acid, 360-03-2; α,α-difluoro-4-(trifluoromethyl)benzeneacetic acid, 73790-11-1; α,α-difluoro-4-(perfluoroisopropyl)benzeneacetic acid, 73790-12-2; α,α-difluoro-4-phenylbenzeneacetic acid, 73790-13-3; α,α-difluoro-1-naphthaleneacetic acid, 73790-14-4; α,α-difluorobenzeneacetamide, 383-19-7; α,α,3,4-tetrafluorobenzeneacetamide, 73790-15-5; *N*-methyl-α,α,3,4-tetrafluorobenzeneacetamide, 73790-16-6; α,α-difluoro-1-naphthaleneacetamide, 73790-17-7; α,α-difluoro-3,4-(dimethylmethylenedioxy)benzeneacetamide, 73790-18-8; *p*-bromo(trifluoromethyl)benzene, 402-43-7; *p*-bromo(perfluoroisopropyl)benzene, 2396-23-8; 3,4-difluorobromobenzene, 348-61-8; 1-bromo-3-fluoro-4-methoxybenzene, 2357-52-0; 1-bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; 1-bromo-3,4-(dimethylmethylenedioxy)benzene, 73790-19-9; ethyl α-oxo-3,4-difluorobenzeneacetate, 345-72-2; DAST, 38078-09-0; α,α-difluorobenzeneacetonitrile, 2002-72-4; diethyl oxalate, 95-92-1; 4,4'-bis(trifluoromethyl)benzil, 73790-20-2; ethyl α-oxo-3-indoleacetate, 51079-10-8; *p*-chlorobenzyl chloride, 104-83-6; 2,2-difluoro-2-(3,4-difluorophenyl)ethylamine hydrochloride, 73790-21-3.

Trifluoroperacetic Acid. Oxidation of Aromatic Rings

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Trifluoroperacetic acid is an oxidizing reagent capable of converting alkylbenzenes to the corresponding aliphatic carboxylic acids. No trace of aromatic carboxylic acid is ever observed. Aromatic heterocyclic compounds do not behave like their hydrocarbon analogues. Quinoline and pyridine are oxidized to the corresponding *N*-oxides, and dibenzothiophene is oxidized to the sulfone. No destruction of the ring is found in these latter three cases. The reaction mixture of hydrogen peroxide and trifluoroacetic acid undergoes a decomposition reaction to form carbon dioxide and fluoroform. The rate of this decomposition is slow compared to the oxidation so that it does not interfere with the primary reaction process. However, attempts to quantify the amount of aromatic carbons in a compound or mixture of compounds must be done with caution.

Recently, Deno described some interesting degradation work[1] which utilized trifluoroperacetic acid. Reagents of this type[2] are known to be a source of positive hydroxyl groups which electrophilically attack certain aromatic rings. This process is believed to proceed through various progressive hydroxylations until the ring is destroyed. If an aliphatic side chain were present, an aliphatic carboxylic acid would be produced. For example, *n*-propylbenzene, upon oxidation with trifluoroperacetic acid, produced butyric acid in good yields. Deno performed this oxidation on numerous other hydrocarbons, and in each case the major product formed was derived from the destruction of the aromatic moiety, with the aliphatic portion of the molecule surviving the oxidation. In all of this work there was also produced a significant amount of minor products which the authors left unidentified. Some quantity of acetic acid was usually produced but the amount of this product was diminished by the addition of sulfuric acid to the reaction mixture at the start of the reaction.[3] In the earlier work[1] the composition was analyzed after distillation of volatile material to obtain a concentrated solution for ^{1}H NMR analysis. Accordingly, volatile or minor products (<5%) would not be observed. The existence of these minor products (sometimes totaling 30–40% of the observed products) sparked our curiosity as to their identity. Several of the published oxidations were repeated and extended to other structures; the product mixtures were analyzed by gas chromatography/mass spectroscopy (GC/MS) under conditions which are known to separate the expected products.

It has been suggested[1,3] that this oxidative degradation should be used to identify and quantify aliphatic side chains on coal and similar materials. Unfortunately, the behavior of some structural types in this reaction is not known, namely, aromatic amines and sulfur compounds which are known to be present in coal. Part of this study fills this gap. Furthermore, no mention of gas evolution was made in the previous studies, and, therefore, material balances could not be calculated. The gases evolved during the reaction have now been identified. The GC analysis also served to quantify the relative abundances of nonvolatile products. For the elucidation of the mechanistic details of the reaction, a partial-oxidation study was performed. During the course of these partial oxidations, reaction intermediates were observed (by mass spectroscopy) and most of them identified.

Results and Discussion

Instability of Reaction Mixture. All of the off gases were allowed to pass through a barium hydroxide scrubber solution. More carbon dioxide was produced in certain reactions than was possible from the amount of organic substrate present. The carbon dioxide produced was collected as barium carbonate and weighed after thorough drying. The barium carbonate was then decomposed with hot concentrated HCl to liberate CO_2. The measured quantity of CO_2 (an ascarite trap) was consistent with that expected for pure barium carbonate. It was hypothesized that the oxidizing reagent was decarboxylating according to eq 1. To test this, we ran a blank (no organic substrate);

$$CF_3CO_2H \xrightarrow{H_2O_2} CHF_3 + CO_2 \qquad (1)$$

indeed, CO_2 slowly evolved. Further, we found that the decomposition of trifluoroacetic acid–hydrogen peroxide (TFA/H_2O_2) reagent was catalyzed by certain materials. For example, in one experiment addition of a small crystal of cuprous chloride to the standard oxidizing reagent

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[1] N. C. Deno, B. A. Greigger, L. A. Messner, M. D. Meyer, and S. G. Stroud, *Tetrahedron Lett.* 1703, (1977).

[2] (a) H. Hart, *Acc. Chem. Res.*, 4, 377 (1971); (b) H. Hart and R. M. Lange, *J. Org. Chem.*, 31, 3776 (1966); (c) M. E. Kurz and P. Kovacic, *J. Am. Chem. Soc.*, 89, 4960 (1967); (d) J. A. Vesely and L. Schmerling, *J. Org. Chem.*, 35, 4028 (1970).

[3] N. C. Deno, B. A. Greigger, and S. G. Stroud, *Fuel*, 57(8) 455 (1978).

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Table I. Exhaustive Oxidation of Representative Aromatic Compounds with Trifluoroperacetic Acid

substrate	products[a] (% yield)
toluene	acetic acid (95)[b]
n-propylbenzene	butyric acid (82), acetic acid (18)
n-pentylbenzene	hexanoic acid (68), pentanoic acid (22), acetic acid (10)
o-xylene	acetic acid (95)[b]
hexamethylbenzene	acetic acid (98)[b]
acenaphthene	succinic acid (80), acetic acid (20)
pyridine	pyridine *N*-oxide (100)
quinoline	quinoline *N*-oxide (100)
dibenzothiophene	dibenzothiophene sulfone (100)

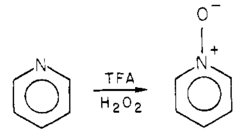
[a] Yields determined by GC relative to internal standards, and the peak identities were determined by mass spectroscopy. [b] Small peaks were not identified.

produced 13.0 mmol of CO_2 in 3 h. Mass spectral analysis of the gas which passed through the barium hydroxide trap revealed the presence of fluoroform. It has been noted that the use of sulfuric acid as cosolvent reduces the amount of side products formed.[3] However, sulfuric acid does not reduce the rate of decomposition of TFA/H_2O_2 to CO_2 and CHF_3.

This decomposition prevents attainment of accurate material balances. Clearly the use of labeled reagents is required for this. For example, if labeled TFA (labeled on the carboxyl group) is employed, then one could measure the amount of labeled CO_2 relative to unlabeled CO_2 and thus quantify the amount of CO_2 which comes from the organic substrate. This could then be related to the mole fraction of aromatic carbons in the substrate. As of yet, this has not been carried out.

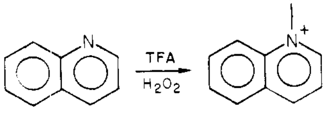
Complete Oxidation. Complete oxidation of an aromatic hydrocarbon is accomplished by slowly adding the compound to a stirred solution of excess trifluoroperacetic acid initially at room temperature. The exothermicity of the oxidation causes the reaction mixture to heat up rapidly. The addition rate of the compound must be controlled in order to maintain a gentle reflux. Reactions are generally complete in 1 h; however, as a rule, reactions are allowed to stand for 2–3 h. The products of the oxidation of aromatic hydrocarbons are all aliphatic carboxylic acids. No aromatic carboxylic acid was found in any reaction mixture. The results of the exhaustive oxidations are presented in Table I.

Aromatic Heterocyclics. Certain heterocyclic structures react rapidly and exothermically with TFA/H_2O_2 but not in the same fashion as their hydrocarbon analogues. Pyridine and quinoline react rapidly to form the corresponding amine *N*-oxide (eq 2a and 2b). The *N*-oxide structure is most resistant to further attack, and even heating for several hours under reflux does not cause further oxidation. Apparently the positively charged *N*-oxide deactivates the aromatic rings sufficiently that hydroxylation cannot occur.[4]



(2a)

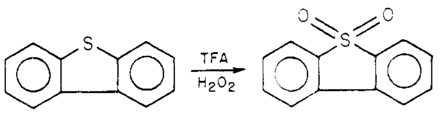
pyridine pyridine *N*-oxide



(2b)

quinoline quinoline *N*-oxide

Aromatic sulfur-containing compounds behave similarly. An example is dibenzothiophene. It is oxidized completely to the corresponding sulfone (dioxide) and then the reaction stops. No trace of sulfoxide was observed 20 min after mixing the dibenzothiophene in the peracid solution (eq 3).



(3)

dibenzothiophene dibenzothiophene sulfone

The results of the oxidation of these heterocyclic compounds are not exactly unexpected. They are presented to make the point that this reaction will have limited utility for coal structure determinations. Molecular units which resemble a thiophene or pyridine (which are believed to be present in coal) should be converted to the corresponding sulfone or *N*-oxide. It is likely that these aromatic heterocyclic moieties will survive the oxidation with structural integrity. The production of the sulfone or *N*-oxides appears to be a quantitative reaction at least for model compounds. The conversion of an alkylbenzene to an aliphatic carboxylic acid has been reported to proceed in yields of 60–80%.[1,3] This latter process is too inefficient for an analytical reaction. Furthermore, acetic acid, a side product produced in the oxidation of compounds with no methyl substituents, cannot be eliminated even by the use of sulfuric acid. Accordingly, one should expect a high methyl group count relative to ethyl, for example, in a typical coal oxidative analysis.

If the trifluoroperacetic acid degradation is used to merely note changes in the aliphatic side-chain composition on a relative basis, as in the case of a coal and a derivatized product, then this method of analysis may be adequate. However, quantitative and absolute structural composition analyses are too equivocal to be of any real value.

Perhaps a more important use of this oxidation would be to identify and even quantify aromatic heterocyclic functionalities as the corresponding *N*-oxides and sulfones, providing, of course, that these functional moieties in coal survive the reaction at least as well as the model compounds.[5] To date no definitive information exists which clearly shows what fraction of the organically bound sulfur and nitrogen in coal is aromatic in nature.

Partial Oxidations. Toluene. The major product formed in the partial oxidation of toluene is acetic acid (eq 4). This product results from the complete oxidation of the aromatic ring. One other product is detected by gas chromatography. The mass spectral analysis identifies this partial oxidation product as *n*-2,4-hexadienoic acid (geometrical isomers not established). This minor product can be envisioned as arising from hydroxylation of the aromatic ring in the position ortho to the methyl substituent. If *o*-cresol is produced, it would react much faster than

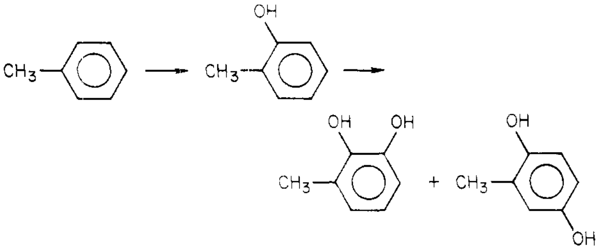
$$\mathrm{PhCH_3} \xrightarrow[\mathrm{H_2O_2}]{\mathrm{TFA}} \underset{88\%}{\mathrm{CH_3CO_2H}} + \underset{12\%}{\mathrm{CH_3CH{=}CHCH{=}CHCO_2H}} \qquad (4)$$

---

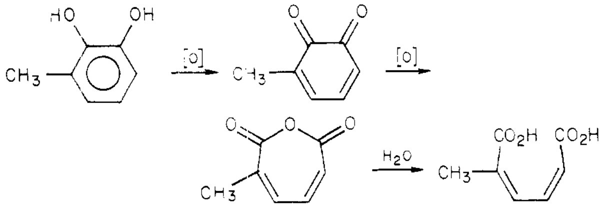
(4) It is known that nitrobenzene, benzoic acid, and benzenesulfonic acid are inert under the reaction conditions (see ref 1). The presence of an electron-withdrawing substituent is believed responsible for ring deactivation. Electrophilic aromatic substitutions are known not to proceed when these functional groups are present. Nitrobenzene has often been used as an inert solvent in Friedel–Crafts alkylations.

(5) The feasibility of this application to coal and processed coal is currently being investigated.

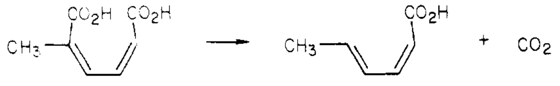
toluene.[2a] The relative rates of trifluoroperacetic acid oxidation reveal that the hydroxyl group is a strong ring activator in electrophilic substitutions. The hydroxylation is likely to produce attack as shown in eq 5. 2,3-Dihydroxytoluene is very susceptible to oxidative cleavage. This process perhaps can be envisioned as in eq 6. The unsaturated dicarboxylic acid produced may spontaneously decarboxylate under the reaction conditions or during the chromatographic analysis. In any event, n-2,4-hexadienoic acid is observed (eq 7).



(5)



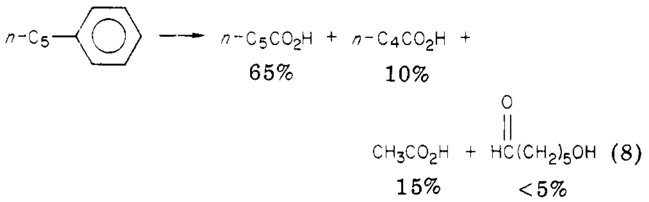
(6)



(7)

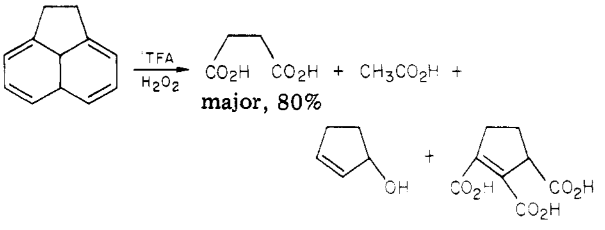
n-2,4-hexadienoic acid

n-Pentylbenzene. The major product in the partial oxidation of n-pentylbenzene is hexanoic acid. Among the minor products are pentanoic and acetic acids and 6-hydroxyhexaldehyde (eq 8). In addition, there was one other product formed which appeared to be related in structure to 6-hydroxyhexanal. It may be 6-hydroxyhexanoic acid. Interestingly, neither butyric nor propionic acid was observed, even though the chromatographic procedure used would have easily revealed their presence. The stability of butyric and propionic acid under the reaction conditions has been demonstrated,[3] so if they had been formed they would have survived. This means that acetic acid is not produced from the higher acid homologues. A mechanism for acetic acid production is not obvious at the present time. However, these results would tend to indicate that the ring carbons[6] are the source of its formation. If one envisions malonic acid as a ring oxidation product, then a subsequent decarboxylation could produce acetic acid.[7]



The formation of 6-hydroxyhexanal is surprising. However, it shows that five carbons make an effective "insulator". The terminal carbon atom of the pentyl side chain is far enough removed from the electron-withdrawing effects of the phenyl ring and is attacked by the electrophilic reagent. Further oxidation of 6-hydroxyhexanal would result in carboxyl formation from the aldehyde. This further oxidation would produce 6-hydroxyhexanoic acid. Positive mass spectral confirmation of this proposed structure was not achieved due to a poorly resolved chromatographic separation.

Acenaphthene. The major oxidation product of acenaphthene is succinic acid. Small quantities of acetic acid, 3-hydroxycyclopentene, and a tricarboxylic acid are also found (eq 9). All of the products may not be primary reaction products. Yet the existence of succinic acid and the two cyclopentene derivatives demonstrates again that the attack of the reagent is directed at the aromatic carbons.



(9)

Conclusion

Trifluoroperacetic acid is an effective electrophilic oxidizing agent. It readily oxidizes aromatic hydrocarbons in an exothermic fashion. When used by itself this reagent is not too useful synthetically. If mild reaction conditions are employed, then a clean reaction product is difficult to achieve. Numerous products often result. If more vigorous conditions are employed, then simple carboxylic acids are produced, which, in general, are obtained more easily and much less expensively by other means.

A word of caution is in order for those who wish to use this powerful oxidant to identify and quantify alkyl substituents on macromolecular structures such as coal or similar material. A quantitative analysis on the reaction products (complete mass balance) is possible only if the carboxyl group of TFA is labeled. Since carbon dioxide gas is produced both from the substrate oxidation as well as from TFA/H_2O_2 decomposition, the total carbon dioxide produced in the course of a reaction would have to be trapped and the ratio of unlabeled to labeled CO_2 determined.

In the early studies,[1,3] analysis of the reaction mixture revealed in general that the expected product (even under the most favorable circumstances) was formed in yields of 60–80%. This is far too low for an analytical reaction and really serves only to give a purely qualitative measurement. If one wanted to determine the relative abundance of the alkyl substituents in a series of similar materials, then use of this reagent might be one way to accomplish this. However, quantitative measurement of these alkyl substituents in the analytical sense is not yet possible by this procedure.

Organically bound nitrogen and sulfur in some bituminous coal accounts for 3 or 4% by weight of the material. A good portion of these heteroatoms are bound as aromatic

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(6) To test the hypothesis that acetic acid is produced from the electrophilic oxidizing reagent TFA/H_2O_2, we treated benzene in an analogous manner as pentylbenzene, and, indeed, a minor product of this reaction is acetic acid. The reaction products were most difficult to analyze by the usual method (GC/MS). However, the presence of acetic acid is confirmed by mass spectral correlation as a reaction product. It is, of course, quite possible that the small amount of acetic acid arises from some secondary reaction during the gas chromatographic analysis, and it may not be a primary reaction product at all.

(7) The production of CO_2 from the substrate has been assumed. This assumption is based on low material balance based on the observed products.

nitrogen and sulfur. The rings which contain these heteroatoms may oxidize to the correspondig *N*-oxide or sulfone. It may be possible to isolate and characterize these units. The remarkable stability of the *N*-oxides of pyridine and quinoline as well as dibenzothiophene sulfone give an indication that these general structure types should survive a TFA/H_2O_2 coal oxidation if indeed they are actually present in this material. Accordingly, direct evidence for heteroatom distribution in coal could be available.

Experimental Section

General Conditions. Trifluoroperacetic Acid. The reagent was prepared by the dropwise addition of 30% aqueous hydrogen peroxide[8] to trifluoroacetic acid (TFA) at 0 °C. The final solution contained no more than 10% water.[9] The ice bath was removed after the peroxide addition was complete. The material to be oxidized was added slowly with stirring to the trifluoroperacetic acid solution. The reaction mixture heated up while the addition of the material continued. The rate of addition was maintained such that the exothermicity of the reaction was controlled. An efficient reflux condenser was mounted on the flask and connected to a carbon dioxide trap (an aqueous solution of barium hydroxide). The barium carbonate produced in this way was decomposed by hot concentrated hydrochloric acid solution. The liberated carbon dioxide was collected in an ascarite trap. This precautionary analysis revealed that the carbon dioxide content of the white precipitate was between 91 and 97% of the theoretical value for pure barium carbonate. Any gas which passed through the CO_2 trap was collected for mass spectral analysis. The composition of the reaction solution was determined periodically throughout the course of the reaction. Minute samples (1 μL) were removed via syringe (through a sidearm equipped with a septum) and analyzed by gas chromatography. Tentative peak assignments were made by coinjections with authentic samples. The workup procedure employed was essentially the same as that described previously[3] except that no ester derivatives were prepared. Instead, the reaction products (free acids) were analyzed on two different columns: 10% SP1200 and 10% SP2300, both 1% phosphoric acid, 6 ft × 0.25 in, and 80/100 mesh of Supelcoport.

The mass spectral data were obtained from a Du Pont 21-490 magnetic-focusing mass spectrometer after the reaction components had been separated on one of the gas chromatographic columns.[10]

Instability of the Reagent. The solution of hydrogen peroxide and trifluoroacetic acid is not stable. The decomposition is greatly facilitated by inorganic chemicals. In one experiment 6.6 mL of 30% H_2O_2 was added to 50 mL of trifluoroacetic acid as previously described. A crystal of cuprous chloride was then added; after 3 h, 13.0 mmol of CO_2 had been produced. The gas which passed through the barium hydroxide solution was collected, and mass spectral analyses revealed the presence of fluoroform (CHF_3).

Complete Oxidation of Substrate. Typical Reaction Stoichiometry. The general reactions were employed to effect complete oxidation. The trifluoroperacetic acid solution was prepared by the dropwise addition of 30% H_2O_2 (10.0 mL, 88 mmol) to trifluoroacetic acid (75.0 mL) at 0 °C. The ice bath was removed and *n*-propylbenzene (0.60 g, 5.0 mmol) added slowly. The reaction time was 2 h. Analysis by gas chromatography revealed there were two products, butyric acid (82%) and acetic acid (18%). The results of the other reactions are summarized in Table I.

Incomplete Oxidation of Substrate. The general reaction conditions previously described were followed with the following exceptions. A cold-water bath was used to maintain lower temperatures during the course of the reaction, and the stoichiometric ratio of the peroxide to substrate was lower from almost 18:1 to 8:1.

Acknowledgment. The authors wish to express their appreciation to Professor N. C. Deno and M. L. Gorbaty for their helpful counsel during the course of this work.

Registry No. Toluene, 108-88-3; *n*-propylbenzene, 103-65-1; *n*-pentylbenzene, 538-68-1; *o*-xylene, 95-47-6; hexamethylbenzene, 87-85-4; acenaphthene, 83-32-9; pyridine, 110-86-1; quinoline, 91-22-5; dibenzothiophene, 132-65-0; acetic acid, 64-19-7; butyric acid, 107-92-6; hexanoic acid, 142-62-1; pentanoic acid, 109-52-4; succinic acid, 110-15-6; pyridine *N*-oxide, 694-59-7; quinoline *N*-oxide, 1613-37-2; dibenzothiophene sulfone, 1016-05-3; trifluoroperacetic acid, 359-48-8.

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[8] Standardization of hydrogen peroxide solutions was accomplished by refractive index. See P. A. Giguere and P. Geoffrion, *Can. J. Res., Sect. B*, 27, 168 (1949).

[9] If a larger amount of water is used, the oxidation of aromatic hydrocarbons is inhibited, N. C. Deno, private communication.

[10] Mass spectral data was obtained by Gollob Microanalytical Co., Berkeley Heights, NJ.

Multiple Extrusion Methods for the Preparation of Sterically Hindered Olefins. An Approach to Tetra-*tert*-butylethylene

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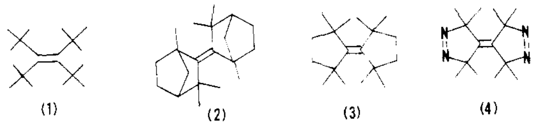
While twofold extrusion procedures have proved to be very useful in the preparation of very sterically hindered olefins, the extremely hindered tetra-*tert*-butylethylene (1) has remained elusive. An approach to 1 based on "tied-back" intermediates such as the selone 13 and diazo compound 14 was investigated. Although 1,1-diphenyl-2,2-di-*tert*-butylethylene (16) could be prepared by a combination of twofold extrusion and reductive cleavage, no significant formation of 1 could be detected by using analogous procedures, the major product being the azine 18. Reaction of 14 with selenofenchone directly gave 2,2′-bifenchylidene (2) as the only olefinic product.

Approaches to the synthesis of very sterically hindered olefins and investigations of the chemical and physical properties of these compounds have recently attracted much attention.[1] These investigations may prove very useful in understanding the nature of sterically hindered environments. In this area the ultimate synthetic goal of a number of research groups is the extremely hindered tetra-*tert*-butylethylene (1)[2-5] (Chart I).

Chart I



(1) (2) (3) (4)

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[1] For recent reviews, see: (a) T. T. Tidwell, *Tetrahedron*, 1855 (1978); (b) J. F. Liebman and A. Greenberg, *Chem. Rev.*, 76, 311 (1976).

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