$\times 10^{-3}$ s^{-1}, $k_{OH^-}[OH^-]$ is $(0.6 \pm 0.2) \times 10^{-3}$ s^{-1}, and k_{Et_2NH} is $(2.5 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}.[6] The Et_2NH-dependent term is 27 ± 3% of k_{obs} under the conditions of the product study, but **9a** is only 16 ± 1% of the reaction products. This indicates that a substantial part of the Et_2NH-dependent term may be due to ester aminolysis (eq 2), which generates the hydroxylamine **6**.[7] Indeed, at pH 11.2 (μ = 1.0 M, T = 25 °C) in the absence of Et_2NH, **6** is isolated in only 3 ± 1% yield.

The presence of **9a** shows that the nucleophilic displacement of eq 1 can compete with S_N1 solvolysis of **2a** under aqueous conditions. The decomposition of the more reactive ester **2b**[2b] in an Et_2NH buffer identical with that described previously generates **9b** in 1.0 ± 0.1% yield. This compound is similar in reactivity to the suspected carcinogenic metabolites of polycyclic aromatic amines.[2b] The substituent effects noted in these product studies indicate that if ρ^+ is −6.0 for the S_N1 solvolysis of **2** in an aqueous solution,[8] then ρ^+ is ca. −3 for the S_N2 substitution of **2** by Et_2NH. This relatively low sensitivity to the aromatic substituent is in accord with expectations.[2b]

These results demonstrate that nucleophilic attack on the nitrogen of ester derivatives of *N*-arylhydroxylamines can compete with S_N1 solvolysis in aqueous solutions, but the solvolysis will predominate at low to moderate concentrations of the nucleophile (≤1 M). The results with OH^- show that acyl transfer (eq 2) can also occur efficiently. We are continuing to examine the nature of the bimolecular nucleophilic displacement reactions of **2** in an effort to understand the factors that determine the site of nucleophilic attack.

Experimental Section

The syntheses of **2a** and **2b** have been described.[2b,4] All water used in the kinetic and product studies was distilled, deionized, and then distilled again in an all-glass apparatus. The purification of CH_3CN has been described.[9] All reactions were run in glassware or plasticware that had been soaked in an EDTA solution (pH ≈ 12) and rinsed with deionized water. All aqueous solutions contained 5% CH_3CN by volume, and ionic strength was maintained at 0.5 M with KCl; pH was maintained with phosphate, borate, or carbonate buffers or KOH. $(Et)_2NH$ was distilled from CaH under a N_2 atmosphere prior to use.

Kinetics. The appropriate solution (3 mL) was transferred to a thunberg cuvette and outgassed with a rapid stream of N_2 for ca. 30 min before it was equilibrated at 40 °C in the thermostated cell holder of a Cary 2290 UV–vis spectrophotometer. Reactions were initiated by injection of 15 μL of a ca. 0.015 M stock solution of **2a** in CH_3CN to obtain an initial concentration of ca. 7.5×10^{-5} M. Progress of the reaction was monitored at 233 and 260 nm. The absorbance vs time data were fit to the appropriate rate equation by nonlinear least-squares methods. The pH of solutions was measured at 40 °C after the kinetic run. An apparent pK_w of 13.52 ± 0.02 was obtained for the solvent system at 40 °C by measurement of pH at known concentrations of OH^- in the range 0.01–0.50 M.

Product Studies. These studies were run at the same concentrations as the kinetic runs on a 25-mL scale. The buffer was outgassed with N_2 for 3–4 h before the reaction was initiated. After ca. 10 half-lives, the products were quantified by HPLC (μ-Bondapak-C_{18} column, 6/4 MeOH/H_2O, 1.0 mL/min, 250 nm, 20-μL injections). Comparisons were made to authentic compounds in all cases by HPLC and GC/MS. It was necessary to quench the KOH solutions with appropriate amounts of 1 M KH_2PO_4 to avoid oxidation of the hydroxylamine **6** during quantification.

^{18}O Experiment. The addition of 0.5 mL of 45% ^{18}O-enriched H_2O (determined by MS analysis of a sample of lauric acid generated by hydrolysis of lauroyl chloride in $[^{18}O]H_2O$) to 1.0 mL of a 0.75 M KOH solution generated a 0.5 M KOH solution with an ^{18}O enrichment of ca. 15%. After outgassing of the solution and incubation at 40 °C for an appropriate time, the mixture was brought to 7.5×10^{-4} M in **2a** by injection of a ca. 1 M stock solution of **2a** in CH_3CN. After completion, the reaction was quenched by addition of 1 M KH_2PO_4 and the reaction products were extracted into CH_2Cl_2 (3 × 5 mL), dried briefly over Na_2SO_4, concentrated, and analyzed by GC/MS on a Hewlett-Packard 5890 gas chromatograph equipped with a 5971A mass-selective detector. The column used was a 25 m × 0.1 mm fused silica column with a 0.1 μ-bonded methyl silicone stationary phase. The reaction was run in duplicate and compared to duplicate runs in ordinary H_2O.

Et_2NH Reactions. These reactions were run under conditions similar to the other product studies except that Et_2NH was used as the buffer, ionic strength was maintained at 1 M, and reactions were done at 25 °C. The hydrazine **9a** was compared to an authentic sample prepared in an earlier study.[10] An authentic sample of **9b** was prepared by decomposition of **2b** in neat Et_2NH. After 24 h, the Et_2NH was removed by rotary evaporation, and the residue was taken up into CH_2Cl_2. This solution was extracted with 5% $NaHCO_3$, dried over Na_2SO_4, and evaporated to dryness. The yellow oil was then purified by chromatography on silica gel (CH_2Cl_2 eluent): IR (neat) 3286, 3015, 2972, 1614, 1514, 1251 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.07 (6 H, t, J = 7.0 Hz), 2.24 (3 H, s), 2.75 (4 H, q, J = 7.0 Hz), 4.20, (1 H, s, broad) 6.78 (d, J = 8.4 Hz), 6.99 (d, J = 8.4 Hz); GC/MS m/e 178 (M^+), 163, 149, 135, 106, 91; high-resolution MS m/e 178.1492, $C_{11}H_{18}N_2$ requires m/e 178.1471.

The yield of **9a** was obtained by HPLC as described previously. Quantification of the yield of **9b** was performed by GC/MS on the same column used for the ^{18}O analysis. The authentic samples of **9a** and **9b** were used to calibrate peak areas in a standard fashion.

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Supplementary Material Available: Table of rate constants vs pH for **2a** (1 page). Ordering information is given on any current masthead page.

(6) Hydrolysis in phosphate and acetate buffers at pH < 7 provided k_0 under these conditions, $k_{OH^-}[OH^-]$ was obtained from measurements in KOH solution at pH 11.2, and k_{Et_2NH} was obtained from the slope of k_{obs} vs $[Et_2NH]$ at pH 11.2 in the Et_2NH concentration range 0.0–1.0 M.

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Photochemistry of Large-Ring 2-Phenylcycloalkanones in Various Environments. Intramolecular Para Coupling Products of Acyl Benzyl Biradicals

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The photochemistry of five- and six-membered cycloalkanones has played an important role in mechanistic organic chemistry and in our knowledge of biradicals.[1,2] The photolysis of 2-phenylcyclopentanone and -cyclo-

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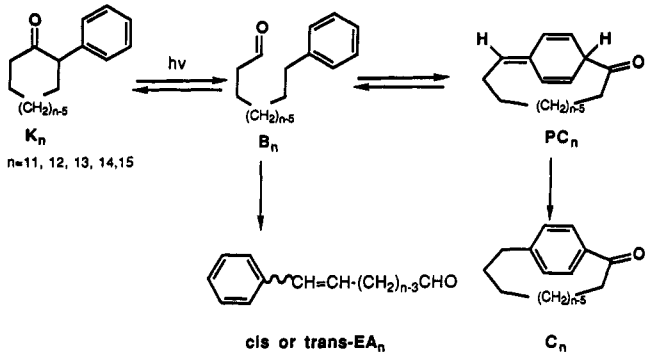
Scheme I



hexanone yields alkenals in good yields.[3,4] However, for the photochemistry of large-ring unsubstituted cycloalkanones, the dominant primary process if γ-hydrogen abstraction, which affords cyclobutanol derivatives,[5] although 2-methyl-substituted cyclododecanones undergo both α-cleavage and γ-hydrogen abstraction.[6,7] We report the photochemistry of large-ring 2-phenylcycloalkanones[8] (11- to 15-membered) that produce cyclophanes as major products under different conditions.

The 2-phenylcycloalkanones K_n (where n labels the original ring size, Scheme I) were prepared from corresponding cycloalkanones by conventional synthetic methodologies[9] and characterized by ^1H NMR, IR, UV, and MS. The photolyses of K_n in different solvents, such as DMF, CH_3CN, MeOH, n-C_6H_{14}, and C_6H_6, result in formation of the cyclophanes, C_n, as the major products. In DMF, the photolysis of K_n produces over 90% cyclophanes, even at high conversion of the starting ketone. This result implies that C_n are photochemically stable relative to K_n under the reaction conditions in DMF. However, the products (Table I) C_n from K_n (n = 13–15) are photochemically active in n-C_6H_{14}, C_6H_6, and MeOH;[10] thus, for the product distribution studies the conversion of K_n (n = 13–15) was controlled below 15%. The photolysis products were separated and characterized by ^1H and ^{13}C NMR, IR, UV, and MS. ^1H NMR spectra of cyclophanes are especially characteristic, all displaying two doublets in the phenyl region, the characteristic pattern of the aromatic AA'XX' four protons in a para unsymmetrically substituted benzene ring.[11]

The effect of microenvironmental conditions on the photolysis of K_n was investigated by conducting the photolyses in aqueous solutions of anionic micelles (sodium dodecylsulfate, SDS) and cationic micelles (dodecyltrimethylammonium chloride, DTCl, and hexadecyltrimethylammonium chloride, HTCl) and on the zeolite surfaces (Na-LZ-105 and NaX). Micelles offer a hydrophobic organic cage of the order of 10's of angstroms in size surrounded by charges,[12] and K_n resides in the cage. This restricted environment presumably affects the motion of K_n and of the photochemically produced biradicals inside the micelle cage. Therefore, it may affect the chemistry that occurs inside the micelle. Other types of restricted environments are the surface of solids and micropores of zeolites. The molecular sieve NaX, a faujasite zeolite, possesses an 8-Å pore to its 13-Å internal supercages.[13] so that the K_n can diffuse throughout the porous internal surface of the zeolite. Once K_n is transformed to a cyclophane within a supercage, the cyclophanes cannot be extracted by conventional extraction methods due to the increase in kinetic size from K_n to C_n.[8a] Therefore, the cyclophanes must be extracted after the dissolution of the entire zeolite framework with HCl followed by neutralization with NaOH. Because Na-LZ-105 is a pentasil-type zeolite possessing ~5.5-Å channel openings,[14] K_n cannot be inside the channel and the cyclophanes are formed on the external surface only and can be easily extracted by an organic solvent.

Table I. Product Distribution for Photolysis of 2-Phenylcycloalkanones[a]

K_n, n =	C_n	*cis*-EA_n	*trans*-EA_n	C_n	*cis*-EA_n	*trans*-EA_n
		DMF			Hexane	
11	98	0	2.0	91	5.3	3.5
12	92	3.2	4.8	86	5.8	8.6
13	92	6.0	2.0	60	27	13
14	86	8.1	6.1	48	12	39
15	93	4.8	2.3	64	6	30
		SDS Micelles			DTCl Micelles	
11	90	10	0	100	0	0
12	89	5.6	5.3	98	0.5	1.6
13	60	40	0	65	18	17
14	86	0	14	96	2.9	1.0
15	70	11	19	94	4.8	1.4
		NaX			Na-LZ-105	
11	93	0	7.0	94	0	6.0
12	90	0	10	92	0	8.0
13	91	2.2	7.0	95	0	5.0
14	80	0	20	90	6.9	2.9
15	78	0	22	100	0	0

[a] Vide infra (2) in Experimental Section.

The results in Table I clearly show that the microheterogeneous environments, such as micelles and zeolite surfaces, do not strongly influence the product distribution produced in the photolysis of K_n. The photolysis of K_n was also carried out at low temperature (−55 °C both in n-C_6H_{14} and DMF; −85 °C in n-C_6H_{14}) and under the influence of a magnetic field (field strength 2.2 kG). No effect on the products of photolysis of K_n was found, although both temperature and magnetic field affect the lifetime of B_n dramatically.[15]

The formation of cyclophanes (C_n) is postulated to result from para coupling of the biradical intermediate B_n to produce a precursor (PC_n) to the isolated C_n (Scheme I). Related para couplings have been reported in the dimerization of cumyl radicals[16a,b,17] and from CIDNP experi-

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ments.[16c] A para coupling of the $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ radical pair produced by photolysis of dibenzyl ketone (DBK) has been proposed to produce a semibenzylic product,[17] which then thermally cleaved back to the radical pair or was stablized by a hydrogen shift to yield 1-phenyl-4-methylacetophenone (PMAP). It was later discovered that PMAP was produced in varying yields by photolysis of DBK in micelles,[18] on porous silica,[19] and on zeolites.[20] However, in the case of K_n the intramolecular para coupling of acyl and benzyl biradical centers is the major process to stabilize the intermediate under various conditions. To date, only when K_n is photolyzed in the solid state as its cyclodextrin complex is the intramolecular disproportionation of acyl benzyl biradical, producing cis and trans alkenals, the major process.[21]

In summary, the dominant products from the photolysis of large α-phenylcycloalkanones are the cyclophanes formed by the intramolecular para coupling of the acyl benzyl biradical intermediate. This tendency to form cyclophanes is preserved under a variety of environmental conditions (organic solvents, micelles, and zeolites).

Experimental Section

^{1}H NMR spectra were obtained at 300 MHz for the cyclophanes and at 400 MHz for the alkenals and the 2-phenylcycloalkanones. ^{13}C NMR spectra were obtained at 75 MHz. Preparative TLC was performed on 1-mm thick plates of Merck silica gel 60 F254s with concentrating zone. Column chromatography was carried out with ICN Industries, Inc., 60–200-μm silica gel.

(1) Preparation of 2-Phenylcycloalkanones. K_n, except for K_{14}, were prepared from corresponding cycloalkanones (Aldrich). For the synthesis of K_{14}, tetradecanone was prepared from tetradecanedioic acid (Nippon Mining).[22] The following is a typical example of the preparation of K_n.

Cyclododecanone (5 g, 0.027 mol) was treated with 15.1 mL of 2 M (0.0303 mol) solution of phenyllithium in 150 mL of THF at −78 °C under Ar to yield 6.9 g of the crude tertiary alcohol (approximately 80% pure by NMR, 78% yield based on cyclododecanone). The crude alcohol was dehydrated by treatment with 130 mg of toluenesulfonic acid in 250 mL of benzene for 2 h to yield 6.3 g of 80% pure alkene (98% yield). The resulting crude alkene was purified by silica gel chromatography with hexane elutant to yield 4.4 g of material (92% purity by NMR). The resulting alkene (3.2 g, 0.0132 mol) was treated with 14.8 mL of 1 M solution of borane in THF (which was diluted with 40 mL of THF) in an ice bath for 2 h. The solution was then allowed to warm to room temperature. To this solution was added 2 mL of water, then 5.0 mL of 3 M NaOH, and then 1.43 mL of 30% H_2O_2 to yield 3.4 g (94% pure by NMR, 100% yield) of the secondary alcohol. The secondary alcohol was vigorously stirred with 2.98 g of pyridinium chlorochromate in 20 mL of dry CH_2Cl_2 for 4 h to yield 2.7 g of α-phenylcyclododecanone, K_{12} (80% purity by NMR). Purification of the material by flash chromatography with 5% ether in hexane yielded 2.0 g of 99% pure material (62% yield based on secondary alcohol).

The ketones K_n were characterized by ^{1}H NMR, MS, UV, and FTIR. Their salient spectral features are the following.

K_{11}: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5 H), 4.05 (dd, J = 11.26 Hz, 2.22 Hz, 1 H), 2.6–2.2 (m, 3 H), 1.9–1.7 (m, 2 H), 1.6–1.2 (m, 13 H); IR (CCl_4) 3087, 3067, 3029, 2935, 2870, 2851, 1708, 1494, 1470, 1452 cm^{-1}; UV (hexane) λ_{max} = 260 nm (π–π* transition of benzene ring) 299 nm (n–π* transition of carbonyl), ε = 319, 354; MS m/z 244 (M^+).

K_{12}: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5 H), 4.04 (dd, J = 12.06 Hz, 2.62 Hz, 1 H), 2.50–2.20 (m, 3 H), 1.90 (m, 1 H), 1.60–1.20 (m, 16 H); IR (CCl_4) 3086, 3064, 3029, 2932, 2867, 2852, 1709, 1550, 1547, 1469 cm^{-1}; UV (hexane) λ_{max} = 266, 300 nm, ε = 3.52, 305; MS m/z 258 (M^+).

K_{13}: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5 H), 3.86 (dd, J = 11.02 Hz, 3.18 Hz, 1 H), 2.60–2.20 (m, 3 H), 1.80–1.20 (m, 19 H); IR (CCl_4) 3086, 3064, 3028, 2933, 2863, 1710, 1494, 1462, 1453 cm^{-1}; UV (hexane) λ_{max} = 260, 298 nm, ε = 242, 253; MS m/z 272 (M^+).

K_{14}: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5 H), 3.85 (dd, J = 10.00 Hz, 4.84 Hz, 1 H), 2.60–2.20 (m, 3 H), 1.78 (m, 1 H), 1.60–1.20 (m, 20 H); IR (CCl_4) 3084, 3063, 3028, 2932, 2862, 1713, 1493, 1461, 1453 cm^{-1}; UV (hexane) λ_{max} = 260, 297 nm, ε = 246, 275; MS m/z 286 (M^+).

K_{15}: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5 H), 3.78 (dd, J = 9.36 Hz, 5.24 Hz, 1 H), 2.60–2.15 (m, 3 H), 1.73 (m, 1 H), 1.68–1.20 (m, 22 H); IR (CCl_4) 3086, 3064, 3028, 2930, 2858, 1712, 1494, 1460, 1454 cm^{-1}; UV (hexane) λ_{max} = 261, 293 nm, ε = 246, 263; MS m/z 300 (M^+).

(2) Photolysis of K_n. For the analysis of the product distribution in different solvents, a solution of K_n (2–5 mM) in an NMR tube was bubbled with argon for 10 min. The deaerated sample was then irradiated with a medium-pressure mercury lamp (450 W) that was cooled and filtered by a 5.0 × 10^{-4} M solution of $KCrO_4$. The conversion was controlled to be less than 30%. The relative yields and mass balances (all were between 60–80%) of the products were determined by GC analysis, employing the corresponding parent cycloalkanone as an internal standard. The minor products were established as decarbonylation products of secondary photolysis of the alkenals (GC/MS analysis). For low-temperature photolysis, the NMR tube containing the solution of K_n was immersed in the Dewar flask, one side of which is transparent. For the photolysis of K_n in micelles, a solution of K_n in micelles (molar ratio, K_n:micelle = 1:1) was bubbled with Ar before irradiation. The products were extracted with ether. For the photolysis of K_n on zeolites, the K_n was loaded by soaking the zeolite (dried in a 500 °C oven overnight before use) with a given volume of 0.2% K_n in pentane overnight, and pentane was then evaporated under vacuum. The final loading by weight was estimated to be 2%. Before irradiation, the zeolite–K_n complex was degassed under vacuum for 1 h until the vacuum was below 10^{-3} Torr. The zeolite–K_n complex was then irradiated with the medium-pressure mercury lamp (20–40 min). The photolysis products on silicalite or Na-LZ-105 zeolite were extracted with C_6H_6, and the products on X-type zeolite were extracted with $CHCl_3$ after the zeolite was dissolved with 2 N HCl followed by neutralization with NaOH. The product distribution was determined by gas chromatography with a 25-m capillary column (HP-1, cross-linked methyl silicone gum). For the separation of cyclophanes, ~100 mg of K_n in DMF was photolyzed at −55 °C to complete conversion. DMF was evaporated under vacuum. The cyclophane was purified by silica gel flash chromatography with 5% ether in hexane as eluant. For the spectroscopic identification, alkenals were obtained by photolyzing the β-CD+K_n complexes in solid state.[21] The alkenals were separated by preparative TLC with 7% ether in hexane as solvent. A mixture of cis and trans alkenals was obtained.

(3) Identification of Photolysis Products. C_{11}: ^{1}H NMR ($CDCl_3$) δ 7.70 (d, J = 7.23 Hz, 2 H), 7.29 (d, J = 7.23 Hz, 2 H), 2.86 (t, J = 6.48 Hz, 2 H), 2.69 (t, J = 6.24 Hz, 2 H), 1.64 (m, 4 H), 1.20–0.50 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 205.9, 147.5, 137.6, 129.6, 128.2, 38.5, 36.1, 29.2, 28.9, 28.0, 27.1, 26.9, 26.8, 26.7, 25.3; IR (CCl_4) 2932, 2858, 1684 cm^{-1}; UV (hexane) λ_{max} = 249 nm, ε = 1.3 × 10^4; MS m/z (relative intensity) 118 (26), 131 (100), 146 (34), 244 (M^+, 27).

C_{12}: ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 7.87 Hz, 2 H), 7.28 (d, J = 7.87 Hz, 2 H), 2.89 (t, J = 6.54 Hz, 2 H), 2.69 (t, J = 6.12 Hz, 2 H), 1.60 (m, 4 H), 1.5–0.7 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 204.5, 148.3, 135.7, 129.4, 128.2, 39.6, 35.8, 28.9, 27.7, 27.5, 27.2, 27.0, 26.6, 26.0, 25.9, 25.1; IR (CCl_4) 2930, 2858, 1683 cm^{-1}; UV (hexane) λ_{max} = 250 nm, ε = 1.1 × 10^4; MS m/z (relative intensity) 118 (32), 131 (100), 146 (63), 258 (M^+, 34).

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C_{13}: ^1H NMR ($CDCl_3$) δ 7.81 (d, J = 8.34 Hz, 2 H), 7.29 (d, J = 8.34 Hz, 2 H), 2.91 (t, J = 6.57 Hz, 2 H), 2.71 (t, J = 6.12 Hz, 2 H), 1.70 (m, 4 H), 1.35–0.60 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 203.7, 148.4, 135.5, 129.2, 128.3, 38.6, 35.8, 29.1, 28.7, 28.3, 28.1, 27.7, 27.6, 27.0, 26.6, 26.5, 26.3; IR (CCl_4) 2930, 2857, 1681 cm^{-1}; UV (hexane) λ_{max} = 250 nm, $\epsilon = 1.4 \times 10^4$; MS m/z (relative intensity) 118 (37), 131 (100), 146 (81), 147 (31), 272 (M^+, 49).

C_{14}: ^1H NMR ($CDCl_3$) δ 7.81 (d, J = 8.06 Hz, 2 H), 7.26 (d, J = 8.06 Hz, 2 H), 2.89 (t, J = 6.69 Hz, 2 H), (t, J = 6.09 Hz, 2 H), 1.70 (m, 2 H), 1.60 (m, 2 H), 1.40–0.70 (m, 18 H); ^{13}C ($CDCl_3$) δ 203.0, 148.1, 134.7, 129.2, 128.3, 39.0, 35.5, 29.1, 28.4, 28.1, 27.6, 27.4, 27.2, 27.0, 26.8 (2 C's), 25.6, 25.2; IR (CCl_4) 2929, 2857, 1682 cm^{-1}; UV (hexane) λ_{max} = 250 nm, $\epsilon = 1.6 \times 10^4$; MS m/z (relative intensity) 118 (31), 131 (46), 146 (100), 147 (44), 286 (M^+, 64).

C_{15}: ^1H NMR ($CDCl_3$) δ 7.88 (d, J = 6.80 Hz, 2 H), 7.27 (d, J = 6.80 Hz, 2 H), 2.90 (t, J = 8.10 Hz, 2 H), 2.70 (t, J = 6.00 Hz, 2 H), 1.75 (m, 2 H), 1.66 (m, 2 H), 1.4–0.8 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 202.6, 148.2, 135.0, 129.1, 128.4, 37.6, 35.2, 29.2, 29.1, 28.3, 28.14, 28.09, 27.7, 27.5, 27.4, 27.3, 27.2, 26.4, 25.7; IR (CCl_4) 2930, 2857, 1680 cm^{-1}; UV (hexane) λ_{max} = 251 nm, $\epsilon = 1.5 \times 10^4$; MS m/z (relative intensity) 118 (23) 131 (69), 146 (100), 147 (45), 300 (M^+, 59).

***trans*-EA_{11}**: ^1H NMR ($CDCl_3$) δ 9.77 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.38 (d, J = 15.8 Hz, 1 H), 6.22 (dt, J = 15.8 Hz, 6.8 Hz, 1 H), 2.43 (td, J = 7.3 Hz, 1.8 Hz, 2 H), 2.20 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.40–1.20 (m, 8 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 244 (M^+).

***cis*-EA_{11}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.41 (d, J = 11.6 Hz, 1 H), 5.66 (dt, J = 11.6 Hz, 7.2 Hz, 1 H), 2.42 (td, J = 7.3 Hz, 1.8 Hz, 2 H), 2.34 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.20–1.40 (m, 8 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 244 (M^+).

***trans*-EA_{12}**: ^1H NMR ($CDCl_3$) δ 9.75 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.37 (d, J = 15.8 Hz, 1 H), 6.20 (dt, J = 15.8 Hz), 7.0 Hz, 1 H), 2.41 (td, J = 7.2 Hz, 1.8 Hz, 2 H), 2.19 (dt, J = 7.0 Hz, 7.2 Hz, 2 H), 1.8–1.1 (m, 14 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 258 (M^+).

***cis*-EA_{12}**: ^1H NMR ($CDCl_3$) δ 9.75 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.35 (d, J = 11.6 Hz, 1 H), 5.65 (dt, J = 11.6 Hz, 7.2 Hz, 1 H), 2.41 (dt, J = 7.2 Hz, 1.8 Hz, 2 H), 2.31 (m, 2 H), 1.8–1.1 (m, 14 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 258 (M^+).

***trans*-EA_{13}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.38 (d, J = 15.7 Hz, 1 H), 6.23 (dt, J = 15.7 Hz, 6.9 Hz, 1 H), 2.42 (td, J = 7.4 Hz, 1.8 Hz, 2 H), 2.21 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.40–1.20 (m, 12 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 272 (M^+).

***cis*-EA_{13}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.8 Hz, 1 H), 7.30 (m, 5 H), 6.41 (d, J = 11.7 Hz, 1 H), 5.67 (dt, J = 11.7 Hz, 7.2 Hz, 1 H), 2.42 (td, J = 7.4 Hz, 1.8 Hz, 2 H), 2.33 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 2 H), 1.40–1.20 (m, 12 H); IR (CCl_4) 1729 cm^{-1}; MS m/z 272 (M^+).

***trans*-EA_{14}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.38 (d, J = 15.9 Hz, 1 H), 6.23 (dt, J = 15.9 Hz, 6.8 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1729 cm^{-1}; MS m/z 286 (M^+).

***cis*-EA_{14}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.41 (d, J = 11.7 Hz, 1 H), 5.67 (dt, J = 11.7 Hz, 7.3 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1729 cm^{-1}; MS m/z 286 (M^+).

***trans*-EA_{15}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.37 (d, J = 15.9 Hz, 1 H), 6.23 (dt, J = 15.9 Hz, 6.9 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1728 cm^{-1}; MS m/z 300 (M^+).

***cis*-EA_{15}**: ^1H NMR ($CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1 H), 7.30 (m, 5 H), 6.40 (d, J = 11.6 Hz, 1 H), 5.67 (dt, J = 11.6 Hz, 7.4 Hz, 1 H), other hydrogens are overlapped with the hydrogens from the starting ketone and cyclophane; IR (CCl_4) 1728 cm^{-1}; MS m/z 300 (M^+).

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Supplementary Material Available: ^1H NMR spectra of compounds K_{11}–K_{15}, *cis*- and *trans*-EA_{11}–*cis*- and *trans*-EA_{15}, and C_{11}–C_{15}, ^{13}C and two-dimensional ^1H–^1H homonuclear chemical shift correlated NMR of compounds C_{11}–C_{15} (31 pages). Ordering information is given on any current masthead page.

Unexpected Behavior of Limonene in the Oxidative Aminomercuration Reaction with HgO/HBF_4 and Aromatic Amines: Stereospecific Synthesis of 1,2-Diamines

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Solvomercuration–demercuration of alkenes provides a very general and useful method for Markovnikov functionalization of carbon–carbon double bonds.[1] Moreover, by using some mercury salts, an oxidative–demercuration process can occur, leading, in the presence of a nucleophile, to bifunctionalized compounds.[2] Although some attempts directed toward asymmetric induction have been performed by using chiral mercury salts, the enantiomeric excess was low in all cases.[3] The synthetic utility of the above mentioned reaction decreases when unconjugated dienic systems are used because of the competition reaction between the two double bonds; furthermore, side reactions are usually observed when the two double bonds are not equivalent, e.g., in the case of limonene. The monohydroxymercuration of limonene can only be achieved with high chemoselectivity with aqueous micelles,[4] the mercuration always taking place at the less hindered exocyclic double bond.

We report here our preliminary results on the aminomercuration reaction of limonene with HgO/HBF_4 as the mercuration reagent.

Thus, (*R*)-(+)-limonene (1) reacted with HgO/HBF_4 (1 equiv of HgO and 2 equiv of HBF_4, 40% v/v) in the presence of primary aromatic amines (molar ratio 1:1:5) in THF at −20 °C to give rise to mercurial **3**. Heating of **3** at 80 °C for 5 h did not afford the expected diamine **8**,[2] but diamine **4** was obtained as the major product, along with monoamines **5**, **6**, and *p*-cymene (**7**)[5] (Scheme I). Diamine **4** was obtained by high-vacuum distillation of the reaction crude as a very viscous red-orange oil. The ^{13}C NMR and ^1H NMR data show the presence of only one enantiomer.

Single-crystal X-ray analysis established unequivocally the complete structure and absolute 1*R*,2*R*,4*R* configuration for **4a**[6] (Figure 1). The 1*S*,2*S*,4*S* enantiomer **4a'** was obtained from (*S*)-(−)-limonene under the same reaction conditions (see the previous text).

When the mercurial intermediate **3a** was reduced in situ with $NaBH_4/OH^-$, the β-elimination reaction was the most

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