$H_3)_2(CH_2)_{11}Br$, 111772-86-2; $(H_3C)_2CH(CH_2)_{11}Br$, 111772-90-8; $(H_3C)_2CH(CH_2)_{10}C_H3$, 1560-96-9; $HOC(CH_3)_2(CH_2)_{11}Cl$, 111772-87-3; $(H_3C)_2CH(CH_2)_{11}Cl$, 111793-80-7; 1-methyl-1-cyclododecanol, 32400-09-2; methylcyclododecanol, 1731-43-7; 1-butyl-1-cyclododecanol, 16282-71-6; butylcyclododecanol, 102860-64-0; 1-*tert*-butyl-1-cyclododecanol, 111772-83-9; *tert*-butylcyclododecanol, 61682-11-9; 2-(3-adamantyl)-2-propanol, 775-64-4; 2-(3-adamantyl)propane, 773-32-0; 1-butyl-1-cycloheptanol, 3898-34-8; butylcycloheptane, 13152-41-5; 1-butyl 4,4-dimethylcyclohexan-1-ol, 111772-88-4; 1-butyl-4,4-dimethylcyclohexane, 111772-91-9; cyclododecanone, 830-13-7; cycloheptanone, 502-42-1; 4,4-dimethylcyclohexanone, 4255-62-3; 5-methyl-undecan-5-ol, 21078-80-8; 5-methylundecane, 1632-70-8; Raney nickel, 7440-02-0.

The Structures of Marvel's δ-Lactone and "Polymer"

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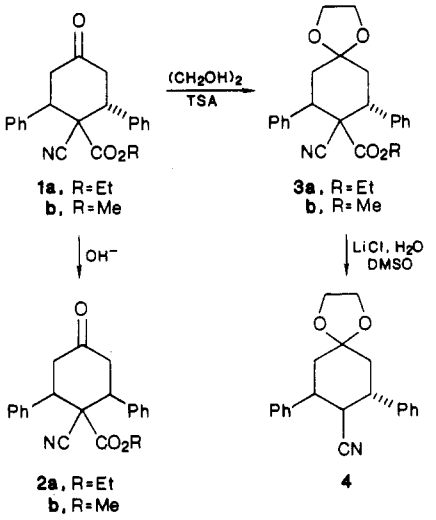
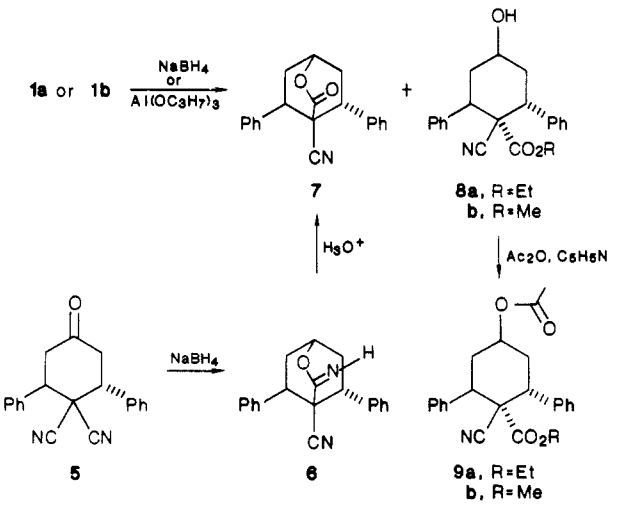
The Michael condensations of 1,5-disubstituted 1,4-pentadien-3-ones with certain addends provide efficient preparations of substituted cyclohexanones.[1] In the course of our studies[2] of Michael adducts, it became necessary to determine the configurations at C-2 and C-6 in two previously reported cyclohexanones: ethyl 1-cyano-2,6-diphenyl-4-oxocyclohexane-1-carboxylate (**1a**)[3] and 2,6-diphenyl-4-oxocyclohexane-1,1-dicarbonitrile (**5**).[4] Marvel and Moore[3] assumed that **1a** was one of the two possible meso isomers (phenyls cis) while NMR data[4c] indicated that the dicyano ketone **5** probably was the trans (±) isomer. We report here chemical and spectroscopic studies that make stereochemical assignments with certainty in **1a** and in **5**. We also present a complete elucidation of the products of the Meerwein–Ponndorf–Verley reduction of **1a** first reported by Marvel and Moore.[3]

Condensation of dibenzalacetone with ethyl cyanoacetate in ethanol or in ethyl ether with Triton B as the catalyst gave the oxo ethyl ester **1a**.[3] This material was converted by further treatment with base into the previously unknown isomeric ester **2a** (Scheme I). The behavior of **1a** parallels that of the trans methyl ester **1b**, which is known to be the labile product of the reaction of methyl cyanoacetate with dibenzalacetone and which can be isomerized by base to the cis isomer **2b**.[4c,5] Further chemical proof of the trans relationship of the phenyl substituents in **1a** was obtained by decarbalkoxylation[6] of the ethylene ketals (**3a** and **3b**) of the oxo esters **1a** and **1b**. In each case, the same cyano ketal **4** was obtained in good yield. The ^{13}C NMR spectrum (Table I) of **1a** exhibits a unique signal for each cyclohexanone ring carbon as expected for a trans relationship of the phenyl groups. In contrast, identical δ values for C-2/C-6 and for C-3/C-5 in **2a** confirm the meso character of this compound, presumably with a C-1 axial cyano group.[4c] The ^{13}C NMR spectrum of the dicyano ketone **5** (recorded also by Kingsbury[4c]) is consistent with a trans compound with rapidly equilibrating chair or twist conformations.

Scheme I



Scheme II



Sodium borohydride reduction of the dicyano ketone **5** gave the imino ester **6** in high yield (Scheme II). Compound **6** was obtained as a mixture of diastereomers about the C=NH unit in a ratio of ca. 7/3 as calculated from the appropriate signals in the ^{13}C NMR spectrum (Table II). Hydrolysis of **6** with aqueous HCl gave the δ-lactone **7** reported earlier.[3] Reduction of the ethyl ester **1a** by aluminum isopropoxide following Marvel and Moore[3] gave a mixture from which the δ-lactone **7** was readily isolated in 43% yield as an ether-insoluble precipitate. The formation of **7** from **5** as well as from **1a** provides conclusive evidence of **5** as the trans (±) isomer. The ether extract gave a syrup, which resisted all attempts at crystallization. The IR and ^1H NMR spectra of this material were inconsistent, however, with the "noncrystalline polymer" suggested[3] as the secondary product of the reduction as evidenced by the presence of the ethyl group. Chromatography of the oil on silica gel gave fractions that proved to be the hydroxy ester **8a**. The oil was identified from spectral data and by conversion to the solid acetate derivative **9a**.

Lactone **7** and the hydroxy ester **8a** also were obtained by $NaBH_4$ reduction of the ethyl ester **1a**. In similar fashion, the methyl ester **1b** was reduced to give **7**, accompanied by the noncrystalline hydroxy ester **8b**, which was characterized spectroscopically and by conversion to

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Table I. ^{13}C NMR Signals of Cyclohexanones and Relatives

compd	shifts[a] C-1	C-2	C-3	C-4	C-5	C-6	CN	others
1a	55.64	47.98	42.85	206.78	41.62	42.35	118.21	ester C=O, 166.00; ester CH_3, 13.37; ester CH_2, 62.63; Ar, 137.16 and 136.55 (ipso), 128.49, 128.40, 128.34, 128.22, 128.15
1b	55.64	48.16	42.85	207.89	41.63	42.34	118.24	ester C=O, 166.61; ester Me, 53.12; Ar, 137.33 and 136.66 (ipso), 129.29, 128.80, 128.72, 128.39
2a	59.20	49.25	43.65	204.34	43.65	49.25	115.92	ester C=O, 166.23; ester Me 13.37; ester CH_2, 62.40; Ar, 136.28 (ipso), 128.62, 128.50, 127.89
2b	59.56	49.34	43.59	204.05	43.59	49.34	115.90	ester C=O, 167.07; ester Me, 53.02; Ar, 136.41 (ipso), 128.89, 128.81, 127.92
3b	57.61	46.05	35.72	108.44	34.69	42.19	118.35	ketal CH_2, 63.78, 63.72; Ar, 138.43 and 137.32 (ipso), 128.47, 128.28, 128.11, 127.88, 127.81; ester C=O, 167.15; ester Me, 52.85
4	39.98	41.49	36.76	108.01	35.86	38.03	119.96	ketal CH_2, 64.34, 64.10; Ar, 141.09 and 140.70 (ipso), 128.56, 127.61, 127.36, 127.14, 126.86
5	45.01	45.64	42.37	198.80	42.37	45.64	113.85	Ar, 135.14 (ipso), 129.55, 129.18, 128.94
8a	56.33	41.72	36.15	65.55	35.33	41.72	118.77	ester C=O, 166.41; ester CH_3, 13.30, ester CH_2, 62.15; Ar, 138.96 and 138.56 (ipso), 128.84, 128.44, 128.34, 128.17, 127.75, 127.60

[a] Shifts in parts per million downfield from Me_4Si in $CDCl_3$ solutions (**3b** in DMSO-d_6).

its solid acetate **9b**. Hydroxy esters produced by $NaBH_4$ reduction of keto esters are known to cyclize under the reaction conditions if the functional groups have the appropriate fixed spacial relationship.[7] We observed no lactol product from further reduction of the δ-lactone as was found in another system.[7] Belletire has reported the facile conversion of dimethyl 4-hydroxycyclohexane-1,1-dicarboxylate to a δ-lactone by treatment with iodotrimethylsilane or by heating the hydroxy diester in benzene under catalysis by *p*-toluenesulfonic acid.[8] The ease of formation of the imino ester **6** and δ-lactone **7** directly from the oxo compounds upon reduction by $NaBH_4$ probably is due to the relatively low energy difference between the chair and boat (twist) conformations in these compounds.

Assignments of the cyclohexyl ring atoms in the ^{13}C NMR spectra of all trans compounds (Tables I and II) were made with the assumption that an axial phenyl group shields the substituted carbon to a greater extent than an equatorial phenyl.[9] Assignments of signals were made by using off-resonance or DEPT techniques.

Experimental Section

Melting points were taken in a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Micro-Analysis, Inc. IR spectra were measured with a Perkin-Elmer Model 281B spectrometer in 10% $CHCl_3$ solutions; only major frequencies are listed. ^1H NMR spectra were taken on a Varian T-60 spectrometer in $CDCl_3$ solutions with Me_4Si as the internal standard. ^{13}C NMR spectra were recorded on Varian CFT-20, Nicolet NT-360, Bruker WM-250, and JEOL FX-90Q instruments. Solutions were dried with anhydrous Na_2SO_4.

Ethyl 1-Cyano-*trans*-2(e),6(a)-diphenyl-4-oxocyclohexane-1(e)-carboxylate (1a). Method A. To a magnetically stirred suspension of 2.156 g (9.20 mmol) of dibenzalacetone in 16 mL of absolute EtOH was added 1.0 mL (1.1 g, 9.4 mmol) of ethyl cyanoacetate followed by 2 drops of Triton B and 4 mL of absolute EtOH. A thick white precipitate separated after about 6 min; 13 mL of absolute EtOH was added, and the solid was stirred with a spatula for a further 10 min. After standing at 0 °C for 1 h, the product was collected, pressed, and washed with cold absolute EtOH. Recrystallization from absolute EtOH containing 2 drops of glacial HOAc gave 1.936 g (61%) of **1a**: mp 140–141.5 °C (lit.[3] mp 137–138 °C); IR 2248, 1730 (br) cm^{-1}; ^1H NMR δ 0.83 (t, *J* = 7, 3 H), 2.57–3.17 (m, 4 H), 3.45–4.17 (m, 4 H), 7.32 (br s, 10 H).

Method B. To a vigorously swirled mixture of 20.00 g (85.4 mmol) of dibenzalacetone and 10.0 mL (10.6 g, 94 mmol) of ethyl cyanoacetate in 350 mL of ethyl ether were added 20 drops of Triton B and 10 mL of absolute EtOH. Most of the starting material dissolved within 10 min, and "feathery, white needles"[3] began to separate after an additional 5 min. After being cooled in the refrigerator for 1 h, the product was collected and pressed as it was washed with ether. Recrystallization from absolute EtOH gave 18.85 g (63%) of **1a**, mp 136–139.5 °C. The ^1H NMR spectrum was identical with that of **1a** prepared by method A.

Ethyl 1-Cyano-*cis*-2(e),6(e)-diphenyl-4-oxocyclohexane-1(e)-carboxylate (2a). A suspension of 516 mg (1.49 mmol) of the ethyl ester **1a** in 15 mL of absolute EtOH was treated with 1 drop of Triton B while being stirred magnetically at room temperature. After 1.7 h, the colorless solution was diluted with 50 mL of water. The resulting emulsion was extracted twice with ethyl ether, and the combined extracts were washed once with water, dried, and evaporated. Crystallization of the oil from ethyl ether–petroleum ether gave 396 mg (77%) of **2a** as tiny needles: mp 137–137.5 °C; IR 2243, 1730 (br) cm^{-1}; ^1H NMR δ 0.70 (t, *J* = 7, 3 H), 2.72 (d of d, br legs, *J* = 14 and 3, 2 H), 3.30 (t, *J* = 14, 2 H), 3.45–3.95 (m, 4 H), 7.42 (s, 10 H). Anal. Calcd for $C_{22}H_{21}NO_3$ (mol wt 347.4): C, 76.06; H, 6.09; N, 4.03. Found: C, 75.91; H, 6.07; N, 3.92.

Preparation of Ethylene Ketals. General Procedure. The ketone was heated under reflux with constant water separation in the given volume of benzene containing ethylene glycol and *p*-toluenesulfonic acid monohydrate (TSA). The cooled mixture was treated with excess 0.5 M NaOH solution and shaken with water. The benzene layer was washed twice with water, dried over anhydrous K_2CO_3, and processed as indicated in the individual preparations.

Ethyl 1-Cyano-*trans*-2(e),6(a)-diphenyl-4,4-(ethylenedioxy)cyclohexane-1(e)-carboxylate (3a). A mixture of 10.00 g (28.8 mmol) of the ethyl ester **1a**, 10 mL of ethylene glycol, and 0.60 g of TSA in 200 mL of benzene was boiled for 2.25 h. The dried benzene was removed, and the resulting oil was crystallized from ethyl ether to yield 9.072 g (81%) of **3a**: mp 118–119 °C; IR 2242, 1734, 1117, 1024 cm^{-1}; ^1H NMR δ 0.72 (t, *J* = 7, 3 H), 1.97 (t, *J* = 3, 1 H), 2.27 (t, *J* = 3, 1 H), 2.67 (t, *J* = 14, 1 H), 2.83 (t, *J* = 14, 1 H), 3.5–4.18 (m, 8 H), 7.35 and 7.37 (both s, 10 H). Anal. Calcd for $C_{24}H_{25}NO_4$ (mol wt 391.5): C, 73.64; H, 6.44; N, 3.58. Found: C, 73.43; H, 6.27; N, 3.38.

Methyl 1-Cyano-*trans*-2(e),6(a)-diphenyl-4,4-(ethylenedioxy)cyclohexane-1(e)-carboxylate (3b). A mixture of 30.0 g (90.1 mmol) of ketone **1b**,[5a,b] 30 mL of ethylene glycol, and 1.8 g of TSA in 600 mL of benzene was boiled for 3.3 h. The dried benzene solution was evaporated to dryness under reduced pressure, and the residual oil was dissolved in 350 mL of boiling ether. Cooling resulted in the deposition of 23.6 g (69%) of **3b** as a white powder: mp 125.5–127 °C; IR 2240, 1738, 1117 cm^{-1}; ^1H NMR δ 1.95 (t, *J* = 3, 1 H), 2.18 (t, *J* = 3, 1 H), 2.63 (t, *J* = 14, 1 H), 2.80 (t, *J* = 14, 1 H), 3.20 (s, 3 H), 3.63 (d, *J* = 4, 1 H), 3.83–4.17 (m, 5 H), 7.33 and 7.37 (both s, 10 H). Anal. Calcd for $C_{23}H_{23}NO_4$ (mol wt 377.4): C, 73.19; H, 6.14; N, 3.71. Found: C, 73.42; H, 6.28; N, 3.73.

Decarbalkoxylations. General Procedure. A mixture of the ester, LiCl, and water in Me_2SO was heated with magnetic stirring up to the given oil bath temperature and maintained until the evolution of CO_2 [determined by precipitation of $BaCO_3$ from $Ba(OH)_2$ solution] had ceased. In each reaction, precipitation

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Table II. ^{13}C NMR Signals of Imino Ester 6 and δ-Lactone 7

compd	shifts[a] C-1	C-3	C-4	C-5	C-6	C-7	C-8	CN	others
6[b]	72.94 (72.19)	163.05 (165.99)	49.31 (52.71)	44.17 (43.89)	34.00 (33.77)	31.49 (31.11)	38.77 (38.60)	116.15	Ar, 139.40 (138.94) and 136.04 (135.88) (ipso), 129.13, 129.04, 128.74, 128.62, 128.44, 127.92, 127.65
7	74.89	167.78	52.31	43.16	34.05	31.05	39.31	114.93	Ar, 138.85 and 134.86 (ipso), 129.06, 128.83, 128.75, 128.17, 128.04

[a] Shifts in parts per million downfield from Me_4Si in $CDCl_3$. [b] Shifts in parentheses are due to the minor diastereomer.

of Li_2CO_3 in the reaction flask accompanied the CO_2 evolution. The cooled solution was diluted with ice and water and worked up as given in the individual case.

***trans*-2(e),6(a)-Diphenyl-4,4-(ethylenedioxy)cyclohexane-1(e)-carbonitrile (4). Method A.** A mixture of 13.129 g (34.79 mmol) of the cyano methyl ester **3b**, 3.108 g (73.3 mmol) of LiCl, 3.2 mL (200 mmol) of water, and 130 mL of Me_2SO was heated to 173 °C over the course of 4 h.[6] (Vigorous CO_2 evolution and precipitation of Li_2CO_3 occurred at ca. 140 °C.) Workup gave an off-white precipitate, which was collected, washed well with water, taken up in acetone, and filtered to remove a small amount of insoluble material. The solution was concentrated to about 40 mL and diluted with an equal volume of methanol, giving 9.732 g (88%) of the cyano ketal **4** as needles: mp 146–148 °C; IR 2240, 1110 cm^{-1}; ^1H NMR δ 1.67–2.67 (m, 4 H), 3.33–3.80 (m, 3 H), 3.92 (nar m, 4 H), 7.38 and 7.45 (s and m, 10 H). Anal. Calcd for $C_{21}H_{21}NO_2$ (mol wt 319.4): C, 78.97; H, 6.63; N, 4.39. Found: C, 79.06; H, 6.86; N, 4.43.

Method B. A mixture of 2.003 g (5.12 mmol) of the cyano ethyl ester **3a**, 488 mg (11.5 mmol) of LiCl, 0.6 mL (30 mmol) of water, and 20 mL of Me_2SO was heated from 147 to 170 °C over the course of 4.5 h. Isolation and recrystallization of the product as in method A gave 1.267 g (78%) of **4** as needles with mp 145.5–147 °C. The ^1H NMR spectrum of the product was identical with that of **4** prepared from **3b**.

3-Imino-4-cyano-*trans*-5,8-diphenyl-2-oxabicyclo[2.2.2]octane (6). To a magnetically stirred suspension of 4.099 g (13.7 mmol) of the dicyano ketone **5**[4a-c] in 80 mL of absolute EtOH at room temperature was added 544 mg (14.4 mmol) of $NaBH_4$. The mixture was stirred for 23 min and then treated with an additional 103 mg (2.72 mmol) of $NaBH_4$ and 8 mL of absolute EtOH. After being stirred for a total of 1.5 h, the mixture was diluted with 200 mL of water and then cooled in an ice bath. The white precipitate was collected, washed with water, and recrystallized from acetone–water to yield 3.820 g (93%) of the imino ester **6** (mixture of diastereomers) as white plates: mp 178–179 °C; IR 3340, 3300, 2254, 1682, 1383, 1073 cm^{-1}; ^1H NMR δ 1.90–2.90 (m, 4 H), 3.37–3.83 (m, 2 H), 4.82 (m, $W_{1/2}$ = 9, 1 H), 7.22 (nar m, includes NH, 6 H), 7.48 (s, 5 H). Anal. Calcd for $C_{20}H_{18}N_2O$ (mol wt 302.4): C, 79.44; H, 6.00; N, 9.27. Found: C, 79.70; H, 5.85; N, 9.08.

Acid Hydrolysis of Imino Ester 6. A suspension of 306 mg (1.01 mmol) of **6** in 12 mL of 2 M HCl was stirred magnetically for a total of 21 h. (The mixture was diluted three times with water: 25 mL after 3 min, 10 mL after 1.5 h, and 10 mL after 5.5 h.) The white precipitate was collected, washed with water, and recrystallized from acetone–MeOH to give 238 mg of 4-cyano-*trans*-5,8-diphenyl-2-oxabicyclo[2.2.2]octan-3-one (**7**): mp 233.5–234.5 °C; IR 2255, 1765 cm^{-1} [lit.[3] 2265, 1766 cm^{-1}]; ^1H NMR (DMSO-d_6) δ 2.0–3.1 (m, 4 H), 3.37–4.08 (m, 2 H), 5.25 (m, $W_{1/2}$ = 9, 1 H), 7.0–7.7 (m, 10 H). The mixture melting point with **7** prepared from **1b**[3] was 234–235.5 °C, and the ^1H NMR spectra of the two δ-lactone samples were identical.

A further 25-mg sample with mp 232.5–233.5 °C was obtained by concentration of the mother liquor: total yield of **7**, 86%.

Reduction of 1a. Method A.[3] To a warm suspension of 2.000 g (5.76 mmol) of **1a** in 10 mL of 2-propanol were added 2.70 g (13.2 mmol) of aluminum isopropoxide and 10 mL of 2-propanol. The solution was distilled slowly through an uncooled vertical condenser to which was attached a short path still body. The distillate gave a negative 2,4-DNP test for acetone after 35 min. After another 15 min, a white solid separated from the reaction mixture (4.6 mL of distillate had been collected). The mixture was cooled in an ice bath, acidified with 20 mL of 3 M HCl, and poured into a separatory funnel. The suspension was shaken with ethyl ether, and the aqueous phase was discarded. The ether suspension was washed once with water and then filtered to yield the δ-lactone **7** as a white powder. Recrystallization from acetone–MeOH gave 709 mg of **7** with mp 234–235.5 °C [lit.[3] mp 227–228 °C]. The melting point undepressed upon admixture with **7** prepared by $NaBH_4$ reduction of the methyl ester **1b**. Concentration of the mother liquor gave two additional crops of **7**: 31 mg with mp 234.5–235.5 °C and 17 mg with mp 234–235 °C; total yield, 43%.

The combined ether extracts were dried and evaporated to give 1.263 g of a white foam whose ^1H NMR spectrum was in good agreement with that expected for a hydroxy cyano ethyl ester. When dissolved in 95% EtOH, the cold solution deposited 36 mg of the δ-lactone **7**, mp 232.5–233.5 °C. The oil that resulted from evaporation of the mother liquor could not be crystallized from a variety of solvents. A 528-mg sample of the oil chromatographed on silica gel was found to be methyl 1-cyano-2(e),6(a)-diphenyl-4(e)-hydroxycyclohexane-1(e)-carboxylate (**8a**) as a homogeneous colorless oil: IR 3608, 3470, 2244, 1734 cm^{-1}; ^1H NMR δ 0.77 (t, J = 7, 3 H), 2.07 (OH, removed by D_2O exchange, 1 H), ~1.83–2.77 (m, 4 H), 3.65 (q, J = 7, 2 H), ~3.5–3.93 (m, 2 H), 4.50 (m, W = 34, 1 H), 7.3 (s, 10 H). Anal. Calcd for $C_{22}H_{23}NO_3$ (mol wt 349.4): C, 75.62; H, 6.63; N, 4.01. Found: C, 75.35; H, 6.87; N, 3.84.

Method B. To a magnetically stirred suspension of 3.020 g (8.69 mmol) of **1a** in 45 mL of absolute EtOH were added 303 mg (8.01 mmol) of $NaBH_4$ and 8 mL of absolute EtOH at room temperature. Complete dissolution occurred within 2 min followed by precipitation within another 5 min. After a total reaction time of 45 min, the mixture was diluted with 150 mL of water. The flask was cooled at 0 °C as the amorphous material was worked with a glass rod. The product was collected, washed with water, and crystallized from acetone–MeOH to yield 1.039 g (39%) of the δ-lactone **7**, mp 234–235.5 °C.

The mother liquor was evaporated to give 1.84 g of a pale yellow glass whose IR and ^1H NMR spectra were consistent with the hydroxy cyano ester **8a** obtained as the byproduct from method A. This material was not investigated further.

Ethyl 1-Cyano-*trans*-2(e),6(a)-diphenyl-4(e)-acetoxycyclohexane-1-carboxylate (9a). A solution of 512 mg (1.47 mmol) of **8a** in 4 mL of pyridine and 4 mL of acetic anhydride was allowed to remain at room temperature for 20 h. Crushed ice and 5 mL of 6 M HCl were added, and the resulting gum gradually solidified at 0 °C when worked with a glass rod. The solid was collected, washed well with water, and crystallized from 95% EtOH to yield 418 mg (73%) of **9a** as white needles: mp 122–122.5 °C; IR 2241, 1730 cm^{-1}; ^1H NMR δ 0.75 (t, J = 7, 3 H), 2.05 (s, 3 H), ~2.0–2.77 (m, 4 H), 3.65 (q, $J \cong$ 7, 2 H), ~3.7–3.95 (m, 2 H), 5.52 (m, W = 31, 1 H), 7.32 (nar m, 10 H). Anal. Calcd for $C_{24}H_{25}NO_4$ (mol wt 391.5): C, 73.64; H, 6.44; N, 3.58. Found: C, 73.40; H, 6.15; N, 3.53.

Sodium Borohydride Reduction of 1b. To a magnetically stirred suspension of 14.00 g (42.0 mmol) of **1b** in 220 mL of absolute EtOH were added 1.62 g (42.8 mmol) of $NaBH_4$ and 35 mL of absolute EtOH at room temperature. After 2.5 h, the suspension was diluted with 700 mL of water, stirred for 15 min, and cooled at 0 °C for 1.5 h. The white powder was collected, washed with water, and recrystallized from acetone–MeOH to give 6.12 g of the δ-lactone **7**, mp 234–235.5 °C. The mp was undepressed upon admixture with **7** prepared by hydrolysis of the imino ester **6**. Anal. Calcd for $C_{20}H_{17}NO_2$ (mol wt 303.4): C, 79.18; H, 5.65; N, 4.62. Found: C, 79.28; H, 5.66; N, 4.52.

The solid obtained by concentration of the mother liquor was recrystallized from acetone–MeOH to give an additional 675 mg of **7** with mp 235–236.5 °C; total yield, 54%.

The foam obtained by evaporation of the main mother liquor was chromatographed in two parts on silica gel. Elution with CH_2Cl_2 and 10% MeOH–CH_2Cl_2 gave a total of 4.51 g (32%) of methyl 1-cyano-*trans*-2(e),6(a)-diphenyl-4(e)-hydroxycyclohexane-1(e)-carboxylate (**8b**) as a colorless glass: IR 3600, 3460, 2241, 1738 (sh at 1750) cm^{-1}; ^1H NMR δ 1.97–2.67 (m, 4 H), 3.22 (s, 3 H), 3.55–3.95 (m, 2 H), 4.52 (m, $W \cong 40$, 1 H), 7.32 (s, 10 H). Anal. Calcd for $C_{21}H_{21}NO_3$ (mol wt 335.4): C, 75.20; H, 6.31; N, 4.18. Found: C, 75.42; H, 6.52; N, 3.99.

Methyl 1-Cyano-*trans*-2(e),6(a)-diphenyl-4-acetoxycyclohexane-1(e)-carboxylate (9b). A solution of 707 mg (2.11 mmol) of **9a** in 6 mL of pyridine and 1.5 mL of acetic anhydride was allowed to stand at room temperature for 17 h. Crushed ice and 6 mL of concentrated HCl were added with stirring. The resulting white powder was collected, washed with water, and recrystallized from 50% EtOH to give 555 mg (70%) of the acetate **9b** as tiny white crystals: mp 122.5–124 °C; IR 2244, 1735 cm^{-1}; ^1H NMR δ ~2.07 (s, 3 H), 2.0–2.67 (m, 4 H), 3.23 (s, 3 H), 3.60–3.97 (m, 2 H), 5.53 (m, $W \cong 38$, 1 H), 7.33 (s, 10 H).

When recrystallized again from EtOH–water, **9b** showed mp 142–143 °C. When another sample of the lower melting form of **9b** was recrystallized similarly but with seeding by the 143 °C material, the precipitate had mp 142–143 °C. Seeding of a solution of the higher melting polymorph gave **9b** with mp 123 °C in part and then 143–144 °C. Anal. Calcd for $C_{23}H_{23}NO_4$ (mol wt 377.4): C, 73.19; H, 6.14; N, 3.71. Found: C, 73.34; H, 6.15; N, 3.71.

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Registry No. (±)-**1a**, 111904-71-3; (±)-**1b**, 63087-40-1; **2a**, 111904-72-4; (±)-**3a**, 111904-73-5; (±)-**3b**, 111904-74-6; (±)-**4**, 111904-75-7; (±)-**5**, 62940-83-4; (±)-(*E*)-**6**, 111904-76-8; (±)-(*Z*)-**6**, 111957-24-5; (±)-**7**, 111904-77-9; (±)-**8a**, 111904-78-0; (±)-**8b**, 111904-80-4; (±)-**9a**, 111904-79-1; (±)-**9b**, 111904-81-5; PhCh=CHCOCH=Ph, 538-58-9; EtO_2CCH_2CN, 105-56-6.

Preparation of Nitronium Tetrafluoroborate Free of Nitrosonium Ions

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In the course of our studies[1] on aromatic nitrations with nitronium tetrafluoroborate (NO_2BF_4), we were unable to obtain this salt with purities greater than about 80% from commercial sources.[2] The major impurity was found to be nitrosonium tetrafluoroborate ($NOBF_4$). During the course of their nitration studies, Yoshida and Ridd[3] found that commercial sources of NO_2PF_6 contained considerable amounts of $NOPF_6$ as an impurity. They described a method to separate $NOPF_6$ from NO_2PF_6 on the basis of solubility differences, but this technique is not readily applicable to the purification of NO_2BF_4. Although Olah et al.[4] have reported on the preparation of pure NO_2BF_4 by treating NO_2F with BF_3, we could not locate a commercial source of NO_2F; its preparation is quite elaborate.[5] Kuhn[6] reported two methods for the preparation of NO_2^+ salts, one from nitric acid, and the other from alkyl nitrate esters. The latter method reportedly gives a pure product.

It was suspected that the commercial samples of NO_2BF_4 were prepared by the method of Olah and Kuhn[7] where 95% red fuming nitric acid, anhydrous HF, and anhydrous BF_3 are combined in CH_2Cl_2 (eq 1). The source then of

$$HNO_3 + HF + 2BF_3 \rightarrow NO_2BF_4 + H_2O{\cdot}BF_3 \quad (1)$$

the large amounts of $NOBF_4$ in these samples probably arises in part from the large amounts of dissolved nitrous oxides in the nitric acid[8] (eq 2). Utilizing nitric acid that

$$N_2O_4(N_2O_3) + BF_3 + HF \xrightarrow{HNO_3} NOBF_4 + NO_2BF_4 + H_2O{\cdot}BF_3 \quad (2)$$

is free of nitrous oxides should provide NO_2BF_4 free of $NOBF_4$. Indeed, when purified anhydrous nitric acid was used in the preparation, the product was better than 95% NO_2BF_4, and no $NOBF_4$ could be detected in the sample (vide infra).

The determination of the nitronium ion and nitrosonium ion content in samples of NO_2BF_4 is not a trivial matter. An adaptation of the method of Yoshida and Ridd[3] was found suitable for determining NO_2^+ content. The method employs nitrating a twofold excess of 4-nitrotoluene directly in an NMR tube (CD_3CN) with a weighed amount of the NO_2BF_4 to be analyzed. Integration of the methyl signals of the formed 2,4-dinitrotoluene and unreacted 4-nitrotoluene gives the amount of NO_2^+ in the sample. It is known from previous work that this nitration reaction is quantitative with NO_2BF_4. Performing this reaction directly in the NMR tube reduces the limits of error in the analysis since workup and isolation are eliminated. Under these conditions, 4-nitrotoluene is inert with $NOBF_4$.

The determination of NO^+ in the presence of NO_2^+ is much less straightforward. This can be determined qualitatively by both Raman and infrared spectroscopy. Raman spectra of solid samples of NO_2BF_4 with small amounts of $NOBF_4$ showed only the symmetrical stretching frequency of NO_2^+ at 1400 cm^{-1}. It was only when these samples were dissolved in a solvent (e.g. 96% or 100% H_2SO_4) that the symmetrical stretching frequency of NO^+ at 2325 cm^{-1} was seen. The presence of NO^+ in samples of NO_2BF_4 could also be readily detected by preparing the 1:1 complex with 18-crown-6 ether in CH_2Cl_2.

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