H, Ph H, m). The minor isomer **4q** was eluted second (0.45 g, 13%) and recrystallized from hexane/ether (1:1): mp 122–4 °C; ^{1}H NMR ($CDCl_3$) δ 2.1 (3 H, CH_3, s), 2.5 (3 H, CH_3, s), 5.75 (2 H, 2 CH, s), 6.32 (1 H, CH, s), 7–8.2 (13 H, Ph H, m); IR (Nujol) ν_{max} 1690 (CO), 1200–1100 (characteristic bands of dioxolane ring) cm^{-1}.

2,3-Dihydroxy-1-phenyl-3-(2-methoxyphenyl)propan-1-one (3r). After workup, the crude solid residue was dissolved in ethyl acetate. From the solution, stored at 0 °C for 3 days, the minor isomer crystallized out as needles: mp 140–2 °C (lit.[32] mp 143–5 °C); ^{1}H NMR ($CDCl_3$) δ 2.85 (1 H, OH, d, J = 8.4 Hz, D_2O exch), 3.9 (3 H, OCH_3, s), 4.0 (1 H, OH, d, J = 6 Hz, D_2O exch), 5.3 (1 H, CH, dd, J = 6, 2.7 Hz, AB system after D_2O exch, J = 2.7 Hz), 5.38 (1 H CH, dd, J = 8.4, 2.7 Hz, AB system after D_2O exch, J = 2.7 Hz), 6.75–7.65 (7 H, Ph H, m), 8.1 (2 H, Ph H, m); IR (Nujol) ν_{max} 3500–3350 (OH), 1690 (CO) cm^{-1}. The mother liquor of the above recrystallization was evaporated and then chromatographed on a silica gel column with hexane/ethyl acetate (4:1). The less mobile phase was the major isomer (1.6 g, 60%): mp 98–100 °C, upon recrystallization from ether/hexane (4:1); ^{1}H NMR ($CDCl_3$) δ 3.3 (1 H, OH, s, D_2O exch), 3.5 (3 H, OCH_3, s), 3.7 (1 H, OH, d, D_2O exch), 5.43 (1 H, CH, AB system, J = 3.3 Hz), 5.53 (1 H, CH, AB system, J = 3.3 Hz), 6.7–7.9 (9 H, Ph H, m); IR (Nujol) ν_{max} 3350 (OH), 1690 (CO) cm^{-1}; MS m/e 272 (M$^{\bullet+}$), 137, 136, 135, 105 (base peak), 77, 51.

2,4-Bis(2-methoxyphenyl)-5-benzoyl-1,3-dioxolane (4r). When a slight excess of 2-methoxybenzaldehyde was used, formation of **4r** occurred even at 0 °C. With a 1:1.5 molar ratio phenylglyoxal/aldehyde, formation of **4r** occurred in 50% yield together with 50% yield of **3r**; the yield based on both the starting substrate and starting aldehyde was quantitative. After workup, 3.4 g of a thick oil was obtained. The fine needles (0.5 g, 20%) recovered after dissolution of the crude oil in ether corresponded to the minor isomer **3r** (mp 140–2 °C). The mother liquors of the above recrystallization were evaporated to dryness and chromatographed on a silica gel column with hexane/ethyl acetate (4:1) and gave in the order: **4r** (1.9 g, 49%, thick oil) as a mixture of two isomers in the ratio 60:40 and the major isomer **3r** (0.7 g, 26%). Major isomer **4r**: mp 98–100 °C; ^{1}H NMR ($CDCl_3$) δ 3.3 (3 H, OCH_3, s), 3.8 (3 H, OCH_3, s), 5.29 (1 H, CH, AB system, J = 6.3 Hz), 5.38 (1 H, CH, AB system, J = 6.3 Hz), 6.65 (1 H, CH, s), 6.9–8.0 (13 H, Ph H, m). Minor isomer **4r**: ^{1}H NMR ($CDCl_3$) δ 3.5 (3 H, OCH_3, s), 3.8 (3 H, OCH_3, s), 5.25 (1 H, CH, AB system, J = 5.7 Hz), 5.9 (1 H, CH, AB system, J = 5.7 Hz), 6.7 (1 H, CH, s), 6.9–8.0 (13 H, Ph H, m); IR (film) ν_{max} 1690 (CO), 1200–1000 (characteristic bands of dioxolane ring) cm^{-1}; MS m/e 390 (M$^{\bullet+}$), 285 (M – PhCO), 254, 136, 135, 121, 105 (base peak), 77, 65.

2,3-Dihydroxy-1-phenyl-3-(2-hydroxyphenyl)propan-1-one (3s). After usual workup, 2.6 g of a solid residue was obtained. The solid was dissolved in ethanol. On standing, 1.9 g (73%) of one isomer **3s** crystallized out (mp 142–5 °C). No traces of the isomer reported in the literature[34] were found: ^{1}H NMR (CD_3OD) δ 4.7 (3 H, 3 OH, s, D_2O exch), 5.4 (1 H, CH, AB system, J = 3 Hz), 5.5 (1 H, CH, AB system, J = 3 Hz), 6.8–7.7 (7 H, Ph H, m), 8.15 (2 H, Ph H, m); IR (Nujol) ν_{max} 3400–3200 (OH), 1675 (CO) cm^{-1}; MS m/e 258 (M$^{\bullet+}$ < 1), 122 (100), 121 (90), 105 (90), 93, 77, 65, 51.

2-Hydroxy-2-phthalidylacetophenone (5t). After usual workup, 2.7 g of a thick oil was recovered. The crude oil was dissolved into hexane/ether (1:1) and stored at 0 °C for few days. On standing, only one isomer **5t** crystallized out. Upon filtration (1.9 g, 71%) and recrystallization from ether it melted at 122–4 °C. No traces of the other isomer were found: ^{1}H NMR ($CDCl_3$) δ 3.65 (1 H, OH, d, J = 7.5 Hz, D_2O exch), 5.5 (1 H, CH, dd, J = 7.5, 4.2 Hz, after D_2O exch, AB system, J = 4.2 Hz), 5.7 (1 H, CH, AB system, J = 4.2 Hz), 7.3 (1 H, Ph H, m), 7.6 (6 H, Ph H, m), 8.1 (2 H, Ph H, m); IR (Nujol) ν_{max} 3500 (OH), 1770 (CO, five-membered lactone), 1670 (CO) cm^{-1}; MS m/e 268 (M$^{\bullet+}$), 134, 133, 105 (base peak), 77, 51.

3-Benzoylisocoumarin (6t). Upon heating under reflux for 3 h 1 g of **5t** with 0.2 g of *p*-toluenesulfonic acid in benzene (50 mL), **6t** was recovered in quantitative yield (0.92 g): mp 130–1 °C, after recrystallization from hexane/ethyl acetate (7:3); IR (Nujol) ν_{max} 1735 (CO, six membered lactone), 1670 (CO) cm^{-1}; MS m/e 250 (M$^{\bullet+}$, 60), 145 (M – PhCO, 100), 117 (25), 105 (50), 89 (90), 77 (35), 63 (15), 51 (15).

2,3-Dihydroxy-3-(2-furyl)-1-phenylpropan-1-one (3u). After usual workup, 2.2 g of a thick oil was obtained. The crude oil was eluted from a silica gel column with hexane/ethyl acetate (4:1). The chromatographically more mobile of the two isomers **3u** was the major one (1g, 45%): mp 95–7 °C (recrystallization from ether); ^{1}H NMR ($CDCl_3$) δ 3.0 (1 H, OH, s, D_2O exch), 4.2 (1 H, OH, s, D_2O exch), 5.02 (1 H, CH, AB system, J = 2.7 Hz), 5.42 (1 H, CH, AB system, J = 2.7 Hz), 6.4 (2 H, 2 furyl H, m), 7.3–7.7 (4 H, 3 Ph H + 1 furyl H, m), 8.1 (2 H, Ph H, m); IR (Nujol) ν_{max} 3420 and 3380 (OH), 1680 (CO) cm^{-1}. The less mobile of the two isomers was recovered as a thick oil (0.5 g, 23%): ^{1}H NMR ($CDCl_3$) δ 3.4 (2 H, 2 OH, s broad, D_2O exch), 5.1 (1 H, CH, d, J = 4.2 Hz), 5.45 (1 H, CH, d, J = 4.2 Hz), 6.15 (2 H, 2 furyl H, m), 7.3–8 (6 H, 5 Ph H + 1 furyl H, m).

3,4-Dihydroxy-3-phenylpentan-2-one (3v) and 2,3-Dihydroxy-2-methyl-1-phenylbutan-1-one (3v'). After workup, 2 g of a crude oil was recovered. ^{1}H NMR analysis revealed the presence of two isomers **3v** (53%) in the ratio 60:40 and of two isomers **3v'** (16%) in the ratio 60:40. Purification of the crude residue on a silica gel column with hexane/ethyl acetate (4:1) afforded a first fraction of 1-hydroxy-1-phenylpropan-2-one (0.35 g, 23%) and a second fraction which was a mixture of the four isomers **3v** and **3v'** (1.25 g, 64%). Separation of the isomer mixture (oil) was not achieved. The major isomer **3v**: ^{1}H NMR ($CDCl_3$) δ 1.03 (3 H, CH_3, d, J = 6.3 Hz), 2.2 (3 H, CH_3CO, s), 4–5 (2 H, 2 OH, s broad, D_2O exch), 4.8 (1 H, CH, q, J = 6.3 Hz), 7.2–7.8 (5 H, Ph H, m). The minor isomer **3v**: ^{1}H NMR ($CDCl_3$) δ 1.18 (3 H, CH_3, d, J = 6 Hz), 2.1 (3 H, CH_3CO, s), 4–5 (2 H, 2 OH, s broad, D_2O exch), 4.7 (1 H, CH, q, J = 6 Hz), 7.2–7.8 (5 H, Ph H, m). The major isomer **3v'**: ^{1}H NMR ($CDCl_3$) δ 1.3 (3 H, CH_3, d, J = 6 Hz), 1.5 (3 H, CH_3, s), 4.35 (1 H, CH, q, J = 6 Hz), 4.5 (2 H, 2 OH, broad, D_2O exch), 7.2–7.8 (3 H, Ph H, m), 8.1 (2 H, Ph H, m).

(34) The isomer reported in the literature melted at 167–8 °C (see ref 32).

3,4-Dihydroxy-3,4-diphenylbutan-2-one (3w). The only isomer **3w** formed precipitated directly from the reaction mixture and after filtration was recovered (2.4 g, 93%) and recrystallized from ether/ethyl acetate (1:1); mp 147-8 °C. It was shown to have syn relative configuration[18] by single crystal X-ray diffractometry: ^{1}H NMR (DMSO) δ 2.18 (3 H, CH_3, s), 5.5 (1 H, CH, d, J = 4.5 Hz, s after D_2O exch), 5.75 (1 H, OH, d, J = 4.5 Hz, D_2O exch), 6.0 (1 H, OH, s, D_2O exch), 7.0-7.6 (10 H, Ph H, m); IR (Nujol) ν_{max} 3440 and 3380 (OH), 1700 (CO) cm^{-1}.

1-Hydroxy-1-phenyl-1-phthalidylpropan-2-one (5z) and 2-Hydroxy-1-phenyl-2-phthalidylpropan-1-one (5z'). After workup, 2.85 g of a solid residue was recovered. ^{1}H NMR analysis revealed the presence of only one isomer **5z** (50%) and of two isomers **5z'** (33%) in the ratio 60:40. After the solid residue was dissolved in methanol and stored at 0 °C for 6 days, **5z** crystallized out (1.3 g, 46%): mp 204-5 °C; ^{1}H NMR (DMSO) δ 2.22 (3 H, CH_3, s), 6 (1 H, Ph H, d),[35] 6.35 (1 H, OH, s, D_2O exch), 6.5 (1 H, CH, s), 7.2-7.8 (8 H, Ph H, m); IR (Nujol) ν_{max} 3460 (OH), 1755 (CO, lactone), 1710 (CO) cm^{-1}; MS m/e 282 ($M^{\cdot+}$), 239, 222, 194, 134, 133, 105 (base peak), 77, 43. The mother liquors of the above crystallization were evaporated to dryness, and the residual thick oil was chromatographed on a silica gel column with hexane/ethyl acetate (4:1). The first eluted fraction was a mixture of **5z** and of the minor isomer **5z'**, which was not obtained pure: ^{1}H NMR ($CDCl_3$) δ 1.6 (1 H, OH, s, D_2O exch), 1.8 (3 H, CH_3, s), 6 (1 H, CH, s), 7.2-8.2 (9 H, Ph H, m). The second eluted fraction was the major isomer **5z'** (0.4 g, 16%): mp 135-40 °C, after recrystallization from ethyl acetate; ^{1}H NMR ($CDCl_3$) δ 1.85 (3 H, CH_3, s), 4.5 (1 H, OH, s, D_2O exch), 5.85 (1 H, CH, s), 7.2-8.2 (9 H, Ph H, m); IR (Nujol) ν_{max} 3450 (OH), 1750 (CO, lactone), 1675 (CO) cm^{-1}; MS m/e 282 ($M^{\cdot+}$), 264 (M - H_2O), 222, 211, 194, 177 (M - PhCO), 160, 134, 133, 105 (base peak), 77.

(35) As confirmed by ^{13}C NMR data, the proton at 6 ppm is the proton at position 4 of the isobenzofuran-1-one ring (see ref 31).

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Supplementary Material Available: Elemental analytical data for compounds **3c,e-i,k,m,p,s,u**, **5j,t,z,z'**, and **6t** (1 page). Ordering information is given on any current masthead page.

Chemistry of Singlet Oxygen. 53. Environmental Effects on the Photooxygenation of 2-Methoxy-3-methyl-2-cyclopenten-1-one

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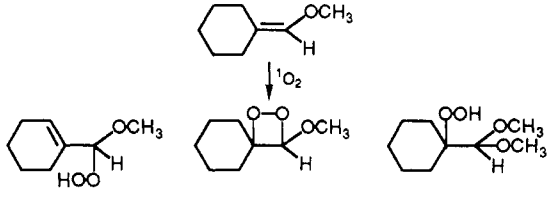
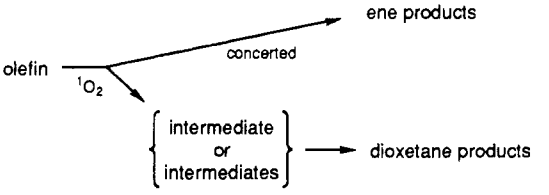
Photooxygenation of 2-methoxy-3-methyl-2-cyclopenten-1-one (1) gives both ene and dioxetane products. The product distribution depends on temperature and solvent. In CD_3OD, the photooxygenation of **1** gives solvent adducts as initial products, and the ratio of stereoisomers is very sensitive to the amount of CD_3OD in the reaction mixture. The results are discussed in terms of possible intermediates for the ene and dioxetane products, especially an exciplex.

Introduction

Environmental effects on the reactions of singlet oxygen have often been used to draw mechanistic conclusions. Solvent and temperature effects on the reaction rates of olefins which give exclusively either ene or [2 + 2] (dioxetane) products are negligible.[1] On the other hand, in cases where both ene and dioxetane products are formed, the product distribution is sensitive to both solvent and temperature.[2] Usually, increased solvent polarity or lower temperature favors dioxetane formation from these olefins. In addition, solvent adducts are often formed from these substrates in methyl alcohol. For example, the exocyclic enol ether gave over 95% of the ene product in benzene at 20 °C, but only 32% in CH_3OH at 20 °C along with 20% of solvent adduct and 48% of dioxetane products.[2e]



The major mechanistic question is whether the products stem from a concerted mechanism or from intermediates such as zwitterions, perepoxides, or exciplexes.[3] An interpretation that is commonly made is that the ene product stems from a concerted reaction, but that the dioxetane is formed from a more polar pathway involving a zwitterion or a perepoxide.



Recently, considerable experimental evidence has been reported that suggests that even the ene reaction proceeds through an intermediate. This intermediate has been suggested to be an irreversibly formed perepoxide on the basis of isotope effect studies.[4] However, Gorman has recently suggested that this intermediate is a reversibly formed exciplex because of the negative activation enthalpy associated with many such reactions.[5] Gorman has

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