(s), 1457 (m), 1402 (w), 1362 (s), 1342 (w), 1256 (w), 1236 (m), 921 (w), 913 (w), 845 (w), 748 (m), 741 (m), 713 (m), 360 (w), 343 (m), 329 (m) cm^{-1}.

Anal. Calcd for $C_{10}H_{12}N_4O_8$: C, 37.98; H, 3.83; N, 17.72. Found: C, 38.30; H, 3.86; N, 17.50.

1-Acetamido-3,5,7-tribromoadamantane (6). The photolysis of 5.4 g (0.012 mol) of 1 in 800 mL of acetonitrile was carried out in the same manner as described above for the conversion of 2 to 3. The solids obtained by flash evaporation of the clear solution were extracted with boiling *n*-heptane several times, removing 0.9 g of unchanged 1 as confirmed by IR spectrum. The undissolved solids were taken up in methanol, and the solution was neutralized dropwise with aqueous KOH. The solution was dispersed in water, and the separated solids were collected on a filter. The dried solids were taken up in boiling acetone, and the solution was filtered, concentrated, diluted with water to the cloudpoint, and chilled overnight to give 1.68 g (32%) of 6, mp 286–289 °C dec. Recrystallization from acetone–water gave needles: mp 290–292 °C dec; NMR [$(CD_3)_2SO$] δ 1.78 (3 H, s, CH_3), 2.50 (6 H,[24] s, CH_2 β to $NHCOCH_3$), 2.73 (6 H, s, CH_2 δ to $NHCOCH_3$), 7.88 (1 H, s, NH); IR (KBr) 3280 (s), 3070 (w), 2940 (w), 1635 (s), 1550 (s), 1448 (m), 1371 (m), 1343 (m), 1320 (s), 1305 (m), 1214 (w), 850 (m), 725 (m), 608 (w), 486 (w) cm^{-1}.

Anal. Calcd for $C_{12}H_{16}Br_3NO$: C, 33.52; H, 3.75; Br, 55.75; N, 3.26. Found: C, 33.73; H, 3.74; Br, 55.83; N, 3.02.

Acknowledgment. Appreciation is expressed to Dr. S. Bulusu for obtaining and interpreting the mass spectrum of 5 and to Ms. V. Hogan and Mr. J. Bobinski for obtaining the NMR spectra.

Registry No. 1, 7314-86-5; 2, 40950-19-4; 3, 21336-48-1; 4·HCl, 21336-47-0; 5, 75476-36-7; 6, 75476-37-8; adamantane, 281-23-2.

Oxidative Coupling of Ketone Enolates by Ferric Chloride†

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Metallic oxidants have been widely employed in oxidative couplings of phenols,[2] yet only recently have comparable methods appeared for oxidatively dimerizing ketones to give 1,4-diketones. Surprisingly, while cupric salts have been used to couple ketone enolates,[3-5] ferric chloride, commonly used in phenolic oxidations, is reported to be ineffective for such couplings.[3,6]

We find that in spite of previous observations, ferric chloride is an effective oxidant for the preparation of 1,4-diketones from ketone enolates. Examples of ketones whose enolates have been coupled with ferric chloride are given in Table I. Entry 10 demonstrates that esters can also be dimerized by this method. In most respects enolate dimerizations with ferric chloride are quite similar to those induced by cupric chloride. However, while dimerizations with cupric chloride are relatively sensitive to steric congestion around the carbanion,[3] the ferric system offers the advantage of not being so.

The coupling reaction is performed by adding a solution of anhydrous ferric chloride[7] in dry dimethylformamide to an enolate in tetrahydrofuran.[8] The enolates can be prepared in conventional ways, e.g., with lithium diisopropylamide (LDA) at dry ice temperatures (kinetic enolates) or with potassium hydride (thermodynamic enolates).[9] Stirring the mixture overnight at room temperature was generally sufficient to ensure completion of the oxidation.[10] After an extractive workup, the products could be isolated with standard techniques.

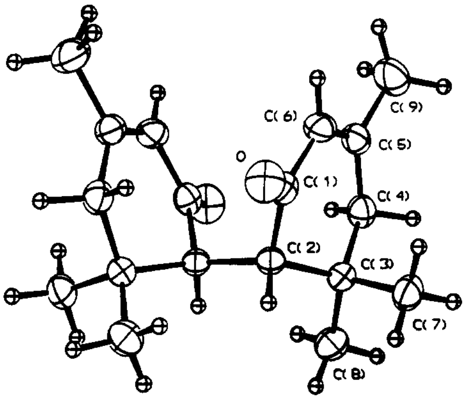

Figure 1. ORTEP drawing of *dl*-1,1′,5,5,5′,5′-hexamethyl[4,4′-bicyclohexenyl]-3,3′-dione. Selected bond distances (Å): C(1)–O, 1.229 (1); C(1)–C(2), 1.510 (2); C(1)–C(6), 1.461 (2); C(2)–C(2)′, 1.560 (2); C(2)–C(3), 1.560 (2); C(5)–C(6), 1.332 (2). The ring adopts a half-chair conformation in which C(2) and C(3) are 0.37 and −0.33 Å out of plane formed by C(1), C(4), C(5), and C(6). The C(1)–C(2)–C(2)′–C(1)′ torsion angle is 55.7°.

Where more than one enolate anion is possible, the structure of the product depended on the particular enolate prepared.[11] Thus, the structure of dimer 3 as shown in Table I was that expected from oxidation of the kinetic enolate. Spectral data for this compound, however, were not unequivocal, and a single-crystal X-ray structure de-

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† Contribution No. 2807.

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[2] For reviews see T. Kametani and K. Fukumoto, *Synthesis*, **657** (1972), and references therein.

[3] Y. Ito, T. Konoike, T. Harada, and T. Saegusa, *J. Am. Chem. Soc.*, **99**, 1487 (1977).

[4] Y. Ito, T. Konoike, and T. Saegusa, *J. Am. Chem. Soc.*, **97**, 2912 (1975).

[5] Y. Kobayashi, T. Taguchi, and E. Tokuno, *Tetrahedron Lett.*, 3741 (1977); Y. Kobuzaski, T. Taguchi, and T. Morihawa, *ibid.*, 3555 (1978).

[6] Oxidation of propiophenone and butyrophenone with ferric chloride has been reported to give 1,4-diketones and products derived from these diketones along with other products. The enolate anions, however, were not oxidized, and, further, the reaction is not general since with acetophenone or aliphatic ketones only products derived from aldol-like condensations were obtained. H. Inoue, M. Sakata, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **46**, 2211 (1973).

[7] Ferric chloride must be anhydrous for successful couplings. In our experience, commercial anhydrous ferric chloride was often not sufficiently dry and was usually contaminated with insoluble iron oxides. We found it better to dry the hydrated reagent with thionyl chloride and, since the anhydrous solid is extremely hygroscopic, handle it under an atmosphere of dry nitrogen.

[8] If THF was substituted for DMF, the yields were much lower. Similar solvent effects have been noted for phenolic oxidations by ferric chloride [S. Tobinaga and E. Kotani, *J. Am. Chem. Soc.*, **94**, 309 (1972)] and by Saegusa for the cupric oxidation of ketone enolates.

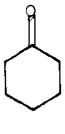
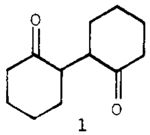
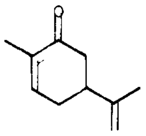
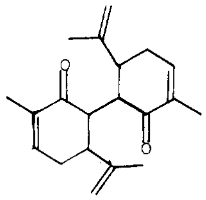
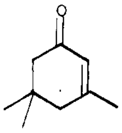
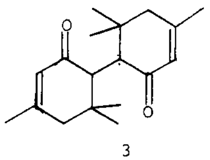
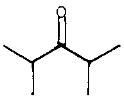
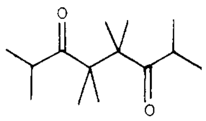
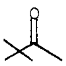
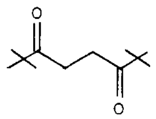
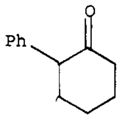
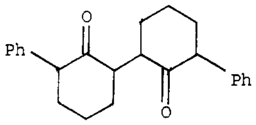
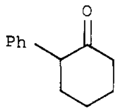
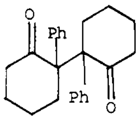
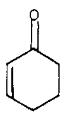
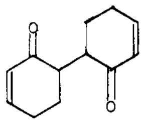
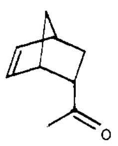
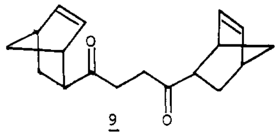
[9] C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).

[10] The reaction can be followed by various standard methods. We found gas chromatography particularly useful due to the large retention time differences between the starting materials and the dimers. Such analyses revealed that the reaction mixtures were composed of primarily dimers and undimerized starting materials. Smaller amounts, generally 10% or less, of self-condensation products were also observed. The dimer yields given, aside from losses due to isolation and purification, generally reflect the percent conversion to dimers. In experiments with cyclohexanone, increasing the amount of ferric chloride used did not substantially alter the conversion to the dimer.

[11] The oxidations presented here were done on enolates composed of essentially only one regioisomer. Under these conditions the dimerization appears to be regiospecific. When a mixture of enolates is present, oxidation with $FeCl_3$ will give a statistical distribution of all possible dimers based on the original concentrations of enolates.

0022-3263/80/1945-5408$01.00/0

Table I

entry	carbonyl compd	dimer	yield, %
1		 1	45[a]
2		 2	60
3		 3	63
4		 4	52[b]
5		 5	60[b]
6		 6	43
7		 7	40
8		 8	23
9		 9	50
10	$CH_3C(O)OCH_2CH_3$	$CH_3CH_2OC(O)CH_2CH_2C(O)OCH_2CH_3$ 10	69

[a] References 13 and 14. [b] Reference 15. [c] Yield via GC analysis.

termination of the *dl* isomer of dimer **3** was performed.

The result of the X-ray work confirmed the structure of dimer **3** (see Figure 1). The molecule is situated about a crystallographic 2-fold axis and is unusual in that the bond connecting the two rings is axial to both rings rather than equatorial as might have been anticipated. Space-filling models suggest, however, that the methyl groups on C(3) and C(3)′ interact less with axial bonds than with equatorial bonds.

Experimental Section

Melting points were taken on samples in glass capillaries with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 257 or Infracord spectrometers. Nuclear magnetic resonance spectra were recorded with Varian A60, HR-220, or XL-100 spectrometers. Preparative high-performance liquid chromatography (LC) was performed with a Waters Prep LC/500 on silica gel columns. Column chromatography was done on Mallinckrodt Silicar CC-7 silicic acid. Analytical thin-layer chromatography (TLC) was done on Machery Nagel and Co. Polygram Sil G/UV precoated plastic sheets (4 × 8 cm). Preparative TLC was done on Analtech Uniplate silica gel plates. Gas chromatography was performed on a Varian Model 1700 (TC detector) or a Hewlett-Packard Model 5700 (FI detector). Column A refers to a 5 ft × 2 mm glass column packed with 3% OV-101 on 80–100-mesh Gas Chrom Q. Helium flow rates were between 35 and 50 mL/min.

Tetrahydrofuran (THF) was distilled from the sodium benzophenone ketyl and stored under nitrogen. Dimethylformamide (DMF) was distilled at ≤10 torr pressure from calcium hydride and stored under nitrogen. *n*-Butyllithium was obtained from Foote Mineral Co. as a hexane solution. The concentration of *n*-butyllithium was determined by the procedure of Watson and Eastham.[12] The ketones were purchased from the Aldrich Chemical Co. and used as received except as otherwise noted. "1 N HCl" refers to aqueous 1 N hydrochloric acid. "Brine" refers to saturated aqueous sodium chloride. "In vacuo" refers to evacuation of a sample with a mechanical pump. "Drybox" or "glovebox" refers to operations carried out in a nitrogen filled Vacuum Atmosphere Dri-Lab glovebox. A polyethylene glovebag has been used with equal success. The phrase "LDA prepared as usual" means a solution of diisopropylamine (1 equiv, distilled from calcium hydride and stored under nitrogen) was treated at 0 °C with 1 equiv of *n*-butyllithium and stirred 15 min at 0 °C. The ketone dimerizations were carried out in glassware that was previously oven dried and cooled under dry nitrogen. Solutions were prepared under nitrogen in a glovebox or glovebag. A mechanical stirrer was preferred for agitation.

Ferric chloride was dried by refluxing the hydrated reagent with thionyl chloride. Excess thionyl chloride was removed in vacuo and the solid further dried and stored in a vacuum desiccator over potassium hydroxide.

Dissolving ferric chloride in DMF is very exothermic. Although no problems have been experienced because of this, care should be exercised during this operation. The solution was allowed to cool to room temperature before being added to the enolate.

The following preparation is an example of the general procedure used.

5,5′-Diisopropenyl-2,2′-dimethyl[4,4′-bicyclohexenyl]-3,3′-dione (2). LDA (0.12 mol) was prepared as usual in 100 mL of dry THF. *l*-Carvone (15 g, 0.1 mol) was added dropwise to the LDA at −78 °C. After the mixture was stirred for 30 min at this temperature, ferric chloride (17.8 g, 0.11 mol) in 100 mL of dry DMF was added dropwise to the cold solution. The resulting black mixture was allowed to warm to room temperature and stirred overnight. A 250-mL amount of 1 N HCl was added followed by 100 mL of pentane. The layers were separated, and the aqueous one was extracted with pentane (3 × 50 mL). The combined pentane layers were washed successively with 50-mL portions of 1 N HCl, water, and brine. Drying ($MgSO_4$) and solvent evaporation gave a crude product (14.5 g) which was recrystallized by dissolving the sample in hot methanol, adding water to the cloud point, reheating the mixture until clear, and then allowing it to cool. The long needles which separated were isolated by filtration, washed once with 50% aqueous methanol, and dried in vacuo over P_2O_5 to give 9.4 g (63%) of product: mp 105–108 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 6.68 (m, 2 H, $C\mathbf{H}=C(CH_3)CO$), 4.85 (br s, 4 H, $C\mathbf{H}_2=C(CH_3)$), 3.52 (dt, 2 H, J_d = 12 Hz, J_t = 8 Hz, $CH_2C\mathbf{H}CHCO$), 2.52 (d, 2 H, J = 12 Hz, $CH_2CHC\mathbf{H}CO$), 2.30 (m, 4 H, $C\mathbf{H}_2CHCHCO$), 1.77, 1.73, 1.63 (3 s, 12 H, $C\mathbf{H}_3C=CH$ and $C\mathbf{H}_3C=CH_2$); high-resolution mass spectrum calcd for $C_{20}H_{26}O_2$ *m/e* 298.1931, found *m/e* 298.1937. A sublimed sample was analyzed. Anal. Calcd: C, 80.49; H, 8.78; O, 10.72. Found: C, 81.23, 80.92; H, 8.76, 8.72.

[1,1′-Bicyclohexyl]-2,2′-dione (1). Cyclohexanone (0.98 g, 10 mmol) was converted to the enolate with LDA and oxidized with ferric chloride in the manner described above. Chromatography of the product gave 0.259 g of the crystalline meso isomer, 0.122 g of a mixture of meso and *dl* isomers, and 0.07 g of the oily *dl* isomer. For the meso isomer:[10,11] mp 74–75 °C (lit.[10] mp 72–74 °C). For the *dl* isomer: spectral data matches that reported in ref 13.

1,1′,5,5,5′,5′-Hexamethyl[4,4′-bicyclohexenyl]-3,3′-dione (3). Isophorone (1.38 g) was converted to its enolate with LDA and oxidized in the manner described above. High-performance LC (eluent 40% ether in hexane) gave two dimers. The faster eluting dimer (0.157 g) crystallized as fine needles: mp 154–156 °C; IR (CCl_4) 1665 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 6.09 (br s, 2 H, $C\mathbf{H}=C(CH_3)_2$), 2.71 (s, 2 H, $COC\mathbf{H}C(CH_3)_2$), 2.40 (d, 2 H, J = 18 Hz, $(CH_3)_2CC\mathbf{H}_2C(CH_3)=$), 1.99 (d, 2 H, J = 18 Hz, $(CH_3)_2C\mathbf{H}_2C(CH_3)=$), 1.95 (br s, 6 H, $HC=C(CH_3)$), 1.00, 0.95, (2 s, 12 H, $(CH_3)_2C<$). The slower eluting isomer (0.563 g) crystallized as large plates: mp 68–70 °C; IR (CCl_4) 1665 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 5.94 (s, 2 H, $C\mathbf{H}=C(CH_3)$), 2.57 (d, 2 H, J = 18 Hz, $(CH_3)_2CC\mathbf{H}_2C(CH_3)=$), 2.40 (s, 2 H, $(CH_3)_2CC\mathbf{H}CO$), 1.97 (d, 2 H, J = 18 Hz, $(CH_3)_2CC\mathbf{H}_2C(CH_3)=$), 1.90 (s, 6 H, $CH=C(C\mathbf{H}_3)$), 1.17, 1.07, (2 s, 12 H, $(C\mathbf{H}_3)_2C<$). The yield of pure dimers was 52%. The X-ray structure determination was performed on the slower eluting *dl* isomer.

Crystal data: monoclinic, space group $C2/c$; at 24 °C, a = 10.838 (3) Å, b = 8.801 (3) Å, c = 17.889 (5) Å, β = 104.85 (1)°, V = 1649 $Å^3$, Z = 4 (molecules sit on 2-fold axes).

Intensity data: Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, ω scans of 1.0°, 4° < 2θ < 50°, 1459 reflections.

Structure Solution and Refinement. The structure was solved by direct methods. Hydrogen atom positions were initially calculated but ultimately refined. The structure was refined by full-matrix, least-squares techniques: 1053 reflections with $I > 2\sigma(I)$, 143 variables, R = 0.047; the largest peak in the final difference Fourier synthesis had a magnitude of 0.25 e $Å^{-3}$ and was located near C(6). The mathematical and computational details may be found elsewhere.[16]

2,4,4,5,5,7-Hexamethyloctane-3,5-dione (4). The enolate of diisopropyl ketone (0.1 mol) was prepared as usual from LDA and oxidized with ferric chloride as described above. The mixture was worked up as usual to give 11.48 g of crude product. This was chromatographed on 700 g of SiO_2, eluting with 7% ether in hexane to give the dimer as an oil: bp 120 °C (20 mm; evaporative distillation); NMR (60 MHz, $CDCl_3$) δ 3.2 (septet, 2 H, J = 6 Hz, $C\mathbf{H}(CH_3)_2$), 1.28 (s, 12 H, $OCC(CH_3)_2C(CH_3)_2CO$), 1.08 (d, 12 H, J = 6 Hz, $(C\mathbf{H}_3)_2CH$); IR (CCl_4) 1705 cm^{-1}; distilled yield 6 g (52%).

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58; O, 14.14. Found: C, 74.48, 74.70; H, 11.50, 11.51.

2,2,7,7-Tetramethyloctane-3,6-dione (5). The enolate of pinocalone (0.1 mol), generated with LDA, was oxidized with ferric chloride as described above. Workup as usual gave an oil which was distilled to give **5**: bp 60–65 °C (0.45–0.5 mm) [lit.[14] bp 55–60 °C (0.5 mm)]; pale yellow liquid; IR (CCl_4) 1705 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 2.75 (s, 4 H, $COCH_2CH_2CO$), 1.17 (s, 18 H, $(CH_3)_3C$); yield 6 g (60%).

Dimerization of the 2-Phenylcyclohexanone Kinetic Enolate. The kinetic enolate of 2-phenylcyclohexanone (0.10 mol) was prepared as usual from LDA and oxidized with ferric chloride in the manner described above. Five dimer fractions, A–E, were obtained after workup and chromatography. (There are four chiral centers in the molecule giving four *dl* pairs and two meso compounds.) Compounds A–E had similar IR spectra with a carbonyl band at ~1700 cm^{-1}. Other physical data are tabulated in Table II. The yield of dimers isolated was 7.4 g (43%).

Thermodynamic Enolate. The thermodynamic enolate of 2-phenylcyclohexanone (0.1 mol) was prepared with potassium hydride as described by Vedejs.[17] Oxidation with ferric chloride

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(12) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

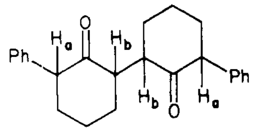
(13) E. G. E. Hawkins and R. Large, *J. Chem. Soc., Perkin Trans. 1*, 280 (1974).

(14) H. Christol, M. Carvich, F. Pietrasanta, and F. Plenat, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 883 (1974).

(15) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Am. Chem. Soc.*, **70**, 1269 (1948).

(16) W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, **18**, 2030 (1979).

Table II. NMR Data



compd[a]	NMR (60 MHz, $CDCl_3$), δ
A	7.25 (br s, 10 H, C_6H_5), 3.9–3.5 (m, 2 H, H_a), 3.2–2.8 (m, 2 H, H_b), 2.5–2.1 and 2.1–1.7 (2 m, 12 H)
B	7.5 (s, 10 H, C_6H_5), 3.9–3.7 (m, 2 H, H_a), 3.2–2.7 (m, 2 H, H_b), 2.7–1.5 (m, 12 H)
C	7.5–7.0 (10 H, C_6H_5), 3.8–3.6 (m, 2 H, H_a), 3.2–2.8 (m, 2 H, H_b), 2.7–1.4 (m, 12 H)
D	7.5–7.0 (10 H, C_6H_5), 4.0–3.6 (m, 2 H, H_a), 3.3–2.8 (m, 2 H, H_b), 2.8–1.2 (m, 12 H)
E	7.5–7.0 (10 H, C_6H_5), 3.9–3.3 (m, 2 H, H_a), 3.1–2.6 (m, 2 H, H_b), 2.4–1.6 (m, 12 H)

[a] Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.2; H, 7.56; O, 9.24. Found (compound B): C, 82.89, 82.70; H, 7.59, 7.72. Found (compound C): C, 83.19, 18.42; H, 7.64, 7.64.

was carried out as usual except that the mixture was heated to ~50 °C for 1 day. The reaction was complete when the blue color turned cloudy green. The diastereomeric dimers **7** were isolated by chromatography and identified by NMR analysis. For isomer 1: ^1H NMR (60 MHz, $CDCl_3$) δ ~7.4–7.1 (m, ~6 H, meta and para aryl H), ~7.2–6.9 (br m, ~2 H, ortho aryl H), 6.7–6.3 (br m, ~2 H, ortho aryl H), 3.1–2.1 (m, 6 H, CH_2CO and $CH_2C(Ph)$), 2.1–1.0 (m, 10 H, $CH_2C(Ph)$ and methylenes); ^1H NMR (220 MHz, $CDCl_3$) δ 7.3–7.08 (m, 6 H), 6.99 (m, 2 H, ortho aryl H), 6.54 (d, 2 H, J = 7 Hz, ortho aryl H), 2.74 (dt, 2 H, J_t = 14 Hz, J_d = 4 Hz, $CH_2C{=}O$), 2.5–2.25 (m, 4 H, $CH_2C{=}O$ and CH_2CPh), 1.95–1.45 (m, 8 H, CH_2CH_2), 1.19 (qt, 2 H, J_q = 13 Hz, J_t = 4 Hz, $PhCCH_2C\mathbf{H}_2CH_2$). The NMR spectrum of the other isomer was similar except for a new broad resonance between δ 6.0 and 5.5 (ortho aryl proton). Variable-temperature NMR (100 MHz) showed that the ortho hydrogens of the aryl groups changed with temperature. This was because the rotation of the phenyl groups was hindered. The coalescence temperature was 69 °C, giving 17 kcal as the activation barrier for the exchange process. The yield of isolated dimers was 40%.

[4,4′-Bicyclohexenyl]-3,3′-dione (**8**). 2-Cyclohexen-1-one (0.96 g, 10 mmol) was converted to its enolate with LDA and oxidized with ferric chloride as described above. The diastereomeric dimers were isolated by high-performance LC (eluant 40% ether in hexane). For isomer 1: yield 0.080 g; white solid; mp 84–86 °C; IR (CCl_4) 3040, 1675 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.97 (dt, 2 H, J_d = 10 Hz, J_t = 3 Hz, $CH_2C\mathbf{H}{=}CHCO$), 6.0 (dt, 2 H, J_d = 10 Hz, J_t = 1.5 Hz, $CH_2CH{=}C\mathbf{H}CO$), 3.27 (dd, 2 H, J = 11 Hz, 7 Hz, $COC\mathbf{H}CH_2$), 2.45 (m, 4 H, $=CHC\mathbf{H}_2CH_2CH$), 1.92 (m, 4 H, $=CH_2CH_2C\mathbf{H}_2CH$). For isomer 2: yield 0.140 g; white solid; mp 90–100 °C; IR (CCl_4) 3040, 1675 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.93 (dt, 2 H, J_d = 10 Hz, J_t = 4 Hz, $CH_2C\mathbf{H}{=}CHCO$), 6.02 (dt, 2 H, J_d = 10 Hz, J_t = 3 Hz, $CH_2CHC\mathbf{H}CO$), 2.88 (t, 2 H, J = 7 Hz, $COC\mathbf{H}CH_2$), 2.42 (m, 4 H, $=CHC\mathbf{H}_2CH_2CH$), 2.0 (m, 4 H, $=CHCH_2C\mathbf{H}_2CH$). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42; O, 16.82. Found: C, 75.20, 75.42; H, 7.46, 7.94.

1,4-Bis(*endo*-5-bicyclo[2.2.1]hept-2-enyl)butane-1,4-dione (9). Pure *endo*-5-acetylnorbornene was obtained from a commercial (Aldrich) sample of the isomer mixture by high-performance LC (eluant 10% ether in hexane). The endo isomer [bp 78–80 °C (20 mm)] shows a characteristic doublet of doublets at δ 6.0 for the olefinic protons in the NMR spectrum. The methine proton α to the carbonyl resonates at δ 3, overlapping with the bridgehead protons.

The enolate of *endo*-5-acetylnorbornene was prepared as usual with LDA and oxidized with ferric chloride as described. The crude product obtained was analyzed by GC (column A, 50–250 °C at 15 °C/min), and the yield of dimer was found to be 50%. Two recrystallizations of the product from ethanol–water gave the dimer as pale yellow needles: mp 69.5–72 °C; IR (CCl_4) 3050, 1710 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.15 (dd, 2 H, J = 5, 3 Hz, olefinic protons), 3.6–2.75 (m, 3 H, 2 bridgehead protons and CHCO), 2.68 (s, 4 H, $OCCH_2CH_2CO$), 2.0–1.1 (m, 4 H, ring protons).

Diethyl Succinate (10). LDA (12 mmol) was prepared as usual in 10 mL of dry THF and cooled to −78 °C. Ethyl acetate (0.97 mL, 0.88 g, 10 mmol; distilled from P_2O_5) was added dropwise via syringe. After 10 min, ferric chloride (1.78 g, 11 mmol) was added dropwise as a solution in 10 mL of dry DMF. The mixture was allowed to warm to room temperature. After being stirred overnight, the mixture was worked up as usual to give 0.67 g of crude product. The NMR spectrum of this material indicated it was diethyl succinate (~89% by weight) contaminated with small amounts of THF and hexane: yield 69%; NMR (60 MHz, $CDCl_3$) δ 4.15 (q, 4 H, J = 7 Hz, $CH_2C\mathbf{H}_2O$), 2.6 (s, 4 H, $COCH_2CH_2CO$), 1.25 (t, 6 H, J = 7 Hz, $C\mathbf{H}_3CH_2O$).

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Registry No. *meso*-**1**, 52690-71-8; *dl*-**1**, 52690-70-7; **2**, 75533-81-2; *meso*-**3**, 75533-82-3; *dl*-**3**, 75533-83-4; **4**, 51513-36-1; **5**, 27610-88-4; **6**, 75533-84-5; **7** (isomer 1), 75533-85-6; **7** (isomer 2), 75533-86-7; **8** (isomer 1), 75533-87-8; **8** (isomer 2), 75533-88-9; **9**, 75533-89-0; **10**, 123-25-1; *l*-carvone, 6485-40-1; cyclohexanone, 108-94-1; isophorone, 78-59-1; diisopropyl ketone, 565-80-0; pinocalone, 75-97-8; 2-phenylcyclohexanone, 1444-65-1; 2-cyclohexen-1-one, 930-68-7; *endo*-5-acetylnorbornene, 824-60-2; ethyl acetate, 141-78-6.

Supplementary Material Available: Table of atomic coordinates and thermal parameters (1 page). Ordering information is given on any current masthead page.

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Substituent Effects upon the Equilibration of 4-Cyano-1,4-dihydro-1-(substituted benzyl)nicotinamides with 1-(Substituted benzyl)nicotinamide Cations

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We have used the ring-substituted benzyl group ($XC_6H_4CH_2$) as a substituent on a nitrogen atom as a probe of charge generation (or charge neutralization) on that nitrogen atom in the transition states for a number of reactions of heterocyclic molecules.[1-3] This substituted benzyl group has a number of features which are attractive in its use as such a probe. (i) Substituents on the meta and para ring carbon atoms are relatively remote from the nitrogen atom, and so substituent effects are primarily electronic without any significant contribution from steric or solvation effects. (ii) The substituted phenyl ring is

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