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.

Acknowledgment. The authors would like to thank Professor Richard Arnold (Southern Illinois University) for discussions that led to this study.

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-methylphenanthrene, 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

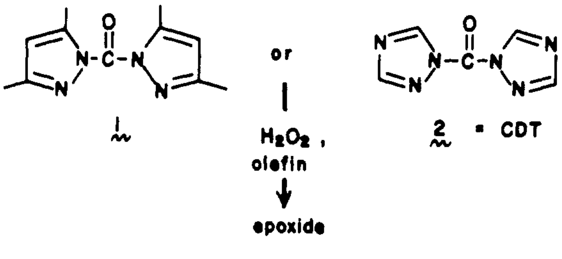

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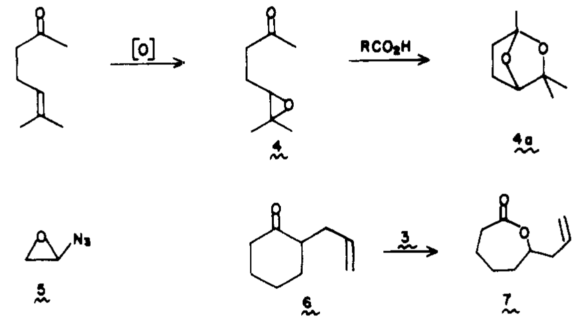
Table I. Epoxide Yields with CDT/H_2O_2 in THF

	registry no.	yield, %	registry no.
cyclopentene	142-29-0	98	285-67-6
cyclohexene	110-83-8	99	286-20-4
cyclododecenes		99	286-99-7
norbornene	498-66-8	95	278-74-0
tetramethylethylene	563-79-1	99	5076-20-0
cholesteryl acetate	604-35-3	92[a]	55400-50-5

[a] By NMR; all others were by GLC.

Scheme II



from H_2O_2 and benzoyl isocyanate (eq 1), but when we found that 3 had been isolated,[5] we used it in its crystalline form.

$$C_6H_5CONCO \xrightarrow{H_2O_2} \underset{3\ (BPC)}{C_6H_5CONHCO_3H} \xrightarrow{olefin} \text{epoxide} \quad (1)$$

Synthetic Applications. The use of CDT and BPC for epoxidation of olefins was examined after optimum conditions had been established. For the CDT/H_2O_2 system, best results were obtained when CDT was added to a chilled solution of olefin (1 M) in THF containing H_2O_2 (3 M). A total of 2 equiv of CDT was added in three portions at ~5-min intervals; reaction was complete in ~30 min. Table I shows yields under these conditions.

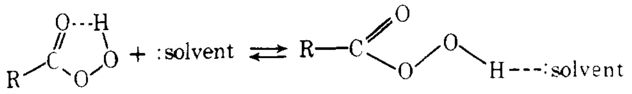
The limited solubility of crystalline BPC in $CHCl_3$ led us to examine its usefulness for epoxidation in THF, even though its reactivity is considerably diminished in the latter solvent (vide infra). Typically, BPC and olefin (both 0.5 M) in THF were allowed to react overnight at room temperature. If olefin was still present after this time, an additional 0.5 equiv of BPC was added. Table II gives yields (GLC) of epoxides.

Either reagent gave >90% isolated yields (1-g scale) of the epoxide 4 (Scheme II), a substance prone to acid-catalyzed rearrangement.[6] A recent report suggests further utility of BPC for sensitive epoxides; the epoxide 5 of vinyl azide was prepared in high yield with this reagent while conventional peracids gave rearranged products, even in the presence of buffers.[7] Neither reagent attacked isophorone, and the reaction of BPC with 2-allylcyclohexanone gave the Baeyer–Villiger reaction rather than epoxide.[8]

The action of CDT/H_2O_2 on arenes was briefly examined. Benzene, toluene, *p*-xylene, and naphthalene were recovered unchanged, while phenanthrene was recovered only to the extent of 75%; diphenic acid (9%) was the sole oxidation product obtained. Disappearance of mesitylene (11%), anisole (6%), and *m*-dimethoxybenzene (35%) was also observed. Experiments with *m*-chloroperbenzoic acid and these arenes showed that only the dimethoxybenzene was attacked under these conditions (2 h, THF, 25 °C).[9] With the BPC reagent, phenanthrene gave diphenic acid while naphthalene gave a complex mixture.

Epoxidation Rates. Many of the previous studies concerning the solvent dependence of peracid epoxidation rates have relied on titrimetric assay for the disappearance of peracid; relatively few have employed a method for the determination of actual epoxide formed.[10] Since we have found that the slowest rates reported, say for *m*-chloroperbenzoic acid epoxidations, reflect decomposition of the peracid rather than epoxidation, we have used GC analysis of epoxides exclusively as an indication of reaction rates. Unfortunately, stoichiometric reaction of CDT and olefins in the presence of slight excesses of H_2O_2 in THF failed to give good second-order kinetic plots. Reaction rates slowed dramatically as the olefin concentration decreased, suggesting that a second reaction was consuming the epoxidizing agent (this was subsequently shown to be $^1O_2$ formation and will be discussed below). However, *initial* rates of epoxidation could be measured for reactions proceeding up to 50%. Results of the initial rate studies are given in Table III.

These rates reveal an insensitivity of the CDT-derived reagent to solvent basicity. For conventional peracids, rates decrease as the Lewis basicity of the solvent increases; good correlations exist between epoxidation rates and shifts in the infrared stretching frequency of the peracid O–H bond in a given solvent.[11] This trend is attributed to the disruption of the intramolecular hydrogen bond which is apparently necessary for the epoxidation reaction (eq 2).



(2)

The crystalline BPC reagent was used in rate studies under second-order conditions; good plots were obtained with dialkyl- and higher alkylethylenes, but monosubstituted olefins gave poor plots due to peracid decomposition. Results with cyclododecenes (commercial mixture) are shown in Table IV. These results resemble those obtained for conventional peracids.

Competition studies using olefin pairs in excess established further similarities between these experiments and other peracids.[12]

Table II. Epoxidation with BPC in THF

olefin	registry no.	yield, %	registry no.	olefin	registry no.	yield, %	registry no.
1-heptene	592-76-7	81[a]	5063-65-0	*cis*-4-methyl-2-pentene	691-38-3	99	1192-31-0
1-octene	111-66-0	68[a]	2984-50-1	*trans*-4-methyl-2-pentene	674-76-0	79	
1-decene	872-05-9	61[a]	2404-44-6	1-methylcyclohexene	591-49-1	89	1713-33-3
trans-5-decene	7433-56-9	92	53248-86-5	1-methylcyclopentene	693-89-0	92	16240-42-9
trans-2-heptene	14686-13-6	84	14925-96-3	cyclohexene		99	
2-octenes		92	3234-26-2	allylbenzene	300-57-2	73[a]	4436-24-2
cis-stilbene	645-49-5	54	17619-97-5	α-methylstyrene	98-83-9	95	2085-88-3
trans-stilbene	103-30-0	59		β-methylstyrene	637-50-3	92	4436-22-0
indene	95-13-6	95[b]	768-22-9				

[a] 1.5 equiv of BPC. [b] By NMR.

Table III. Epoxidation Rates of Cyclohexene[a]

	THF	$CHCl_3$	Et_2O	DMF
perbenzoic acid[11]	4.3	472	5.8	2.2
CDT + H_2O_2	710	790	700	250

[a] $M^{-1}\,s^{-1}$, × 10^4.

Table IV. Solvent Dependence of the Rate of Epoxidation of Cyclododecenes with BPC

solvent	$CHCl_3$	MeOH	THF	EtOH
rate (× 10^4), $M^{-1}\,s^{-1}$	1450	9.5	6.4	4.8

Table V. Rates of Olefin Epoxidation Relative to Cyclohexene (THF, 25 °C)

	CDT/H_2O_2	BPC
1-heptene	<0.01	<0.01
trans-2-heptene		0.67
norbornene	0.5	1.1
cyclopentene	1.1	
1-methylcyclohexene	9.2	24
tetramethylethylene	>100	>100

Singlet Oxygen. When CDT is added to a solution of H_2O_2 in THF, rapid gas evolution occurs and, if measured by means of a buret, 2.0 (±0.1) mol of gas is generated from 1 mol of CDT. When the THF solution contains excess cyclohexene, or is saturated with diphenylanthracene (DPA), only 1 mol of gas is liberated. From the fomer solution cyclohexene oxide (>90% yield based on CDT) is obtained, while DPA endoperoxide can be isolated in high yield from the latter solution. Finally, if excess 1-decene is present, 1.5 mol of gas is liberated and the corresponding epoxide is obtained (30% yield). These results are most economically accommodated by Scheme III.

The intermediate is partitioned between two pathways: epoxide formation at a rate dependent on olefin concentration and olefin reactivity (k_2), or $^1O_2$ formation by reaction with more H_2O_2. The $^1O_2$ may then decay to $^3O_2$ or be trapped by DPA. The efficiency of this latter process is dependent on $k_4[DPA]/k_d$, a ratio expressed as β[13] (the concentration of DPA at which 50% of the $^1O_2$ is trapped).

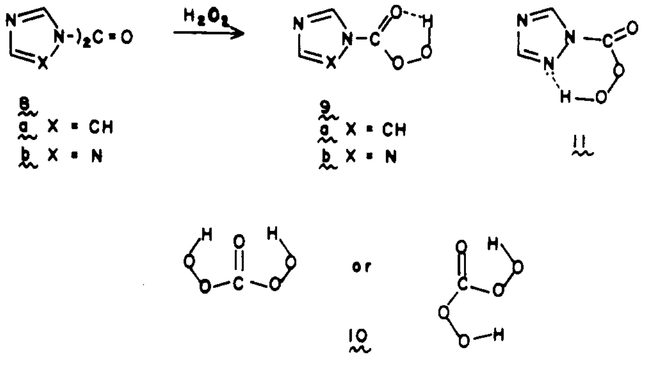
In order to put these observations in more quantitative form, we determined the β value for DPA in THF (0.016 M) and used this value to calculate the yield of $^1O_2$ spectrophotometrically.[14] By measuring the decrease in UV absorbance of DPA, the yield of $^1O_2$ from the CDT/H_2O_2 system was determined to be 95%. This system and others discussed below represent some of the most efficient chemical sources of $^1O_2$ available.[15] Unfortunately, the oxidation of H_2O_2 by the intermediate lowers its value as an epoxidizing agent; unreactive olefins (1-alkenes and particularly arenes) are unable to compete effectively with the $^1O_2$-forming process. Conversely, the reactivity of the intermediate toward the substituted olefins useful for "ene" reactions lowers its value as a $^1O_2$ source.[16]

At room temperature, addition of benzoyl isocyanate to ethereal solutions of H_2O_2 gives oxygen. Using methods described above, we determined that the oxygen was generated in its singlet state and that it was produced in 98% yield. Moreover, the action of H_2O_2 at 25 °C on THF solutions of BPC also results in $^1O_2$ formation, a result which implicates BPC as the intermediate in the oxidation of H_2O_2. Whether the immediate precursor to $^1O_2$ in this (or related[17]) reactions is the elusive H_2O_3 has yet to be experimentally tested.

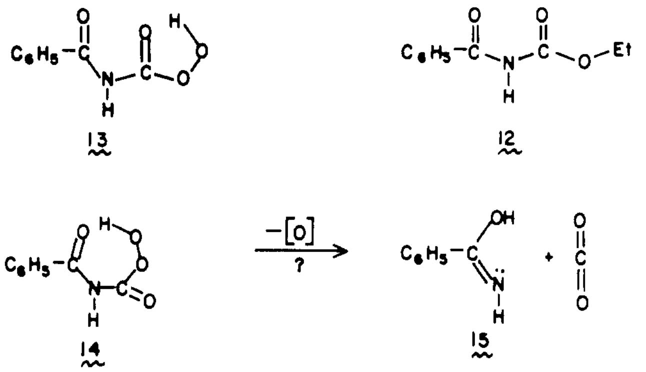
Scheme III

$$\begin{tikzcd}
\mathrm{CDT} + H_2O_2 \arrow[r] & \left[\text{intermediate}\right] \arrow[r, "k_2\,[\text{olefin}]"] \arrow[d, "k_5\,[H_2O_2]"] & \text{epoxide} + CO_2 \\
{}^3O_2 & \left[{}^1O_2\right] \arrow[l, "k_d"'] \arrow[r, "k_4\,[\text{DPA}]"] & \text{endoperoxide} + H_2O + CO_2
\end{tikzcd}$$

Scheme IV



Scheme V



Recently the reaction of some dienes with oxygen to yield endoperoxides has been observed via intermediates other than singlet oxygen.[34] Therefore, the isolation of DPA endoperoxide in our systems is less than proof that $^1O_2$ is generated. Unfortunately, the detection of $^1O_2$ through its other characteristic reactions, e.g., dioxetane formation from electron-rich olefins,[35] ene reactions,[36] or sulfide to sulfoxide oxidations,[37] is precluded by the presence of powerful oxidants in our systems.

Structure. Attempts directed at isolation or spectroscopic observation (low temperature IR) of the intermediate in the CDT/H_2O_2 system were unsuccessful; therefore, evidence in support of **11** (Scheme IV) is far from convincing. One indication that a peculiar hydrogen bond exists in the intermediate is the observed insensitivity of epoxidation rate to solvent basicity. A second indication arises from the *failure* of the corresponding imidazole-derived reagent **8a** to epoxidize olefins under conditions in which **8b** gives high yields of epoxides. Given the similar reactivity of reagents 8 toward oxygen nucleophiles,[18] both should react smoothly with H_2O_2. Either **9a** or **9b** would have the conventional peracid conformation shown, and either might yield the peroxy carbonates **10.** Yet only the CDT system gives epoxides, a result hard to reconcile if **9a** or **10** is the actual epoxidizing agent. Only the triazole-derived reagent may assume the conformer 11 in which a different intramolecular H bond exists, a feature which could permit extrusion of CO_2 as epoxidation occurs.

The structures proposed for BPC rest on IR evidence; carbonyl stretching frequencies occur at 1782 and 1670 cm^{-1}, while the model **12** (Scheme V) shows absorptions at 1786 and

Table VI. Yields of Epoxides and Recovery of Olefins in Epoxidations with *N*-Benzoyl-*N'*-*tert*-butylcarbodiimide and H_2O_2

olefin	% epoxide	% olefin	material balance, %
trans-5-decene	90	1	91
cis-4-methyl-2-pentene	88		
trans-4-methyl-2-pentene	86		
trans-β-methylstyrene	1	16	17
cyclohexene	74	0	74
1-octene	51	24	75
2-octenes	76	10	86
1-heptene	53	35	88
trans-2-heptene	89	2	91
1-decene	69	37	100
1-methylcyclohexene	0	1	1
1-methylcyclopentene	0	0	0

Table VII. Epoxidation with 18/H_2O_2

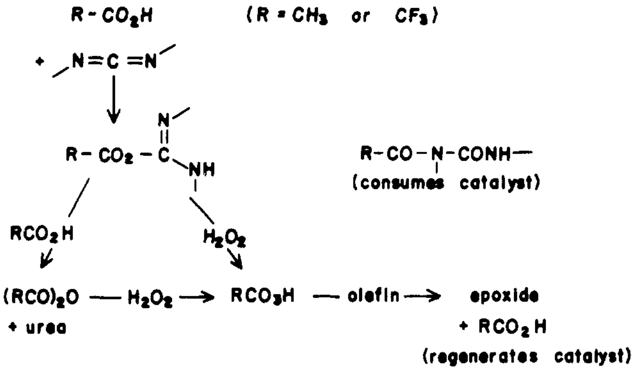
	epoxide, %	recovered olefin, %
1-heptene	0	67
1-octene	10	72
1-decene	5	81
trans-5-decene	20	70
trans-2-heptene	0	50
2-octenes	24	47
cis-4-methyl-2-pentene	34	42
trans-4-methyl-2-pentene	24	59
1-methylcyclohexene	0	0
1-methylcyclopentene	0	0
cyclohexene	41	25
cis-stilbene	7	
trans-stilbene	14	
α-methylstyrene	27	
β-methylstyrene	22	40
indene	20	

1718 cm^{-1}. If the high frequency absorptions are assigned to the urethane carbonyls, the shift in benzoyl absorptions (1718 → 1670 cm^{-1}) is hard to rationalize in a structure such as **13**. However, a structure involving a seven-membered hydrogen bond[19] as in 14 would readily accommodate this spectroscopic shift. Whether 14 does indeed form CO_2 and 15 as oxygen transfer occurs is presently a matter of conjecture.

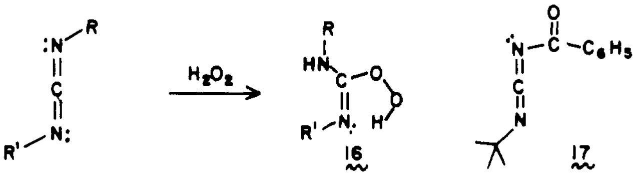
Other Dehydrating Agents. (1) Carbodimides. The commercially available dicyclohexylcarbodiimide (DCC) failed to epoxidize cyclododecenes in THF containing H_2O_2 even when acidic (HCl or HBF_4) or basic ($NaHCO_3$) catalysts were present. Acetic or, better, trifluoroacetic acids were effective epoxidation catalysts, but it is likely that the actual epoxidizing agents in these cases were the corresponding peracids. Further, epoxidation ceased after a few turnovers with these "catalysts" and acylureas could be found in the reaction mixture. Scheme VI depicts the probable events in this system.

The carbodiimide derived from α-phenylethylamine[20] reacted slowly with H_2O_2 without catalyst, but epoxide yields were low. Although faster epoxidation was observed in the presence of toluenesulfonic acid, we felt that structural modification of the carbodiimide was more likely to enhance the formation of adducts such as **16** (Scheme VII) than further search for catalysts. Accordingly, we prepared the benzoyl derivative 17 of Mitsunobu,[21] described as highly sensitive to moisture. Indeed, moderate to fair yields of epoxidation occurred with this reagent (Table VI).

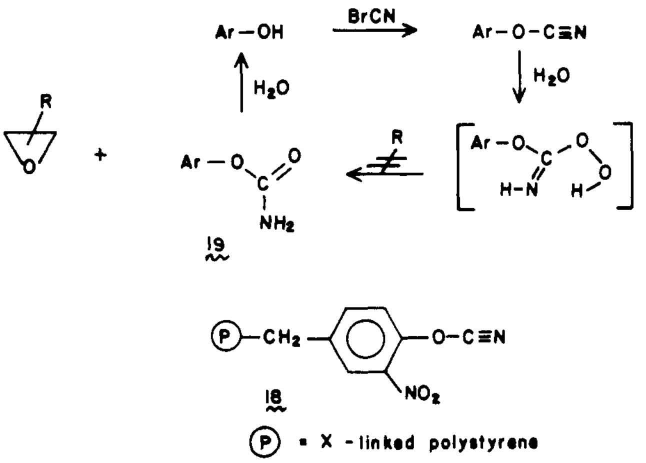
Scheme VI



Scheme VII



Scheme VIII



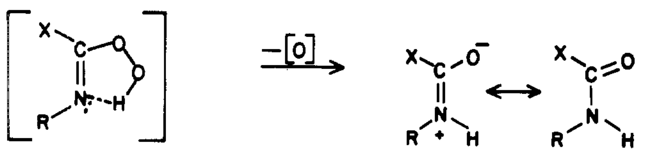
Control experiments disclosed that the epoxide products were unstable to the reaction conditions; i.e., neither H_2O_2 nor the carbodiimide alone had effect on epoxide, but the combination of the two destroyed some 60% of the epoxide under the reaction conditions. Therefore, the degree of epoxidation in Table VI is more accurately reflected by the disappearance of olefin than the appearance of epoxide. A recent report[22] of the isolation of a fragile *arene* oxide from such reaction mixtures is remarkable.

Again, $^1O_2$ was observed in the absence of olefin, but in low (~10%) yield (based on carbodiimide).

(2) Cyanates. Aryl cyanates, once available only with difficulty, have become readily accessible by the direct cyanation of phenols devised by Grigat[23] (eq 3). The structural and electronic characteristics of the phenols can be varied without reduction in yields of the cyanates, and these possibilities attracted our curiosity; 1-naphthyl cyanate was prepared, but it failed to react with H_2O_2 (or with other oxygen nucleophiles) even with acid or base catalysts in THF or $CHCl_3$. The polymer-bound nitro-substituted cyanate 18 (Scheme VIII), however, reacted readily with H_2O_2 without catalyst, and epoxides were indeed formed from olefins. Once again the epoxides, particularly those of trisubstituted olefins, proved unstable to the reagent system, and only low yields could be obtained. These results are summarized in Table VII.

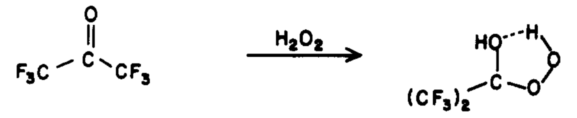
$$ArOH + BrCN \xrightarrow{R_3N} ArOCN \qquad (3)$$

Scheme IX



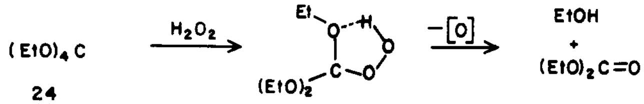
20 X = ArCONH−; R = *t*-Bu

21 X = ArO⁻; R = H

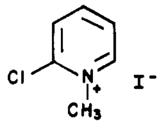


22 **23**

Scheme X



24 **25**



26

The other product, i.e., the polymer-bound aryl carbamate **19** (Scheme VIII), could easily be converted to the phenol (stirring with aqueous THF) and thence recycled to the cyanate. The ease of separating the polymer-bound components from these solutions was helpful, but the reagent does not provide enough epoxide to be considered synthetically useful. As a source of $^1O_2$, however, the system was very good, and at least 60% of $^1O_2$ could be obtained as determined by trapping with DPA.

(3) Ethyl Orthocarbonate. The structures of the intermediates involved in the carbodiimides or cyanate experiments are reasonably formulated as **20** and **21** (Scheme IX), respectively. As in peracids, intramolecular H bonds are present and the remaining π bond permits the generation of a neutral substance after oxygen transfer. In an effort to test the necessity of the π bond, we examined the reaction of H_2O_2 with ethyl orthocarbonate. Some evidence on this point may be inferred from the known ability of hexafluoroacetone (**22**) to mediate Baeyer–Villiger reactions and aromatic hydroxylations with H_2O_2,[24] and even olefin epoxidations.[25]

The addition of ethyl orthocarbonate (**24**) to olefin–H_2O_2 mixtures in THF does indeed result in epoxidation. Yields (not optimized) are low (Table VIII), and once again $^1O_2$ can be detected as its adduct with DPA.

As with the other reagents, little may be said concerning the structure of the actual epoxidizing agent, although **25** (Scheme X) appears to be a reasonable candidate. Finally, we examined the pyridinium salt **26**, useful for a number of dehydration reactions.[26] While olefin disappearance was observed, epoxide yields were low and the colored side products which developed during the course of the reaction precluded attempts to detect $^1O_2$.

Conclusion

It appears that the action of dehydrating agents on H_2O_2 usually produces intermediates capable of olefin epoxidation.

Table VIII. Epoxidation with Ethyl Orthocarbonate (A) or Pyridinium Salt (B) with H_2O_2

olefin	epoxide, % A	epoxide, % B	olefin loss B, %
6-methyl 5-hepten-2-one	22	0	4
trans-β-methylstyrene	14	0	6
1-methylcyclohexene	11	3	30
cyclooctene	6	5	6
cyclohexene	0	20	6

The generation of peroxyacids by the perhydrolysis of anhydrides can be considered as a special case of this general reaction.

Experimental Section

All reagents were purchased from Aldrich Chemical Co. except cholesterol, which was obtained from Baker Chemical Co., cyclododecene, which was purchased from Eastman Kodak, and 98% hydrogen peroxide, which came from FMC Corp. All infrared spectra were taken on a Beckman Model IR-5A infrared spectrometer; solids were run as potassium bromide pellets and liquids neat. NMR spectra were run on a Varian Model T-60 nuclear magnetic resonance spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Büchi Schmeltzpunktbestimmungs apparatus and are reported uncorrected. Gas chromatography was performed on either a Varian A-90 thermal conductivity gas chromatograph or a Perkin-Elmer Model 800 flame ionization gas chromatograph under the conditions and on the columns specified. Epoxides were prepared as standards by epoxidation with *m*-chloroperoxybenzoic acid with sodium carbonate added for acid-sensitive epoxides. Solvents were dried as follows: tetrahydrofuran was distilled from lithium aluminum hydride after being refluxed under nitrogen to a red color from triphenylmethane; benzene was distilled from sodium using benzophenone as an indicator; chloroform was distilled from phosphorus pentoxide; ether was distilled from calcium hydride; ethanol was distilled from magnesium ethoxide; and dimethylformamide was distilled from barium oxide under reduced pressure.

Preparation of *N,N*′-Carbonylbis(3,5-dimethylpyrazole) (1). *N,N*′-Carbonylbis(3,5-dimethylpyrazole) was prepared according to Staab as follows.[3] 3,5-Dimethylpyrazole (3.48 g, 37 mmol) was dissolved in 50 mL of dry THF. Condensed phosgene (7.2 mL, 9.4 mmol) was added to 100 mL of dry THF; 10 mL of this solution was then added dropwise to the stirred solution of the pyrazole over a 10-min period at room temperature. The precipitated pyrazole hydrochloride salt was filtered, the solvent was removed from the filtrate in vacuo to yield a white solid, and the melting point was 85–87 °C (lit.[3] 86–87 °C). This was stored under nitrogen and used without further purification: IR 2960, 1720, 1584, 1442, 1150 cm^{-1}.

Epoxidation of Olefins with 1 and H_2O_2. A solution of 436 mg of **1** (2 mmol) in 25 mL of dry THF was added dropwise to a THF solution containing 1 mmol of olefin, 1 mmol of decane as an internal GLC standard, and 2 mmol of 98% H_2O_2. The solution was stirred, and the products were analyzed by gas chromatography using a 5 ft × 1/8 in. SE-30 on Chromosorb W column at 115 °C, 20 mL/min He flow rate: t_R = 3.1 (cyclohexene), 5.2 (cyclohexene oxide), 2.9 (cyclopentene), 5.0 (cyclopentene oxide), and 7.9 min (decane).

Preparation of 1-(Trimethylsilyl)-1,2,4-triazole. The procedure of Biskofer[4] was modified as follows. 1,2,4-Triazole (13.8 g, 0.197 mol) was refluxed overnight under nitrogen with 24.2 g of hexamethyldisilazane (0.150 mol). The reaction flask was cooled to room temperature, and then the product was fractionally distilled under nitrogen. The fraction boiling at 72–74 °C/11 mmHg was collected. The yield was 25.5 g of a clear liquid product (96.5%).

Preparation of 1,1′-Carbonylbis(1,2,4-triazole)(2, CDT). A benzene solution of 14.1 g of 1-(trimethylsilyl)-1,2,4-triazole (0.1 mol) was stirred at room temperature as phosgene was bubbled through the mixture until no more was absorbed. The mixture was flushed with dry nitrogen and filtered under nitrogen in a glovebox. The yield of product was 13.3 g (81.2%). The product was a white solid which was very sensitive to moist air and had a melting point of 142–145 °C in a sealed capillary (lit.[4] 144–145 °C): IR 3139, 1760, 1481, 1376 cm^{-1}; NMR (CD_3CN) δ 9.35 (s), 8.20 (s).

Epoxidation of 6-Methyl-5-hepten-2-one with CDT/H_2O. 6-Methyl-5-hepten-2-one (1 g, 7.94 mmol) was dissolved in dry THF, and 1.0 mL (98%) of H_2O_2 was added. The solution was stirred at room temperature as 1.5 g (1 equiv) of CDT dissolved in 25 mL of dry THF was slowly added. After the addition, the reaction mixture was stirred for 1 h and then a second equivalent of CDT was added as a solid with stirring for two more hours. The THF was removed in vacuo, and the residue was taken up in CCl_4 and extracted with water to remove excess H_2O_2 and 1,2,4-triazole. The organic layer was dried over sodium sulfate and the CCl_4 removed to yield the crude epoxide. No acetal rearrangement product was detected by gas chromatography. A microdistillation yielded 917 mg (92%) of the epoxide:[28] IR 1715, 1397, 1358, 1165 cm^{-1}; NMR (CCl_4) δ 2.57 (m, 3), 2.13 (s, 3), 1.67 (m, 2), 1.25 (s, 6).

Preparation of *N*-Benzoylperoxycarbamic Acid (3, BPC). A three-neck, round-bottom flask (500 mL) equipped with a dropping funnel, a low temperature thermometer, a magnetic stirrer, and a nitrogen inlet and exhaust was charged with dry ether (120 mL) and H_2O_2 (4 mL, 98%). This solution was cooled to −15 °C in an ice–isopropyl alcohol bath, and benzoyl isocyanate[27] (29.3 g, 25 mL, 0.199 mol) in dry ether (120 mL) was added with stirring over a period of 30 min. During the addition, the temperature was maintained between −12 and −7 °C. As the addition of benzoyl isocyanate was carried out, the precipitate of BPC appeared. After the addition of benzoyl isocyanate was completed, the reaction was stirred for an additional 2 h at −20 °C. The precipitated solid benzoylperoxycarbamic acid was rapidly filtered and washed with cold ether, room temperature CH_2Cl_2, and then pentane and air-dried for 15 min: yield 19.5 g (54%); mp 113–115 °C dec (lit.[5] 98–105 °C). Iodometric titration of the benzoylperoxycarbamic acid indicated a purity of 92.3%. It is stable indefinitely in the freezer (no decomposition was discernible in a sample stored at −25 °C for 17 months) and has moderate stability in solution (a 0.2 M THF solution lost 5% of its activity in 10 h at 25 °C), but its decomposition is accelerated by H_2O_2 or certain olefins.

Reaction of Olefins with BPC. A 5-mL round-bottom flask was charged with BPC (200 mg, 1 mol, based on 90% purity of the crystalline BPC) and dry THF (1 mL). To this slurry was added a THF solution of the olefin and an internal standard (1 mL, 1 M olefin, 1 M standard). The flask was tightly stoppered and stirred for 16 h. After the period of stirring was completed, the crude reaction mixture was stored in a freezer at −35 °C until analysis of the reaction mixture could be made. The crude reaction mixture was analyzed by gas–liquid chromatography for the presence of epoxide and olefin.

Kinetic Measurements (General Procedure) for CDT/H_2O_2. To a solution of 142.3 mg (1 mmol) of decane and 82.1 mg (1 mmol) of cyclohexene was added 0.2 mL of 98% H_2O_2 (8.25 mmol). Solvent was added to make the volume 10 mL, and 325 mg of CDT (2 mmol) was added in 15 mL of solvent. The reaction was allowed to proceed in a water bath at 25 °C; 2-mL aliquots were taken from the reaction at 10-min intervals, quenched with 1 M sodium bisulfite, extracted with pentane, dried over sodium sulfate, and analyzed by gas chromatography on a 6 ft × 1/4 in. 15% SE-30 Chromosorb W column at 115 °C, 20 mL/min He flow: t_R = 5.2 (cyclohexene oxide) and 7.9 min (decane).

Competitive Rate Constant Determination with CDT/H_2O_2. Competitive rate experiments were run with the following pairs of olefins: 1-heptene/2-heptene, 1-octene/2-octene, 2-heptene/cyclohexene, 2-octene/cyclohexene, 1-methylcyclohexene/cyclohexene, cyclopentene/cyclohexene, norbornene/cyclohexene, and 2,3-dimethyl-2-butene/cyclohexene.

A THF solution, 1 M in each olefin in the pair to be tested (5 mmol of each olefin), was placed in a 50-mL three-neck flask under nitrogen. A 0.1-mL amount of 98% H_2O_2 was added, followed by 41 mg of CDT (0.25 mmol) dissolved in dry THF. After 10 min, gas chromatographic analysis under the conditions shown in Table V gave the competition constants. (A gas chromatography standard of the two respective epoxides was prepared for calibration.)

Pseudo-First-Order Competition Constants for Olefins with BPC. A 5-mL round-bottom flask equipped with a magnetic stirrer was charged with a THF solution of olefin A (1 M) and a THF solution of olefin B (1 M), such that the total volume present was 1 mL and the total olefin concentration was 1 M. To this solution of olefins was added BPC (20 mg, 1 mmol, based on a 90% purity of the crystalline BPC) with rapid stirring. The reaction mixture was tightly stoppered and stirred at room temperature for 4 h or until a potassium iodide-peroxide test was negative. The reaction mixture was then analyzed by gas–liquid chromatography for the epoxides present.

Reaction of 6-Methyl-5-hepten-2-one with BPC. An Erlenmeyer flask which had been washed in concentrated ammonium hydroxide was charged with 6-methyl-5-hepten-2-one (2.5 g, 0.02 mol) and dry THF (20 mL). This solution was chilled in an ice bath, and to it was added BPC (3.6 g, 0.02 mol, based on 100% purity for the crystalline BPC) over a period of 5 min. The reaction was allowed to stir in the cold for a period of 30 min and then was allowed to warm to room temperature and stir for an additional 30 min. The benzamide present was separated by precipitation with pentane (50 mL) followed by filtration. The filtrate was concentrated in vacuo, and the residue was vacuum distilled to yield 2.24 g (79%) of the epoxide, identical in all respects with that obtained from CDT/H_2O_2.

Reaction of Allylcyclohexanone with BPC. To a stirred solution of allylcyclohexanone (138 mg, 1 mmol) in dry THF (1 mL, freshly distilled from sodium benzophenone) was added BPC (181 mg, 1 mmol, based on 100% purity of the crystalline BPC) as the solid material in small portions. After the addition was complete, the reaction was stirred for an additional hour. The reaction mixture was diluted with pentane (10 mL), and the precipitated benzamide was separated by filtration. The resulting filtrate was concentrated in vacuo and taken up in CCl_4. The proton magnetic resonance and infrared spectra of this material proved to be identical with those previously reported[8] for 6-hydroxynon-8-enoic acid lactone: NMR (CCl_4) δ 1.1–2.9 (m, 10, $-CH_2-$), 4.22 (m, 0.7, $-OCH-$), 5.0 (m, 2, $-HC{=}CH_2$), 5.8 (m, 1, $-CH{=}CH_2$); IR 1715, 1637, 1172 cm^{-1}. The integration of the lactone $-OCH-$ proton at 0.7 is probably representative of an approximate yield of 70% in the reaction. The presence of starting material was substantiated by the presence of a shoulder in the infrared spectrum at 1698 cm^{-1}, the position of the original ketone carbonyl band.

Reaction of Indene with BPC. A 5-mL round-bottom flask which had been washed with concentrated ammonium hydroxide and dried was equipped with a magnetic stirrer and charged with indene (232.3 mg, 2 mmol) and dry THF (2 mL). To this solution was added BPC (400 mg, 2 mmol, based on 90% purity of the crystalline BPC) in small portions over a 5-min period. After the BPC addition was completed, the reaction was tightly stoppered and allowed to stir for 7 h at room temperature. At this time, gas chromatographic analysis of the crude reaction mixture showed the presence of olefin and a potassium iodide test showed the presence of little peroxide. An additional portion of BPC (200 mg, 1 mmol) was added in small portions, and the reaction was stirred for an additional 12 h at room temperature. At this time, gas chromatography showed the absence of olefin. Benzamide was separated from the reaction mixture by dilution with pentane (50 mL) followed by filtration. The filtrate was concentrated in vacuo, and the oily residue was molecularly distilled (110 °C, 1 torr). The yield was 124 mg of a mixture which appeared to be 86% epoxide, 10% ketone, and 4% olefin by proton magnetic resonance integration: NMR (CCl_4) δ 2.9 (m, 2, β-H epoxide), 4.0 (m, 2, epoxy H), 7.2–7.6 (m, 4, PhH), 3.25 (s, 2, allylic H of olefin), 3.4 (s, 4, α-H ketone); IR (neat) 1754, 829, 758, 723 cm^{-1}.

Standard Oxidation of Arenes with *m*-Chloroperoxybenzoic Acid. Solutions (0.1 M) of benzene, naphthalene, phenanthrene, toluene, *p*-xylene, mesitylene, anisole, and *m*-dimethoxybenzene were prepared in dry THF with 1 equiv of decane as an internal gas chromatography standard. A 1-mL amount of each solution was pipetted into a 5-mL flask followed by the addition of 20 mg of 85% *m*-chloroperoxybenzoic acid (0.1 mmol). The solutions were stirred at room temperature and analyzed by gas chromatography on a Varian Model 1200 A flame ionization instrument using a 5 ft × 1/8 in. 5% SE-30 on 60/80 DMCS column.

Oxidation of Arenes with CDT/H_2O_2. The solutions prepared above were treated with 0.05 mL (90%) of H_2O_2 followed by 16.4 mg (0.1 mmol) of CDT. The solutions were stirred for 2 h at room temperature and analyzed by gas chromatography as above.

Oxidation of Phenanthrene with CDT/H_2O_2. Phenanthrene (178 mg, 1 mmol) and 226 mg of hexadecane (1 mmol) as an internal standard were placed in a 100-mL three-neck flask under nitrogen. Chloroform was added, then 0.2 mL (98%) of H_2O_2, and the reaction flask was stirred as 360 mg (2 mmol) of CDT was added in three equal portions over a 30-min time period. The reaction was stirred for 4 h at room temperature. Gas chromatographic analysis on a 6 ft × 1/4 in. 15% SE-30 on Chromosorb W column at 250 °C showed about a 20% loss of phenanthrene. The reaction mixture was filtered and subjected to TLC (ethyl acetate), which showed phenanthrene (R_f 0.60) and two other spots with low R_f values. Chloroform was added to the reaction mixture. Extraction with 1 N sodium hydroxide, neutralization with hydrochloric acid, back-extraction into fresh $CHCl_3$, desiccation with sodium sulfate, and evaporation of the $CHCl_3$ yielded 15 mg of a white solid (9%) identified as diphenic acid: mp 227–228 °C (lit. 227–229 °C); IR 1677, 1288, 1261, 758, 749 cm^{-1}. None of the other products were isolated or identified.

Reaction of Phenanthrene with BPC. A flask was charged with phenanthrene (178 mg, 1 mmol), *n*-hexadecane (183 mg) as an internal standard, chloroform (1 mL), and 4,4′-thiobis(6-*tert*-butyl-3-methylphenol)[30] (10 mg). To this stirred solution was added BPC (181 mg,

Table IX

solvent	R_f(9,10-DPA)	R_f(DPA peroxide)
3:1 petroleum ether/ benzene	0.44	0.22
benzene	0.63	0.51

0.9 mmol, based on 90% purity of the crystalline BPC). After 30 min, an additional portion of $CHCl_3$ (2 mL) was added to maintain ease of stirring and the reaction was allowed to stir for 2 h at room temperature, at which time it was determined by gas–liquid chromatography that 80% of the original phenanthrene remained. An additional portion of BPC (362 mg, 1.8 mmol) was added at this time and the stirring continued. After 96 h, the remaining phenanthrene constituted 30% of the original amount. Again an additional portion of BPC (362 mg, 1.8 mmol) was added to the reaction. The mixture was stirred for an additional 90 h, for a total of 186 h. At this time, only 9% of the starting phenanthrene remained. The reaction mixture was poured into pentane (100 mL) and the solid material was filtered off. This solid was taken up in ethyl acetate (10 mL) and subjected to thin-layer chromatography (methyl acetate/silica gel). Phenanthrene and benzamide were identified by comparison with known standards. At least two additional spots were observed (R_f 0.5 and 0). The ethyl acetate solution was extracted with sodium hydroxide solution (1 N, 10 mL), and this base extract was acidified and reextracted with ether (10 mL). On thin-layer chromatography the material recovered showed only the two unknown spots (R_f 0.5 and 0). This ether solution of acidic compounds was treated with dicyclohexylamine, and the resulting precipitate was filtered, washed with ether, and partitioned between ether and aqueous hydrochloric acid (2 N). The ether layer was dried (Na_2SO_4) and evaporated. The solid residue was recrystallized from acetone, mp 228–229.5 °C. The infrared spectrum was identical with that of diphenic acid.

Purity of CDT by Gas Evolution. An 84-mg amount of CDT was placed in dry THF in a three-neck flask attached to a 60-mL dropping funnel loaded with aqueous THF. The system was saturated with dry carbon dioxide and equilibrated on a gas measuring line. The aqueous solution was then added, and the amount of gas evolved was measured; 7.9 mL of carbon dioxide was evolved (97% of theoretical).

Gas Evolution from CDT and H_2O_2. A solution of 94 mg of CDT (0.555 mmol, based upon 97% purity) in 50 mL of dry THF was placed in a 60-mL dropping funnel attached to a 100-mL flask containing 1 M H_2O_2 in THF. The system was attached to a gas measuring buret and saturated with carbon dioxide. The system was equilibrated at 25 °C, and then the CDT solution was added to the H_2O_2; 28 mL of gas was evolved (2.04 equiv of gas at 25 °C). Similar experiments were attempted with benzoyl isocyanate, but in each case 1 equiv of gas was evolved upon reaction with either water or hydrogen peroxide. This experiment was repeated three times with similar results. The CDT gas evolution experiment was repeated with a saturated solution of 9,10-diphenylanthracene (DPA) (0.05 M) present. When 0.467 mmol of CDT was decomposed on a gas measuring line by H_2O_2 in the presence of 9,10-diphenylanthracene, 11.4 mL (1 equiv) of gas was evolved at 25 °C. The gas was determined not to be oxygen by its failure to ignite a smoldering wooden splint.

Qualitative Trapping of Singlet Oxygen with 9,10-Diphenylanthracene (DPA). A solution of 50 mg of DPA (0.15 mmol) in dry tetrahydrofuran (2 mL, freshly distilled from sodium) was stirred under nitrogen, and then 0.25 mL (98%) of H_2O_2 was added. A solution of 1 mmol of dehydrating agent in 4 mL of dry THF was slowly added (dropwise by syringe). After the evolution of gases had subsided, the products were analyzed by thin-layer chromatography on commercial alumina plates. The R_f values of the various standards are shown in Table IX and were identical with the endoperoxide prepared by photosensitized oxygenation of DPA.

Partitioning Experiments. A stock solution was prepared by taking 831 mg of cyclohexene (10 mmol), 86.5 mg of decane (0.61 mmol) as an internal GLC standard, and 0.3 mL (98%) of H_2O_2. An aliquot of the solution was titrated with sodium thiosulfate for iodine liberated from potassium iodide to determine the actual H_2O_2 concentration. It contained 0.097 mmol of H_2O_2/0.1 mL. This solution, 9.7 mL, was equilibrated on a gas measuring line and saturated with dry CO_2. Then 86.3 mg (97%) of CDT (0.510 mmol) was added and the gas evolution measured. A 10.6-mL amount of gas was evolved (0.88 equiv). The amount of epoxide present was analyzed by gas chromatography with an internal standard; 90.3% epoxidation was accounted for. At this concentration of secondary olefin, the reaction goes almost completely by the epoxidation pathway.

The experiment was repeated using the same amount of the primary olefin, 1-decene. Gas analysis showed 15.1 mL of gas evolved/ 70.6 mg of CDT (1 equiv = 10.5 mL at 25 °C). This represents 1.44 equiv of gas evolved from the experiment. Gas chromatography of the epoxide relative to the internal standard showed 0.28 equiv of epoxide was formed.

Yields of Singlet Oxygen by UV Loss of 9,10-Diphenylanthracene. The ultraviolet spectra of DPA and its endoperoxide were measured on a Cary 15 recording spectrophotometer; DPA showed a large maximum at 373 nm with an extinction coefficient of 13 000. The endoperoxide had absolutely no absorption at this wavelength. A 2×10^{-2} M solution of DPA in THF was prepared. A 50-mL aliquot of this solution was pipetted into a 100-mL flask previously washed with a 0.50 M solution of EDTA to remove any traces of metal ions. The system was kept under nitrogen during this procedure. Then 0.1 mmol of the dehydrating agent was added to the flask along with 0.25 mL of 90% H_2O_2. The solution was stirred for 4 h, at which time TLC showed the presence of the endoperoxide. The whole solution was transferred to a 100-mL volumetric flask and diluted with dry THF to 100 mL. The solution was then diluted 1:100 again with THF. The ultraviolet spectrum of this solution was then compared with that of a similarly treated aliquot of the original DPA solution. The results are shown in Table X.

Determination of the β Value for 2-Methyl-2-pentene in THF. The β value for 2-methyl-2-pentene in THF was determined by following the reaction of diphenylfuran with singlet oxygen inhibited by 2-methyl-2-pentene. The rate of diphenylfuran decay was followed by fluorescence. A stock solution was prepared which contained 1.06×10^{-5} M zinc tetraphenylporphine and 1.77×10^{-5} M diphenylfuran. A 1.98×10^{-2} M solution of 2-methyl-2-pentene in THF was prepared. Ten mixtures of 5 mL of stock solution and various aliquots of the 2-methyl-2-pentene solution diluted to a total volume of 10 mL were prepared so that the final concentrations of Zn–TPP and diphenylfuran in all of the solutions were 5.3×10^{-6} and 8.85×10^{-6} M, respectively. Nine solutions had concentrations of 2-methyl-2-pentene ranging from 9.9×10^{-2} to 2.96×10^{-2} M. All of these solutions, as well as six blank samples (no 2-methyl-2-pentene), were saturated with oxygen and photolyzed in the fluorimeter described in Chart I. The method is described in ref 14, and the decay curves were analyzed by the PDP 11/45 computer. The β value was determined to be 0.062 M. Using this figure, the β value for DPA in THF could be calculated as 0.016 M.

Epoxidation of Cyclohexene with *N,N'*-Carbonyldiimidazole and H_2O_2. *N,N'*-Carbonyldiimidazole (2 mmol), purchased from Aldrich Chemical Co., was added to 25 mL of dry THF containing 1 mmol of cyclohexene at room temperature. After 10 min, GLC analysis showed no trace of epoxide in the mixture. After 30 min, a peak for cyclohexene oxide was detected (1.5%). A parallel experiment (same conditions) using 1,1'-carbonylbis(1,2,4-triazole) showed 60% epoxidation after 10 min and 90% epoxidation after 30 min.

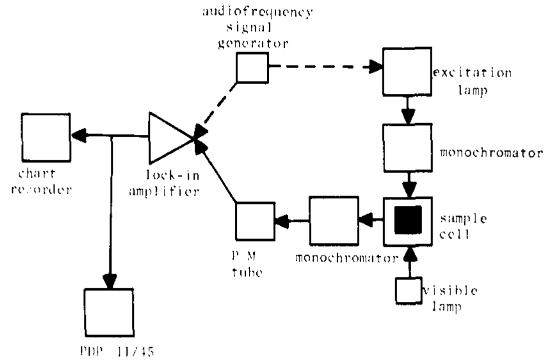
Epoxidation with *N*-Benzoyl-*N'*-*tert*-butylcarbodimide (17) and H_2O_2. After considerable experimentation, the following procedure was found to give best results. A tube, sealed at one end, was equipped with a magnetic stirrer and then charged with the carbodiimide,[21] 60 mg (0.3 mmol), olefin standard (0.1 mmol), and ethereal H_2O_2, 0.6 mmol (150 λ of a 4 M solution). The tube was stoppered with a serum cap, chilled in liquid nitrogen, and carefully sealed in a flame.

Table X. Singlet Oxygen Determination by UV Decay

dehyd. agent	mmol	init. abs.	final abs.	mmol DPA used[a]	$^1O_2$, %
none		1.300	1.300	0.000	0.00
CDT	0.167	1.240[b]	1.125	0.088	94.1
benzoyl isocyanate	0.100	1.240[b]	1.172	0.055	98.0
polymer-bound cyanic ester	0.107	1.302	1.255	0.037	61.7

[a] At 2×10^{-2} M DPA, 56% of $^1O_2$ is trapped; at 1.9×10^{-2} M, 55% is trapped. [b] Solutions were 1.9×10^{-2} M at the start.

Chart I. Diagram of Fluorimeter for β-Value Determinations[a]



[a] Excitation lamp, Hanovia 200-W Xe–Hg lamp powered by a Schoeffel LPS 251 lamp power supply; monochromator, Jarrell-Ash Model 82-410 monochromator with 250 μm slits; photomultiplier, Heath EV-701-93 photomultiplier tube; visible lamp, Norelco Q/CL 500-W tungsten halogen lamp powered by a Nobitron SR 100 DC power supply run at 90 V; lock-in amplifier, Ithaco Dynatrac 391A lock-in amplifier; audiofrequency signal generator, Heath Model EUW-27 sine-square wave generator run at 100 Hz.

Table XI. Control Experiments for the Epoxidation of 1-Methylcyclohexane with *N*-Benzoyl-*N′*-*tert*-butylcarbodiimide and Hydrogen Peroxide

expt	solvent	carbodiimide, mmol	olefin, mmol	epoxide, mmol	H_2O_2, drops	recovery
1	THF			0.1	1–2	96% epoxide
2	THF	0.1	0.1			94% olefin
3	THF	0.1		0.1		100% epoxide
4	THF	0.1		0.1	1–2	41% epoxide

The reaction mixture was allowed to warm to room temperature and stir overnight (15–20 h). After this room-temperature period, the reaction mixture was stored in liquid nitrogen until gas–liquid chromatographic analysis of the crude reaction mixture could be accomplished (results in Table VI).

Stability of 1-Methylcyclohexene and 1-Methylcyclohexene Oxide to a Variety of Conditions. 1-Methylcyclohexene and 1-methylcyclohexene oxide together with an internal standard were subjected to various conditions (Table XI) for 18–24 h, after which gas–liquid chromatography of the mixture determined the recovery of epoxide or olefin.

Reaction of Carbodiimide 17 and H_2O_2 with 1-Methylcyclohexene. A tube sealed at one end and equipped with a magnetic stirrer was charged with *N*-benzoyl-*N′*-*tert*-butylcarbodiimide (20 mg, 0.1 mmol) and a solution of olefin and internal standard (0.1 mL, 1 M olefin and 1 M standard in THF). An ethereal solution of hydrogen peroxide (0.05 mL, 4 M) was added, and the tube was stoppered with a serum cap. Samples were removed periodically and subjected to gas–liquid chromatography without workup (Table XII).

Preparation of Polymer-Bound *o*-Nitrophenyl Cyanate (18). A round-bottom flask was charged with polymer-bound *o*-nitrophenol[29] (18 g, 1.9 mmol/g), cyanogen bromide (18 g), and ethanol-free $CHCl_3$ (300 mL). The mixture was cooled in an ice–acetone bath for 20 min under an argon atmosphere. Using a wire addition funnel, *N*-methylmorpholine (4.0 g, 4.5 mL, 40 mmol) in ethanol-free $CHCl_3$ (100 mL) was added over a 1-h period with constant cooling. The reaction was allowed to stir for an additional 1.5 h in the cold, at which time the polymer was filtered and washed with a large volume of ethanol-free chloroform. The *o*-nitrophenyl cyanate polymer was dried in vacuo overnight: IR (KBr) 2278 cm^{-1} (–OC≡N). Nitrogen analysis confirmed the presence of 1.7 mmol/g of cyanic ester on the polymer; polymeric *o*-nitrophenol, 2.59% N; polymeric *o*-nitrophenyl cyanate, 5.07% N.

Table XII

rxn time	% olefin	% epoxide
15 min	84	0
30 min	79	0
45 min	74	0
1 h	71	0
1 h 30 min	64	3
2 h	60	4
2 h 30 min	57	5
3 h 30 min	50	7
4 h	42	11

Table XIII

olefin	% epoxide	% olefin	material balance, %
1-heptene	0	67	67
1-octene	10	72	82
1-decene	5	81	86
trans-5-decene	20	70	90
trans-2-heptene	0	50	50
cis,trans-2-octene	24	47	71
cis-4-methyl-2-pentene	34	42	76
trans-4-methyl-2-pentene	24	59	83
1-methylcyclohexene	0	0	0
1-methylcyclopentene	0	0	0
cyclohexene	41	25	66
cis-stilbene	7		
trans-stilbene	14		
β-methylstyrene	22	40	62
indene	20		
allylbenzene	0	78	78

Reaction of 18 and H_2O_2 with Olefins. A 5-mL round-bottom flask equipped with a small magnetic stirrer was charged with 18 (200 mg, 3.4 mmol) and a solution of olefin and internal standard (1 mL, 0.1 M olefin, 0.1 M standard in chloroform). The reaction was initiated by the addition of hydrogen peroxide (1 drop, 90%), and the flask was tightly stoppered and stirred at room temperature overnight (16 h). After this period, the reaction mixture was stored in a freezer (−35 °C) until analysis of the reaction mixture could be made. Normally, analysis was made by gas–liquid chromatography of the crude reaction mixtures; however, in the case of the stilbenes, integration of the epoxy protons vs. an internal standard in the proton magnetic resonance spectrum was employed (Table XIII).

Reaction of Ethyl Orthocarbonate/H_2O_2 with Olefins. Olefin (1 mmol), DPA (50 mg), and H_2O_2 (200 μL) in 2 mL of dry THF were stirred at room temperature as 1 mmol of orthocarbonate[31] in 2 mL of THF was added dropwise. Reaction was complete in 5 min. Epoxide yield was determined by GLC, and DPA endoperoxide was detected by TLC.

Reaction of 2-Chloro-1-methylpyridinium Iodide (26) and H_2O_2 with Olefins. The pyridinium salt[26] was suspended in THF as a solution of H_2O_2, DPA, olefin, and internal standard in THF was added dropwise. Epoxide yields were determined by GLC after 20 h at room temperature. The endoperoxide of DPA could not be seen by TLC.

Epoxidation with *N,N′*-Bis[(+)-α-phenylethyl]carbodiimide and H_2O_2. A solution of *trans*-β-methylstyrene (118 mg, 1 mmol) and 0.2 mL of 98% H_2O_2 in 3 mL of THF was treated with the carbodiimide derived from (+)-α-phenylethylamine (250 mg)[20] and a crystal of toluenesulfonic acid. After being stirred overnight, the precipitated urea was filtered and the filtrate was partitioned between petroleum ether and H_2O_2. The organic phase was dried and evaporated. The residue was subjected to preparative GC, from which 14 mg (~10%) of the pure epoxide was obtained, $[\alpha]^{20}{}_D$ +1.41° (*c* 1.4, EtOH) [lit.[32] $[\alpha]^{20}{}_D$ +70.8° (*c* 4.44, EtOH)]. The small (2%) but real optical yield implies that a chiral epoxidizing agent (rather than peroxytoluenesulfonic acid) had been generated.

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Table XIV. Kinetic Data for 2-Methyl-2-pentene

solvent	k_d, s^{-1} [38]	β, M[36]	k_a (calcd), M^{-1} s^{-1}
acetone	3.8×10^4	8×10^{-2}	4.8×10^5
benzene	4.1×10^4	1×10^{-1}	4.2×10^5
methanol	1.1×10^5	1.7×10^{-1}	8.4×10^5

Table XV. Kinetic Data for 9,10-Diphenylanthracene

solvent	β, M[39]	k_d, s^{-1} [38]	k_a, M^{-1} s^{-1}
benzene	5×10^{-2}	4.2×10^4	8.3×10^5
carbon disulfide	3×10^{-3}	5.0×10^3	1.7×10^6
chloroform	4×10^{-3}	1.7×10^4	4.1×10^6

Appendix

Calculation of the β Value for 9,10-Diphenylanthracene in Tetrahydrofuran. The β value for 9,10-diphenylanthracene in tetrahydrofuran was calculated from the β value of 2-methyl-2-pentene in tetrahydrofuran (0.062 M) as follows. In the absence of quenchers, $\beta = k_d/k_a$, where k_d is the rate constant for the deactivation of singlet oxygen in a given solvent and k_a is the rate constant for reaction of an acceptor with singlet oxygen; k_d is solvent dependent and acceptor independent, whereas k_a is generally considered to be solvent independent. Literature data for the reaction of 2-methyl-2-pentene with singlet oxygen are shown in Table XIV. An average k_a is 5.8×10^5 M^{-1} s^{-1}. In tetrahydrofuran $\beta = 0.062$ M; therefore, $k_d = 3.6 \times 10^4$ s^{-1}. The β value for 9,10-diphenylanthracene is known in different solvents and is shown in Table XV. k_a is calculated from β and k_d.

Registry No.—**1**, 50476-17-0; **1**·HCl, 68854-25-1; **2**, 41864-22-6; **3**, 19619-78-4; **4**, 16262-93-4; **17**, 13335-23-4; **24**, 78-09-1; **26**, 14338-32-0; (*E*)-cyclododecene, 1486-75-5; (*Z*)-cyclododecene, 1129-89-1; (*E*)-2-octene, 13389-42-9; (*Z*)-2-octene, 7642-04-8; 3,5-dimethylpyrazole, 67-51-6; phosgene, 75-44-5; hydrogen peroxide, 7722-84-1; 1-(trimethylsilyl)-1,2,4-triazole, 18293-54-4; 1,2,4-triazole, 288-88-0; hexamethyldisilazane, 999-97-3; 6-methyl-5-hepten-2-one, 110-93-0; benzoyl isocyanate, 4461-33-0; allylcyclohexanone, 94-66-6; 6-hydroxynon-8-enoic acid lactone, 68854-26-2; *m*-chloroperoxybenzoic acid, 937-14-4; phenanthrene, 85-01-8; diphenic acid, 482-05-3; DPA, 1499-10-1; DPA peroxide, 15257-17-7; 2-methyl-2-pentene, 625-27-4; *N,N'*-carbonyldiimidazole, 530-62-1; cyanogen bromide, 506-68-3; *N,N'*-bis[(+)-α-phenylethyl]carbodiimide, 57122-22-2; *trans*-β-methylstyrene, 873-66-5.

References and Notes

(1) Abstracted in part from the PH.D. Thesis of S. Wolf (UCLA, 1977) and A. Mossman (UCLA, 1977); preliminary accounts of this work may be found in *J. Chem. Soc., Chem. Commun.*, 711 (1974), and *J. Org. Chem.*, **43**, 180 (1978).

(2) (a) Dialkyl carbonates also failed, but alkyl chloroformates are effective; R. M. Coates and J. W. Williams, *J. Org. Chem.*, **39**, 3054 (1974); (b) T. Hori and K. B. Sharpless, *ibid.*, **43**, 1689 (1978), and references therein.

(3) H. Staab, *Justus Liebigs Ann. Chem.*, **622**, 36 (1959); **609**, 75 (1957).

(4) L. Biskofer, P. Richter, and A. Ritter, *Chem. Ber.*, **93**, 2804 (1960). Our attempts to prepare the tetrazole-derived reagent failed, owing presumably to oxadiazole formation: R. F. Benson, *Heterocycl. Compd.*, **8**, 79ff (1967).

(5) E. Hoft and S. Ganschow, *J. Prakt. Chem.*, **314**, 156 (1972).

(6) W. K. Anderson and T. Veysoglu, *J. Org. Chem.*, **38**, 2267 (1973).

(7) E. Kyba and D. C. Alexander, *Tetrahedron Lett.*, 4563 (1976).

(8) G. B. Paybe, *Tetrahedron*, **18**, 763 (1962).

(9) Griffin has recently observed oxidation of phenanthrene using *m*-chloroperbenzoic acid in $CHCl_3$ (a much better medium for this reagent) and has succeeded in isolating the corresponding K-region arene oxide: K. Ishikawa, H. Charles, and G. Griffin, *Tetrahedron Lett.*, 427 (1977).

(10) D. Swern, *Org. Peroxides 1971*, **2** (1971).

(11) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 740 (1970), and references cited therein.

(12) Data for typical peracids may be found in K. B. Sharpless, J. M. Townsend and D. R. Williams, *J. Am. Chem. Soc.*, **94**, 295 (1972); A. K. Awasthy and J. Rocek, *ibid.*, **91**, 991 (1969); K. O. Bingham, G. D. Meakens, and G. H. Whitham, *Chem. Commun.*, 445 (1966).

(13) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).

(14) R. H. Young, K. Wehrly, and R. Martin, *J. Am. Chem. Soc.*, **93**, 5774 (1971).

(15) For other chemical sources of $^1O_2$, see J. W. Peters, P. J. Bekowies, A. M. Winer, and J. N. Pitts, *J. Am. Chem. Soc.*, **97**, 3299 (1975).

(16) A discussion of the ambiguities in $^1O_2$ detection may be found in R. F. Boyer, C. Lindstrom, B. Darby, and M. Hylarides, *Tetrahedron Lett.*, 4111 (1975), and ref 33.

(17) E. McKeown and W. A. Waters, *J. Chem. Soc. B*, 1040 (1966); L. L. Smith and M. J. Kulig, *J. Am. Chem. Soc.*, **98**, 1027 (1976); W. C. Danen and R. L. Arudi, *ibid.*, **100**, 3944 (1978); D. B. Denney and J. D. Rosen, *Tetrahedron*, **20**, 271 (1964); J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962); P. A. Giguere and K. Herman, *Can. J. Chem.*,, **48**, 3473 (1970).

(18) H. A. Staab, *Chem. Ber.*, **89**, 1927 (1956); **90**, 1320 (1957).

(19) For critical review of the geometry of H bonds, see J. Donohue in "Structural Chemistry and Molecular Biology", A. Rich and N. Davidson, Eds., W. H. Freeman, San Francisco, Calif., 1968, p 433ff, and G. A. Jeffrey and S. Tagaki, *Acc. Chem. Res.*, **11**, 265 (1978). The structure of the phenyl isocyanate/H_2O_2 adduct, also useful for epoxidation reactions, is still uncertain: N. Matsumura, N. Sonoda, and S. Tsutsumi, *Tetrahedron Lett.*, 2029 (1970).

(20) J. Rebek, D. Brown, and S. Zimmerman, *J. Am. Chem. Soc.*, **97**, 4407 (1975).

(21) O. Mitsunobu et al., *Bull. Chem. Soc. Jpn.*, **45**, 3607 (1972).

(22) S. Krishnan, D. Kuhn, and G. Hamilton, *Tetrahedron Lett.*, 1369 (1977).

(23) E. Grigat and R. Putter, *Chem. Ber.*, **97**, 3012 (1964).

(24) R. D. Chambers and M. Clark, *Tetrahedron Lett.*, 2741 (1970).

(25) L. Kim, U.S. Patent Application 171 734 (1971); *Chem. Abstr.*, **78**, 159400n (1973).

(26) T. Mukaiyama et al., *Chem. Lett.*, 1045, 1159 (1975).

(27) A. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 1805 (1963).

(28) Y. Gaoni, *J. Chem. Soc. C*, 2925 (1968).

(29) R. Kalir, M. Fridkin, and A. Patchornik, *Eur. J. Biochem.*, **42**, 151 (1974).

(30) Y. Kishi, M. Anatani, H. Tanino, and T. Fukuyama, *J. Chem. Soc., Chem. Commun.*, 64 (1972).

(31) J. D. Roberts and R. Z. McMahon, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, 1963, p 457.

(32) P. Renolen and J. Ulgestad, *Bull. Soc. Chim. Fr.*, 634 (1960).

(33) J. A. Howard and G. D. Mendenhall, *Can. J. Chem.*, **53**, 2199 (1975).

(34) J. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977); R. Tang, H. J. Yue, J. F. Wolf, and F. Mares, *ibid.*, **100**, 5248 (1978), and references therein.

(35) S. Mazur and C. S. Foote, *J. Am. Chem. Soc.*, **92**, 3255 (1970).

(36) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).

(37) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968).

(38) P. B. Merkel and D. K. Kearns, *J. Am. Chem. Soc.*, **94**, 7244 (1972).

(39) R. W. Denny and A. Nickon, *Org. React.*, **20**, 312 (1973).