Bond Localization Approach to the Carbon Analogue of the Claisen Rearrangement. Thermolysis of 4-Aryl-1-butenes

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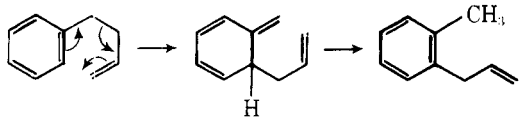
The carbon Claisen rearrangement of 4-phenyl-1-butene, 4-(1-naphthyl)-1-butene, and 4-(9-phenanthryl)-1-butene should yield, respectively, *o*-allyltoluene, 2-allyl-1-methylnaphthalene, and 9-allyl-10-methylphenanthrene. The increased localization of the key aromatic bond in the naphthyl and phenanthryl systems should more closely resemble that in the aliphatic Cope rearrangement. The three systems underwent gas-phase pyrolytic decomposition in the range 350–450 °C. The major pathway (>90%) is rupture of the benzylic–allylic bond to form, respectively, toluene, 1-methylnaphthalene, and 9-methylphenanthrene. Minor pathways include cyclization, hydrogenation, dehydrogenation, and double-bond migration. An upper limit of 1–2%, based on possible gas chromatographic peak coincidence, could be set on the Claisen pathway in the naphthyl and phenanthryl systems. The Claisen product was clearly absent from the phenyl system.

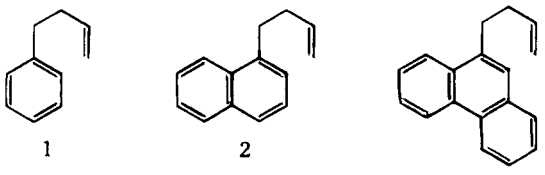
Almost half a century has passed since Hurd and co-workers first examined 4-phenyl-1-butene for a Claisen-type rearrangement, or what we would now call a [3,3] sigmatropic shift (eq 1).[2] A bonafide example of an all-carbon Claisen rearrangement under purely thermal conditions (no base, transition metal, or solid support catalysis) in the absence of the driving force from cyclopropane ring strain is still lacking, despite some very imaginative experiments.[3] We have recently shown that, contrary to earlier thinking, the first step of eq 1 (the [3,3] sigmatropic shift) rather than the second step (the [1,3] sigmatropic shift) is probably rate limiting.[4] The major difference between the easily observed (aliphatic) Cope rearrangement and the still unobserved carbon Claisen rearrangement is the incorporation of one of the reacting double bonds in the latter case into an aromatic ring. The same situation of course obtains in the oxygen Claisen rearrangement, but the strong perturbation by the oxygen atom of the aromatic double-bond frontier molecular orbitals accelerates the reaction sufficiently to make it observable.[4]



(1)

Another approach to accelerating the Claisen-like reaction in the all-carbon system, and the one we take in this paper, is to increase the localization of the aromatic double bond that must react in the first step. Thus, by way of analogy, the diene or ene components of benzene are far less reactive in the Diels–Alder reaction than are the corresponding aliphatic dienes and enes (dienophiles). The logical series on which to test this hypothesis is benzene, naphthalene, and phenanthrene. As the data in Table I show, the bonds in naphthalene and phenanthrene are increasingly alternating. The 1,2 bond in naphthalene has a higher π bond order and a shorter length compared to that in benzene, and the 9,10 bond in phenanthrene has an even higher bond order and shorter length.

Our current approach then is to examine the series in which the aromatic double bond that must react in the first step of the Claisen rearrangement has increasingly higher bond order, as in the series benzene/1,2 bond of naphthalene/9,10 bond of phenanthrene. Cope followed a similar line of reasoning in a highly substituted series of compounds, but the carbethoxy substituents lowered the thermal stability to the point that temperatures in excess of 300 °C could not be achieved before the molecules decomposed.[3] Consequently, we selected the hydrocarbon series **1**–**3** for our studies since their higher thermal stabilities should permit higher temperatures to be achieved. The α-naphthyl isomer **2** was chosen over the β isomer to avoid any ambiguity with possible rearrangement to the γ position. The α isomer has only one available pathway, although addition to the peri position is not inconceivable. We have included 4-phenyl-1-butene (**1**) in this study because Hurd's original investigation was long before the advent of gas chromatography and a small amount of the Claisen product might have been overlooked. Consequently, we report herein the synthesis and thermolysis of 4-phenyl-1-butene (**1**), 4-(1-naphthyl)-1-butene (**2**), and 4-(9-phenanthryl)-1-butene (**3**).



Results

4-Phenyl-1-butene was obtained from commercial sources. The naphthyl (**2**) and phenanthryl (**3**) substrates were obtained by Grignard coupling reactions. Both were initially prepared, isolated, and characterized as products of the coupling between the appropriate arylmagnesium bromide and 4-bromo-1-butene. Improved yields and easier purification, however, were obtained by coupling of the appropriate arylhalomethane with allylmagnesium bromide. Thus, reaction of the allyl Grignard reagent with 1-(chloromethyl)naphthalene yielded the product 4-(1-naphthyl)-1-butene (**2**) in 69% yield.

For the phenanthryl series, the required precursor 9-(bromomethyl)phenanthrene was synthesized in three steps from 9-bromophenanthrene by conversion to the Grignard reagent, reaction with paraformaldehyde, and treatment of the resulting alcohol with PBr_3 in 64% overall yield. The halide was converted by treatment with allylmagnesium bromide to the product 4-(9-phenanthryl)-1-butene (**3**) in 59% yield.

The expected Claisen products for all three series were independently synthesized and characterized to facilitate identification of these materials in pyrolysis mixtures. *o*-Allyltoluene (**4**) was prepared, following Hurd,[2] in one step by the reaction of *o*-tolylmagnesium bromide with allyl bromide. The synthesis of 2-allyl-1-methylnaphthalene (**5**) began with addition of methylmagnesium iodide to 1-indanone to give, after acid-catalyzed dehydration, 1-methylindene in good yield.[5] Ring expansion of the indene by treatment with $CHBr_3$ gave 2-bromo-1-methylnaphthalene in moderate yield.[5] The Grignard reagent from this bromide was treated with allyl bromide to give the desired naphthalene **5** in 56% yield.

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Table I. π Bond Orders and Bond Lengths[a]

compd	bond	π bond order	bond length, Å
benzene	all C–C	0.667	1.397
naphthalene	1,2	0.725	1.365
	2,3	0.603	1.404
phenanthrene	1,2	0.707	1.373[b]
	2,3	0.623	1.406[b]
	3,4	0.702	1.373[b]
	9,10	0.775	1.352[b]
ethylene	only C–C	1.000	1.338

[a] Except as noted, from K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, 1964, pp 88–90. [b] M. J. S. Dewar, "The Molecular Orbital Theory for Organic Chemistry", McGraw-Hill, New York, 1969, pp 166, 172.

For the preparation of 9-allyl-10-methylphenanthrene (**6**), the Grignard reagent from 9-bromophenanthrene was treated with methyl iodide and the resulting 9-methylphenanthrene was brominated and dehydrobrominated. The product of these steps was 9-bromo-10-methylphenanthrene, whose Grignard reagent was treated with allyl bromide to give the desired phenanthrene **6** in 42% yield.

The pyrolyses were carried out in the gas phase by sealing 30–60 μL of a liquid butene or 10–20 mg of a solid butene in a 250-mL glass ampule at −78 °C under 0.01 mm vacuum. The tubes were typically heated for 12 h in a tube furnace at the appropriate temperature. At 380 °C, the phenyl and naphthyl substrates were largely unreacted. Optimal conversion to products was obtained at about 400 °C. At much higher temperatures, there was almost complete conversion to toluene and 1-methylnaphthalene, respectively. The phenanthryl substrate began isomerizing at somewhat lower temperatures, with optimal conversion at about 360 °C and almost complete conversion to 9-methylphenanthrene at higher temperatures.

Figure 1 presents the gas chromatograms for the three reaction mixtures at the optimal temperature for conversion. Very low-boiling products were not examined. The mixtures are remarkably similar, each with 10–13 components and each with the major product being the arylmethane. Products whose structures are reasonably well characterized are drawn into Figure 1. Structures were elucidated by chromatographic peak coincidence with authentic samples, by mass spectrometry (GC/MS), by ozonolysis, or, for major products, by isolation and NMR spectroscopy. Details have been given elsewhere.[6] The peak assignments, including those that are only tentative (1-phenyl-1-propene, 1-phenyl-2-butene, and the 1-phenyl-1-butenes), are shown in Figure 1 for the phenyl derivative. Dihydronaphthalenes have not been excluded but must be at most in a very low proportion. Tentative assignments were omitted for the other two substrates because of lack of space. For the naphthyl substrate, in order of increasing retention time, they included 2-methylnaphthalene, 1-ethylnaphthalene, 1-vinylnaphthalene, and acenaphthalene; not shown but more certain were 1-(1-naphthyl)butane, methylbenzindan, and 1,2,3,4-tetrahydrophenanthrene. For the phenanthryl substrate, tentative assignments included 1′-methyl-1,10-cyclohexenophenanthrene and dihydrotriphenylene; not shown but more certain were 9,10-dihydrophenanthrene, 9-ethylphenanthrene, 1-(9-phenanthryl)-butane, and 1,2,3,4-tetrahydrotriphenylene. In addition, for the naphthyl and phenanthryl systems, peaks were obtained that corresponded to the retention time of the expected Claisen product. These are not shown in Figure 1 but fall at 9.9 min for naphthyl and 35 min for phenanthryl. No peak was found for *o*-allyltoluene in the phenyl system.

The stability of the three expected Claisen products was tested by heating them under the optimal reaction conditions. The naphthyl and phenanthryl products, **5** and **6**, were recovered essentially unchanged. Surprisingly, *o*-allyltoluene was found to isomerize in part to *o*-tolylpropene, methylindan, and tetralin as major components and *o*-xylene, *o*-ethyltoluene, *o*-vinyltoluene, *o*-propyltoluene, and naphthalene as possible minor products (no toluene). Lower boiling materials were not examined. Hurd[2] did not observe decomposition of **1** under his flow conditions. The dissimilarity of the decomposition products of *o*-allyltoluene from those of 4-phenyl-

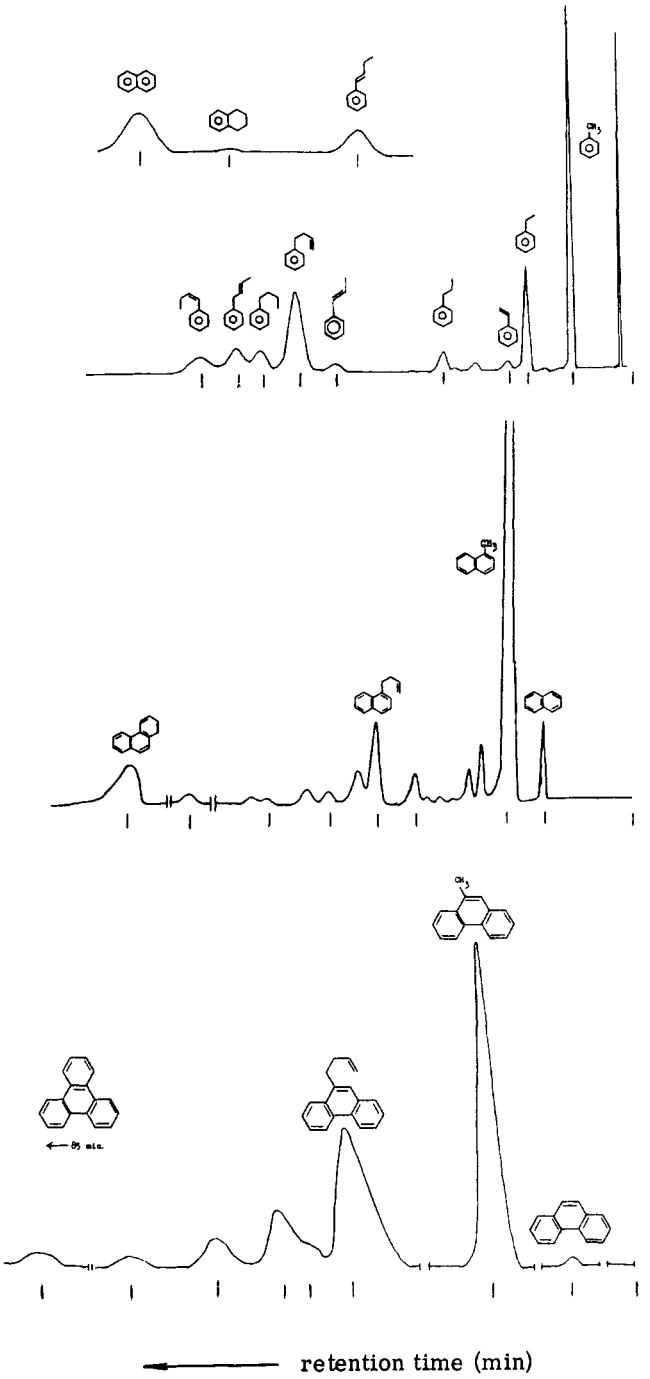
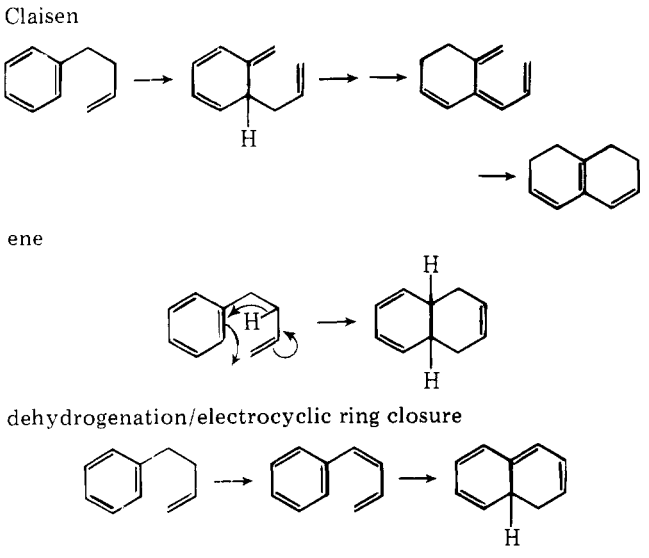


Figure 1. The vapor phase chromatograms of the pyrolysis products of 4-phenyl-1-butene (**1**) (top), 4-(1-naphthyl)-1-butene (**2**) (middle), and 4-(9-phenanthryl)-1-butene (**3**) (bottom). The retention times in minutes are indicated by hashmarks directly under the appropriate peaks. For **1**, the marks (0 is on the far right) correspond to 0, 2.0 (toluene), 3.4, 4.1, 6.1, 9.7, 11.0, 12.2, 13.0, 14.2, 19, 23, and 26 (naphthalene) min. For **2**, they are 0, 2.7 (naphthalene), 4.0, 7.0, 8.3, 9.9, 12.0, 15.6, and 23.4 (phenanthrene) min. For **3**, they are 0, 10 (phenanthrene), 16, 30.5, 31.5, 32.5, 35, 37.5, and 42.5 (triphenylene) min.

Scheme I. Cyclization Pathways



1-butene suggests that the Claisen product is not formed initially and then destroyed under reaction conditions.

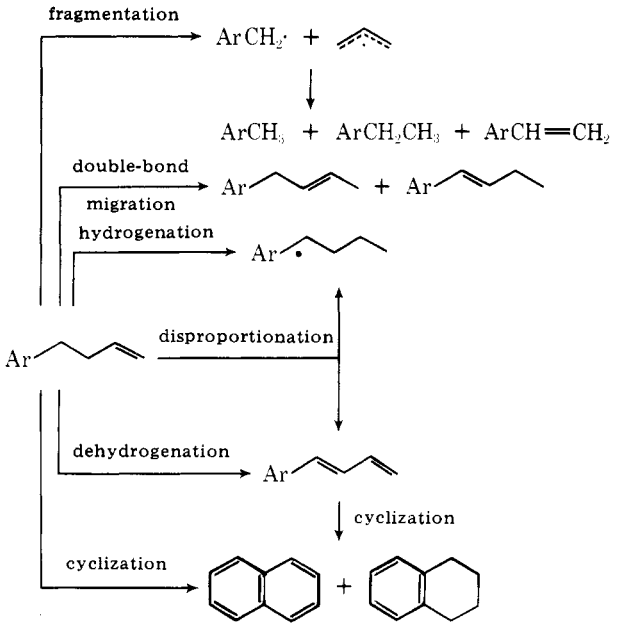
Because peaks were found at the position of the Claisen product for the naphthyl and phenanthryl systems, considerable effort was made to isolate these materials. As they comprised no more than 1–2% of the reaction mixture and were located close to other components, isolation was not successful. Coinjection of the authentic material with the reaction mixture was carried out on numerous different columns. Coincidence was observed on 2.37% Apiezon L, 2% FFAP, 5% SF-96, 3% SE-52, 3% Dow Corning High Vacuum Grease, and 1% Carbowax. Some of the coincident peaks appeared, however, to be slightly broadened or asymmetric. Finally, on 10% FFAP, which gave the best overall product separation, the naphthyl system gave a clear inflection point and the phenanthryl system gave a distinct new peak. Conservatively, one can conclude that at the most there is 1–2% of the Claisen product for naphthyl and phenanthryl; at the least there is none of it. The identity of the peak in each case, if it is not the Claisen product, is not known. Possibly it is a double-bond isomer of the Claisen product.

Discussion

The three 4-aryl-1-butenes react under gas-phase pyrolytic conditions in remarkably similar fashions. The dominant pathway in each case is cleavage of the benzylic–allylic bond to give toluene, 1-methylnaphthalene, and 9-methylphenanthrene, respectively. The benzylic fragment produces the observed major product. The allylic fragment undoubtedly also reacts further, but it does not recombine with the benzylic portion in a Claisen fashion to give *o*-allyltoluene or its congeners.

The hydrogenation, dehydrogenation, hydrogenolysis, disproportionation, and double-bond migration pathways are unremarkable components of many pyrolysis reactions, well known in the petroluem industry. More remarkable is the relatively large portion of dehydrocyclization products, e.g., naphthalene derivatives in the phenyl series, phenanthrenes in the naphthalene series, and triphenylenes in the phenanthrene series. Cyclizations also are common pyrolytic pathways, but they may have special significance in the present context since they may represent a Claisen pathway. Carbonium ion mechanisms are possible but unlikely under our conditions.[7,8] Radical pathways are certainly feasible but appear to be eliminated by our observation that the cyclization product distribution was not significantly affected by the addition of hydroquinone to the reaction mixture.

Scheme II



Scheme I illustrates various mechanisms of cyclization. In the first, originally suggested by Doering,[3] the reaction actually proceeds to the Claisen intermediate, which undergoes a pair of facile [1,5] sigmatropic hydrogen shifts followed by a 6π-electron electrocyclic ring closure. The scheme does not follow the mechanisms further than the ring closure step, since subsequent hydrogen shifts to tetralin or dehydrogenations to naphthalene are straightforward. The second possible cyclization mechanism involves an ene reaction in which the hydrogen shifts onto the aromatic ring. Subsequent hydrogen shifts and dehydrogenation again could lead to the observed product. The third possibility requires an initial dehydrogenation to a 1-aryl-1,3-butadiene, which is known to undergo electrocyclic ring closure to dihydronaphthalenes.[9] Disproportionation[8] and dehydrogenation can produce tetralin as well as naphthalene. Since even *n*-butylbenzene can, under the proper conditions, yield naphthalene, the initial dehydrogenation is quite reasonable. Without further evidence, the dehydrogenation/electrocyclic ring closure process must be considered the most likely route to naphthalenes and, by analogy, to phenanthrenes and triphenylenes in the naphthalene and phenanthrene series, respectively. There is no reason to postulate a Claisen pathway to these products, but it has not been excluded.

The thermal pathways taken by the 4-aryl-1-butenes are shown in Scheme II. At present, the upper limit to the Claisen product is 2% in the most favorable case and 0% in the least favorable case, disregarding the possibility that the ring closure products actually derive from a Claisen pathway. It is clear that little progress can be made in observing the carbon Claisen rearrangement unless the major alternative pathways, in particular the cleavage of the benzylic bond, can be thwarted. It is significant that the successful cyclopropyl system studied by Marvell[3] ties the benzylic and allylic fragments together so that subsequent Claisen-like reactions can occur. Perturbation of the frontier orbitals in the oxygen Claisen rearrangement must accelerate this pathway over that which would produce a phenolate radical. Other sources of activation, such as electron-donating groups on the aromatic ring, might promote the reaction. One type of activation that was successful in the Cope rearrangement[10] failed with 4-phenyl-1-butene. Whereas alumina lowered the reaction temperature of 3,4-diphenyl-1,5-hexadiene, we found that similar conditions led primarily to increased double-bond migration in 4-phenyl-1-butene.

Summary

Increased localization of the aromatic bond that would be involved in the carbon analogue of the Claisen rearrangement does not cause a dramatic increase in the Claisen pathway. For 4-phenyl-1-butene, 4-(1-naphthyl)-1-butene, and 4-(9-phenanthryl)-1-butene, by far the major pathway is the cleavage of the benzylic–allylic bond to form, respectively, toluene, 1-methylnaphthalene, and 9-methylphenanthrene. Optimal temperatures for reaction are 360–400 °C. Other pathways include cyclization, hydrogenation, dehydrogenation, and double-bond migration. The cyclization process probably occurs via a dehydrogenation of the butene to a butadiene, followed by a 6π-electron electrocyclic ring closure. No Claisen product (*o*-allyltoluene) is observed for the phenyl compound, although the product was found to be unstable to reaction conditions. Its decomposition products, however, did not correspond to those of the starting material 4-phenyl-1-butene. Peaks were present at the chromatographic retention time of the expected Claisen products in the other two series, but no more than 1–2% and possibly none since the coincidences may have been misleading. Without modifying the aromatic ring further, e.g., through substitution, the Claisen pathway cannot be observed unless the side chain is appropriately altered to restrict the alternative pathways.

Experimental Section

Instrumental and other general considerations have been dealt with in our previous paper.[4]

Allylmagnesium Bromide. Magnesium (2.63 g, 0.109 mol) was activated with I_2 in oven-dried, N_2-flushed glassware. Allyl bromide (13.82 g, 0.1141 mol) in 50 mL of ether was added so that it just covered the metal. When reaction began, 60 mL of anhydrous ether was immediately added from a second funnel to moderate the reaction rate. The remaining bromide solution was diluted to 200 mL with ether and added dropwise to the graying mixture over a 90-min period. The mixture was gently refluxed for 5 h, cooled, and filtered through a Schlenk tube plugged with glass wool to give Mg-free allylmagnesium bromide. The reagent was used immediately after preparation.

4-(1-Naphthyl)-1-butene (2). Redistilled 1-(chloromethyl)-naphthalene (7.64 g, 0.0434 mol) in 200 mL of anhydrous ether was added dropwise over a 90-min period to allylmagnesium bromide prepared from 4.83 g (0.201 mol) of Mg and 25.18 g (0.210 mol) of allyl bromide. The mixture was refluxed for 14 h, cooled, and treated with 200 mL of saturated NH_4Cl solution. The layers were separated, and the aqueous phase was extracted twice with 100 mL of ether. The combined organic portions were washed with brine until neutral and then dried over anhydrous Na_2SO_4. Rotary evaporation yielded a yellow liquid, which was decanted from the solid coupling product, distilled, and collected in two fractions to yield 5.47 g (69%) of **2**: bp 81–82 °C (0.075 mm);[11] NMR (CCl_4) δ 2.45 (m, 2, allylic), 3.05 (m, 2, benzylic), 4.77–5.16 (m, 2, $=CH_2$), 5.50–6.15 (m, 1, $=CHR$), 7.13–7.95 (m, 7, ArH); IR (film) 3060 (m), 3000 (w), 2980 (w), 2938 (m), 2862 (w), 1630 (m), 1598 (m), 1510 (m), 1397 (m), 993 (m), 911 (s), 798 (s), 790 (s), 777 (s) cm^{-1}; MS (70 eV) *m/e* (rel intensity) 182 (molecular ion, 12), 142 (10), 141 (100), 115 (45), 63 (10), 41 (19), 39 (24); VPC showed the product to be 94% pure and contaminated only by the β isomer. An additional 2.05 g of 90–92% pure **2** was obtained in the other distillation fractions to give a total of 7.52 g (95%). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.68.

9-(Hydroxymethyl)phenanthrene. 9-Bromophenanthrene (10.50 g, 40.8 mmol) in 25 mL of dry THF was added just to cover 0.98 g (40.8 mmol) of I_2-activated Mg. After the reaction was initiated by warming to 38 °C, the remaining bromide solution was diluted with 75 mL of THF and added at a moderate drop rate. When addition was complete, the mixture was stirred at 35 °C for 30 min and then refluxed for 90 min. After the mixture had cooled, 1.26 g (42 mmol) of dry paraformaldehyde was added. The mixture was stirred and refluxed until all of the paraformaldehyde had disappeared (5 h). The cooled reaction mixture was poured into 100 mL of saturated NH_4Cl solution and worked up in the usual fashion. Rotary evaporation of the dried solvent yielded 12.09 g of yellow solid, which was recrystallized from benzene to give 5.03 g (59%) of white crystals: mp 150 °C (lit.[12] 149–149.5 °C); NMR ($CDCl_3$) δ 2.0 (s, 1, OH), 5.3 (s, 2, CH_2), 7.9 (m, 6, ArH), 8.3 (m, 1, ArH), 8.7 (m, 2, ArH); IR (KBr) 3200 (s), 1460 (m), 1440 (m), 1025 (s), 990 (m), 895 (s), 875 (w), 795 (m), 787 (m), 775 (s), 750 (s), 730 (s) cm^{-1}.

9-(Bromomethyl)phenanthrene.[13] 9-(Hydroxymethyl)phenanthrene (5.67 g, 27.3 mmol) was dissolved in 12 mL of CCl_4. The mixture was stirred as 7.74 g (28.6 mmol) of PBr_3 was added dropwise over 10 min. All solids dissolved as the white slurry was heated to reflux. After 40 min, the mixture was cooled. The CCl_4 was decanted into another round-bottom flask and rotary evaporated until the solvent was gone. Absolute CH_3OH (75 mL) was cautiously added. The resulting slurry was stirred overnight and filtered. The filtrate was concentrated and refiltered to give 6.04 g (82%) of white crystals: mp 118.5–119 °C (lit.[13] 118.5–119.5 °C); NMR (C_6D_6) δ 4.15 (m, 2, CH_2), 7.5–8.11 (m, 9, ArH); IR (KBr) 1430 (m), 1195 (s), 880 (m), 770 (m), 750 (s), 730 (s), 700 (s) cm^{-1}.

4-(9-Phenanthryl)-1-butene (3). 9-(Bromomethyl)phenanthrene (6.04 g, 22.3 mmol) in 50 mL of dry THF and 100 mL of ether was added at a moderate drop rate to allylmagnesium bromide (from 2.63 g of Mg and 13.82 g of allyl bromide). The resulting mixture was refluxed overnight, cooled, and worked up in the usual fashion. Rotary evaporation yielded 5.36 g of residue, which was taken up in hot ethanol and cooled to precipitate an oil. The liquor was decanted, the solution was concentrated, and the solid was recrystallized from ethanol to yield 3.04 g (59%) of white needles: mp 44.5–45 °C; NMR (CCl_4) δ 2.4 (m, 2, allylic CH_2), 3.05 (m, 2, benzylic CH_2), 4.9 (m, 2, $=CH_2$), 5.7 (m, 1, $=CHR$), 7.3 (m, 6, ArH), 7.8 (m, 1, ArH), 8.35 (m, 2, ArH); IR (KBr) 3080 (w), 2940 (w), 1650 (w), 1610 (w), 1455 (w), 1435 (w), 1000 (w), 990 (w), 910 (s), 880 (s), 850 (w), 740 (s), 720 (s) cm^{-1}; MS (10 eV) *m/e* (rel intensity) 232 (molecular ion, 19), 191 (100), 165 (10). Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.68; H, 7.16.

***o*-Allyltoluene (4)** was prepared from I_2-activated Mg (1.20 g, 50 mmol), *o*-bromotoluene (8.63 g, 50.5 mmol) (as the Grignard reagent), and 6.20 g (51.2 mmol) of allyl bromide according to the procedure of Hurd.[2]

1-Methylindene was prepared by a modification of Parham's method.[5] Methylmagnesium iodide was prepared in the usual manner from 2.61 g (0.1085 mol) of I_2-activated Mg and 15.73 g (0.1101 mol) of CH_3I in 70 mL of anhydrous ether. 1-Indanone (13.29 g, 0.1005 mol) in 90 mL of dry ether was added dropwise at a rate so as to maintain a gentle reflux. After addition was completed, the reaction mixture was refluxed for 90 min. The mixture was cooled and quenched with 150 mL of ice and 100 mL of 20% H_2SO_4 to give a lime-colored slurry. The ether was removed by distillation, an additional 100 mL of 20% H_2SO_4 was added, and the mixture was heated to a vigorous reflux for 15–20 min. The reaction mixture was cooled, 100 mL of hexane was added, and the resulting mixture was stirred for 10–15 min. The orange organic layer was separated from the green aqueous phase, and the aqueous portion was extracted twice with 100 mL of hexane. The combined organic portions were washed with 100 mL of H_2O, 100 mL of saturated $NaHCO_3$ solution, and 100 mL of brine and dried over anhydrous Na_2SO_4. The solvents were removed by rotary evaporation, and the residue was distilled to give 8.76 g (67%) of slightly yellow 1-methylindene: bp 80–88 °C (20–30 mm) [lit.[5] 76–78 °C (11 mm)]; NMR (CCl_4) δ 2.13 (m, 3, CH_3), 3.21 (m, 2, benzyl), 6.06 (m, 1, vinyl), 7.13 (m, 4, phenyl); IR (film) 3060 (m), 3025 (m), 2980 (m), 2940 (m), 2905 (s), 2895 (s), 1620 (m), 1465 (s), 1440 (m), 1400 (m), 1380 (m), 1000 (m), 940 (m), 910 (m), 765 (vs), 750 (s), 710 (vs) cm^{-1}.

2-Bromo-1-methylnaphthalene. The procedure of Parham was followed with significant modification.[5] Potassium *tert*-butoxide (4.40 g, 40.1 mmol) was slurried with 50 mL of anhydrous ether under a N_2 atmosphere and in an oven-dried apparatus. Redistilled 1-methylindene (4.00 g, 38.4 mmol) was added dropwise to yield an orange slurry. Freshly distilled $CHBr_3$ (9.70 g, 38.1 mmol) was added dropwise over a 35-min period. The slurry immediately became pink, then red, and finally a deep red-violet with precipitation of solid material. A mechanical stirrer was employed to aid mixing of the reagents. The reaction mixture was periodically cooled to 20 °C as it was stirred at room temperature for 2.5 h. The mixture was filtered, and the filter cake was dissolved in water and extracted twice with 30 mL of ether. The ether extracts were combined with the H_2O-washed filtrate, and the combined organics were washed twice with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and rotary evaporated to yield 11.59 g of brown oil. This oil was slurried in 75 mL of absolute ethanol with 1 g of KOH and refluxed for 30 min. The mixture was allowed to stir at room temperature overnight and was then reheated to reflux for an additional 30 min. The solvent was removed by rotary evaporation to give a brown oil and a solid. Hexane (100 mL) was added, and the mixture was heated on a steam bath and filtered. The filter cake was rinsed twice with 50 mL of hot hexane, and the combined hexane portions were concentrated by rotary evaporation to

give 7.02 g of brown oil. The oil was eluted with hexane through 250 g of Alcoa F-20 alumina packed onto a 4.5 × 35 cm column. The second 250-mL fraction yielded 3.02 g of largely unreacted 1-methylindene. Fractions 3–5 yielded a green oil, which was dissolved in absolute ethanol and cooled in a refrigerator to yield 2.36 g (42% based on recovered starting material) of green-tinted white flakes: mp 32–34 °C (lit.[5] 31–32 °C); NMR (CCl_4) δ 2.75 (s, 3, CH_3), 7.47 (m, 6, ArH); IR (KBr) 1590 (m), 1505 (m), 1455 (m), 1380 (m), 1320 (m), 1260 (m), 1125 (s), 995 (s), 865 (m), 820 (s), 810 (vs), 770 (vs), 740 (s) cm^{-1}.

2-Allyl-1-methylnaphthalene (5). The Grignard reagent was prepared in the usual fashion from 0.24 g (10.0 mmol) of I_2-activated Mg and 2.00 g (9.05 mmol) of 2-bromo-1-methylnaphthalene in 50 mL of dry THF. Allyl bromide (2.38 g, 19.7 mmol) in 30 mL of THF was added dropwise to the cooled mixture, and then the mixture was heated to reflux overnight. The mixture was cooled and quenched with 100 mL of saturated NH_4Cl solution and stirred until the phases cleared. The layers were separated, and the aqueous phase was extracted twice with 50 mL of ether. The combined organic layers were washed with 100 mL of saturated NaCl solution and dried over Na_2SO_4. Rotary evaporation of the dried solution left 1.62 g of solid and liquid. Recrystallization from ethanol yielded 120 mg of white solid, mp 231 °C, which is believed to be bis[2-(1-methyl)naphthalene]: NMR (CCl_4) δ 2.45 (s, 6, CH_3), 7.1–8.2 (m, 12, ArH). The mother liquor was distilled to give a 0.20-g first fraction of a mixture of **5** with 1-methylnaphthalene and a 0.93-g (56%) second fraction of pure **5**: bp 95–96 °C (0.4–0.45 mm); NMR (CCl_4) δ 2.58 (s, 3, CH_3), 3.55 (m, 2, allylic), 4.77–5.09 (m, 2, $=CH_2$), 5.95 (m, 1, vinyl), 7.1–8.05 (m, 6, ArH); IR (film) 3070 (m), 3050 (m), 3005 (m), 2980 (m), 2920 (br), 1640 (s), 1600 (m), 1510 (s), 1430 (m), 1390 (s), 1385 (s), 1020 (m), 990 (s), 910 (vs), 860 (m), 815 (vs), 755 (vs), 735 (s) cm^{-1}; MS (70 eV) *m/e* (rel intensity) 183 (11), 182 (molecular ion, 57), 181 (11), 168 (13), 167 (100), 166 (19), 165 (38), 155 (16), 153 (16), 141 (22), 139 (16), 129 (11), 128 (24), 127 (16), 115 (40). An analytical sample was obtained by preparative VPC (¼ in. × 6 ft 4.8% Apiezon L on Chromosorb G AW-DMCS 70/80 column at 195 °C with 27.5 mL/min He flow). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.89; H, 7.91.

9-Methylphenanthrene. The Grignard reagent was prepared in the usual fashion from 10.07 g (0.0392 mol) of 9-bromophenanthrene in 20 mL of THF. Methyl iodide (16.74 g, 0.108 mol) in THF was added to the cool, greenish solution. The reaction was exothermic, and considerable amounts of suspended solid formed. The mixture was refluxed for 20 h, cooled, quenched with saturated NH_4Cl solution, and stirred until both layers cleared. The aqueous phase was extracted with ether, and the organics were washed with NaCl solution and dried over anhydrous $MgSO_4$. The dried solution was filtered and rotary evaporated to give 8.03 g of crude oil. Dissolution in absolute ethanol, treatment with activated charcoal, filtration through Celite, and concentration on the rotary evaporator led to deposition of an oil. The mother liquor was decanted and concentrated to deposit 1.79 g of white crystals, mp 81–86 °C. The remaining oils and concentrates yielded 1.68 g of oily material, which was distilled at 110 °C (0.1 mm) to give a white solid. Recrystallization from ethanol of both products resulted in 2.27 g of white crystals: mp 87–89.5 °C (lit.[14] 90–91 °C); NMR (CCl_4) δ 2.6 (s, 3, CH_3), 7.5 (m, 6, ArH), 7.8 (m, 1, ArH), 8.5 (m, 2, ArH); IR (KBr) 3080 (w), 1630 (w), 1610 (w), 1500 (w), 1445 (w), 1435 (m), 950 (w), 935 (m), 760 (m), 745 (s), 720 (m) cm^{-1}; MS (70 eV) *m/e* (rel intensity) 192 (molecular ion, 100), 191 (56), 190 (12), 189 (21), 165 (17).

9-Bromo-10-methylphenanthrene. The procedure was patterned after that of DeRidder and Martin.[15] To a stirred, ice-cooled solution of 9-methylphenanthrene (2.06 g, 10.7 mmol) in 15 mL of CCl_4 was added dropwise 1.74 g (10.9 mmol) of Br_2 in 7 mL of CCl_4. The addition was completed in 1 h, and the deep red mixture was allowed to warm to 30 °C over a period of 4 h. The solvent and excess Br_2 were removed by rotary evaporation, and the residue was dissolved in hot ethanol. Cooling yielded 2.31 g (80%) of fine needles: mp 121.5–122 °C (lit.[16] 120.5–122.5 °C); NMR (CCl_4) δ 2.83 (s, 3, CH_3), 7.40 (m, 4, ArH), 7.80 (m, 1, ArH), 8.40 (m, 3, ArH); IR (KBr) 3080 (w), 1590 (w), 1490 (m), 1445 (m), 1430 (m), 900 (m), 745 (s), 715 (s), 650 (w) cm^{-1}; MS (70 eV) *m/e* (rel intensity) 272 (39), 270 (40), 192 (17), 191 (100), 190 (36), 189 (65), 188 (11), 187 (15), 165 (24), 163 (15), 95 (12), 94 (14).

9-Allyl-10-methylphenanthrene (6). The Grignard reagent was prepared in the usual fashion from 0.18 g (7.50 mmol) of I_2-activated Mg and 1.97 g (7.27 mmol) of 9-bromo-10-methylphenanthrene in 19 mL of dry THF. Allyl bromide (1.05 g, 8.70 mmol) in dry THF was added dropwise cautiously. The mixture was heated to reflux overnight, cooled, quenched with 50 mL of saturated NH_4Cl solution, and worked up in the usual manner. Rotary evaporation of the dried solution yielded 1.84 g of yellow oil, which crystallized on standing. Initial recrystallization gave 0.70 g (42%) of crystals, mp 89–94 °C. Repeated recrystallization from ethanol yielded better quality material: mp 102.5–104.2 °C; NMR (CCl_4) δ 2.65 (s, 3, CH_3), 3.85 (m, 2, CH_2), 4.90 (m, 2, $=CH_2$), 6.0 (m, 1, =CHR), 7.45 (m, 4, ArH), 7.95 (m, 2, ArH), 8.55 (m, 2, ArH); IR (KBr) 3100 (w), 1650 (w), 1620 (w), 1500 (w), 1450 (w), 1440 (w), 985 (w), 910 (m), 750 (s), 720 (s) cm^{-1}; MS (70 eV) *m/e* (rel intensity) 232 (molecular ion, 47), 218 (19), 217 (100), 216 (19), 215 (33), 203 (19), 202 (52), 189 (21), 165 (12), 101 (11). Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.06; H, 6.92.

Pyrolyses of 4-Aryl-1-butenes. A 10–20-mg amount of solid or 50–60 μL of liquid butene was placed in a 200–250-mL tube, evacuated to 0.01 mm, freeze-thawed twice, and sealed at −78 °C. Pyrolyses were performed at 250–570 °C for 12–14 h in a tube furnace. After reaction, the tip of the tube was exposed and cooled in dry ice to condense the butene. In this manner, a sample was accessible by syringe for VPC study.

Pyrolyses of 4-phenyl-1-butene (1) were examined in the 290 to 570 °C temperature range. At 360 °C, some reaction occurred to yield small quantities of benzene, toluene, and ethylbenzene in addition to unreacted **1**. Almost complete reaction occurred at 400 °C, at which temperature more than ten components were observed (Figure 1). Temperatures above 450 °C yielded mainly toluene and naphthalene. The major products at 360 °C were toluene, ethylbenzene, **1**, and naphthalene in a relative ratio of 62:10:10:8. Product ratios are not indicative of yield because products of retention time greater than naphthalene are not included. Ratios were obtained by triangulation or cutting-and-weighing of the VPC traces. A separation of the product components was attempted by preparative VPC (¼ in. × 6 ft 5% Dow Corning High Vacuum Grease on Chromosorb G AW-DMCS 80/100 at 70 °C), but only toluene and naphthalene were isolated.

Pyrolyses of 4-(1-Naphthyl)-1-butene (2). The optimal temperature of isomerization was determined to be 400 °C (Figure 1). 1-Methylnaphthalene was generally present in excess of 90%. Preliminary component separation was done by filtration through silica gel with pentane to remove tars, followed by distillation to remove the abundant 1-methylnaphthalene and to leave high boiling and high retention time material, e.g., phenanthrene, in the pot. Separation by preparative VPC was not successful.

Pyrolyses of 4-(9-phenanthryl)-1-butene (3) were performed at 260–430 °C. Although some isomerization was observed at 260 °C, more consistent results were obtained between 300 and 360 °C. At 360 °C 9-methylphenanthrene was the major product, and at 400 °C it was the only product. At 360 °C, 9-methylphenanthrene, **3**, and the most abundant butene isomer were present in a 41:30:11 ratio (Figure 1). Careful column chromatography with 1% benzene in hexane on silica gel succeeded in isolating 9-methylphenanthrene and *n*-butylphenanthrene. Separations by preparative VPC and by column chromatography over 10% $AgNO_3$ on silica gel were not successful.

Pyrolyses of *o*-allyltoluene (4), 2-allyl-1-methylnaphthalene (5), and 9-allyl-10-methylphenanthrene (6) were performed in the same manner. Compound **4**, when heated to 400 °C, exhibited considerable reaction. The major products were found to be **4**, *o*-tolylpropene, methylindans, and tetralin. The naphthalene **5** was pyrolyzed at 400 °C with less than 2% isomerization of the starting material. Similarly, phenanthrene **6** was pyrolyzed at 340 °C to give only minimal isomerization.

Ozonolysis of pyrolysis mixtures of **1** and **4** was performed by dissolving 10 μL of the mixture in 1–2 mL of CH_2Cl_2 cooled to −78 °C. A stream of 1.5% O_3 in O_2 was passed through the mixture until a blue color developed. The mixture was allowed to warm until the color disappeared, then recooled to −78 °C, and treated with 1–2 mL of dimethyl sulfide. The mixture was allowed to warm to room temperature before removing the volatiles by rotary evaporation. The sample was thus ready for GC/MS analysis. Since the aromatic rings of the derivatives of **2** and **3** are vulnerable to attack by O_3, a slightly different procedure was used. A sample of the pyrolysis mixture of **1** in 2 mL of CH_2Cl_2 at −78 °C was completely ozonated in 30 s. This reaction time was then used to limit the amount of ozone passage into pyrolysis mixtures of **2** and **3** that had degrees of isomerization comparable to mixtures from **1**. GC/MS indicated that almost no ring opening had occurred in the naphthalene case and very little in the phenanthrene case.

Pyrolysis of 1 and 3 over alumina was modeled after the procedure described by Lutz.[10] Alcoa F-20 alumina was activated by heating to 650 °C for 4 h. The butenes (15–30 mg) were dissolved in distilled heptane and sealed in 10-mL ampules with a 50-fold excess of alumina (w/w). The samples were heated from 100 to 400 °C, cooled, and extracted from the alumina with CH_3OH. The solvent was removed by distillation or rotary evaporation, and the resulting sample was ana-

lyzed by VPC.

Butene **1** began to isomerize at 260 °C to give a 61:39 mixture of **1** and β-ethylstyrene, as determined by coincident retention times through coinjection techniques. At 340 °C, the styrene comprised 80% of the mixture with no starting material detected. Other products appeared to be the other double-bond isomers.

Phenanthrene **3** isomerized quickly at 260 °C. At 300–320 °C, starting material was nearly all consumed to give products other than the Claisen product. The products were not isolated, but by analogy to **1** they appeared to be the double-bond isomers. Heating to 330–340 °C yielded 9-methylphenanthrene and a major new product that was not the desired 9-allyl-10-methylphenanthrene.

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Registry No.—**1**, 768-56-9; **2**, 2489-88-5; **3**, 69258-17-9; **4**, 1587-04-8; **5**, 69258-18-0; **6**, 69258-19-1; allyl bromide, 106-95-6; 1-(chloromethyl)naphthalene, 86-52-2; 9-(hydroxymethyl)phenanthrene, 4707-72-6; 9-bromophenanthrene, 573-17-1; 9-(bromomethyl)-phenanthrene, 24471-57-6; *o*-bromotoluene, 95-46-5; 1-methylindene, 767-59-9; 1-indanone, 83-33-0; methyl iodide, 74-88-4; 2-bromo-1-methylnaphthalene, 20601-22-3; bis[2-(1-methyl)naphthalene], 50418-13-8; 9-methylphenanthrene, 883-20-5; 9-bromo-10-methyl-phenanthrene, 52979-71-2.

References and Notes

(1) This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant no. CHE77-08384).
(2) C. D. Hurd and H. T. Bollman, *J. Am. Chem. Soc.*, **55**, 699 (1933); **56**, 477 (1934).
(3) For a review, see S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 1 (1975). The attempts include those of A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1843 (1941); A. C. Cope, L. Field, D. W. H. MacDowell, and M. E. Wright, *ibid.*, **78**, 2547 (1956); W. v. E. Doering and R. A. Bragole, *Tetrahedron*, **22**, 385 (1966); G. Maas and R. Regitz, *Angew. Chem., Int. Ed. Engl.*, **16**, 711 (1977); E. N. Marvell and C. Lin, *J. Am. Chem. Soc.*, **100**, 877 (1978).
(4) J. B. Lambert, D. M. Fabricius, and J. J. Napoli, *J. Am. Chem. Soc.*, in press.
(5) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956).
(6) D. M. Fabricius, Ph.D. Dissertation, Northwestern University, 1978, Tables II–V.
(7) S. M. Csicsery, *J. Catal.*, **12**, 183 (1968); *ibid.*, **9**, 336 (1967).
(8) A. F. Plate, L. A. Erivanskaya, A. Halima-Mansour, and G. A. Shevtsova in "Mechanisms of Hydrocarbon Reactions: A Symposium", F. Manta and D. Kallo, Eds., Elsevier, New York, 1975, p 345.
(9) P. B. Valkovich, J. L. Conger, F. A. Costiello, T. D. Brodie, and W. P. Weber, *J. Am. Chem. Soc.*, **97**, 901 (1975); C. J. Adams, S. G. Branderberger, J. B. DuBois, G. S. Mill, M. Nager, and D. B. Richards, *J. Org. Chem.*, **42**, 1 (1977).
(10) R. P. Lutz, H. A. J. Berg, and P. J. Wang, *J. Org. Chem.*, **41**, 2048 (1976).
(11) C. Aso, T. Kunitake, and K. Watanabe, *Kogyo Kagaku Zasshi*, **70**, 1001 (1967); *Chem. Abstr.*, **69**, 10788b (1968), reported the bp 99.2–100.5 °C (4.6 mm).
(12) E. Mosettig and J. Van de Kamp, *J. Am. Chem. Soc.*, **55**, 2995 (1933).
(13) W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **59**, 2207 (1937).
(14) W. E. Bachmann, *J. Am. Chem. Soc.*, **56**, 1363 (1934).
(15) R. DeRidder and R. H. Martin, *Bull. Soc. Chim. Belg.*, **69**, 534 (1960).
(16) B. M. Mikhailov and N. E. Chernova, *Zh. Obshch. Khim.*, **21**, 1517 (1951).

New Oxidizing Agents from the Dehydration of Hydrogen Peroxide

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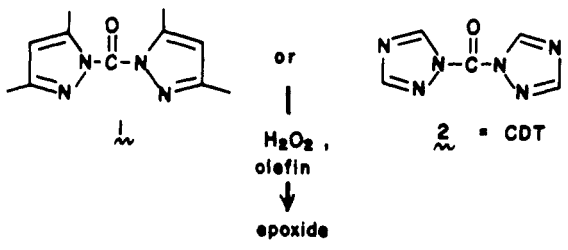
The action of diverse dehydrating agents (activated ureas, isocyanates, cyanates, carbodiimides, and ortho esters) on anhydrous hydrogen peroxide is shown to generate intermediates which are effective epoxidizing agents for olefins. These reagents react rapidly with olefins, operate under mild conditions, and produce neutral byproducts. The applicability of these reagents to synthesis is explored. In the absence of olefins the dehydrating agents react with H_2O_2 to produce singlet molecular oxygen.

A survey of existing epoxidation reagents led us to the premise that new oxygen transfer agents could be devised through the action of chemical dehydrating agents on hydrogen peroxide. We have now examined several such systems. The dehydrating agents were selected to operate under mild conditions (neutral pH, room temperature or below), provide side products of low acidity, and were further designed to have increased oxidation potential through the formation of unusually stable structures (CO_2, amides, ureas) in the oxygen transfer step. These strictures were observed in an effort to develop reagents for direct arene oxidation. While we have not yet succeeded in preparative methods for arene oxides, we detail here our experiences with these systems.

Our initial attempt was directed at monopercarbonic acid, but CO_2 proved unable to mediate the epoxidation of olefins in H_2O_2/THF mixtures even when acidic or basic catalysts were added.[2a] The inertness of CO_2 toward perhydration contrasts sharply with the reactivity of SeO_2,[2b] and we were led to examine more labile CO_2 derivatives. The urea **1**, readily prepared by the action of phosgene on dimethylpyrazole,[3] proved quite reactive. Rapid epoxidation of cyclohexene (50%) and cyclopentene (70%) resulted when **1** was added to anhydrous THF solutions of H_2O_2 containing the olefins (Scheme I).

During the course of these epoxidations, colored side products developed, suggesting that some oxidation of the released pyrazole also occurs. A cleaner system was found in the corresponding 1,2,4-triazole reagent, **2** (carbonylditriazole,[4] hereafter CDT). This reagent, as well as the *N*-benzoylperoxycarbamic acid (**3**, BPC), was examined in some detail. The latter substance was originally generated in situ

Scheme I



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