Aromatic Hydroxylation with Hydrogen Peroxide–Aluminum Chloride

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Simple aromatics were hydroxylated in reasonably good yields with hydrogen peroxide (90 or 30%) in the presence of aluminum chloride. For example, cresols ($o:m:p$ = 60:8:32) and methoxyphenols ($o:m:p$ = 44:1:55) were obtained in 40 and 70% yields, respectively, from toluene and anisole. Very little further oxidation products were formed in contrast to most previous related hydroxylating systems. The initially formed cresols from toluene were found to be only about five times more susceptible than toluene to subsequent reaction. The isomer distributions, relative reactivity, k_{PhCH_3}/k_{PhH} = 19.1, and yields with a series of aromatics were consistent with an electrophile having hydroxyl cation character. Nuclear chlorination, presumably *via* hypochlorous acid, occurred as a minor competing reaction with toluene and anisole but with the less reactive benzene and chlorobenzene became a major reaction pathway. This procedure is compared to other aromatic hydroxylation methods.

In the last decade there have been a number of reports of aromatic substitution by an oxygen entity from peroxides in the presence of Lewis acid catalysts.[1] Although effective reactions of this type have been accomplished with peracids,[2-4] peroxydicarbonates,[5] aroyl peroxides,[6] hydroperoxides,[7] and even dialkyl peroxides,[8] systems involving hydrogen peroxide itself have generally led to rather low yields of monohydroxylated products with nonactivated aromatics. Such was the case with the systems hydrogen peroxide–boron trifluoride etherate[9] and hydrogen peroxide–sulfuric acid.[10]

Very recently an article[11] concerning the hydrogen fluoride catalyzed hydroxylation of aromatic compounds with hydrogen peroxide appeared. With this method, simple aromatics were converted to phenols, although rather large amounts of further hydroxylated products were also found.[11] This article has prompted us to report our observations in a related study.

We have found that moderate to good yields of phenols can be obtained from simple aromatics by treatment with hydrogen peroxide in the presence of aluminum chloride. Furthermore, unlike previous hydroxylation attempts, the reaction is surprisingly free from further oxidation even with very simple aromatics.

Results and Discussion

The slow addition of hydrogen peroxide (0.05 mol of 90%) to a rapidly stirred solution or slurry of aluminum chloride (0.075–0.10 mol) in excess aromatic (0.5–1.0 mol) at 0–5° gave rise after hydrolysis on ice to the products shown in Table I. Thus anisole was oxidized to methoxyphenols in 70% yield, while the alkylbenzenes, toluene, *o*-xylene, and mesitylene, gave around 40% yields of phenolic products. With the less reactive chlorobenzene and benzene less hydroxylation occurred as nuclear chlorination became an important competing process. No phenolic products at all resulted from the attempted hydroxylation of nitrobenzene.

TABLE I

AROMATIC HYDROXYLATION WITH HYDROGEN PEROXIDE–ALUMINUM CHLORIDE[a]

	Phenolic products, ArOH[b]				Aryl chlorides yield,
	Yield,	Isomers			
Aromatic	%[c]	*o*	*m*	*p*	%[d]
Anisole[e]	70	44	<1	55	10
Toluene[f]	40	60	8	32	16
Chlorobenzene	14	26	4	70	20
o-Xylene	35	2,3:3,4 = 60:40			28
Mesitylene	42				19
Benzene	10[g]				28
Nitrobenzene	0				

[a] Aromatic:$AlCl_3$:90% H_2O_2 = 9–20:1.5:1, 0–5°, 2 hr. [b] Less than 3% higher boiling phenolic products were found in the anisole, toluene, xylene, and mesitylene runs investigated. [c] Based on limiting peroxide reagent; determined by glpc as the average of two or more runs in close agreement. Isolated yields of the phenols were generally 2–5% less than the glpc yields. [d] Unreacted H_2O_2 ranged from 5–15% except with chlorobenzene, where 30% of the H_2O_2 was recovered. [e] Hydrogen chloride, 90%. [f] Hydrogen chloride, 88%. [g] In addition *o*- and *p*-chlorophenol were formed in a total amount of 5%.

Yields were approximately the same regardless of whether a 1:1 or higher ratio of aluminum chloride:peroxide was used. In a control run without aluminum chloride, the peroxide was recovered unchanged after 24 hr. The stoichiometry of the hydroxylation reaction is shown in eq 1.

$$ArH + H_2O_2 + AlCl_3 \longrightarrow ArOH + HCl + AlCl_2OH \quad (1)$$

Significantly, most of the reactions were quite clean, perhaps due in part to the large surplus of aromatic used. Other reaction products were hydrogen chloride (90%) and some 10–30% of ring-chlorinated aromatics. In almost every case a small amount (5–15%) of unreacted hydrogen peroxide was recovered after hydrolysis. With the aromatics studied, higher boiling phenolic products or tars amounted to less than 3% except for benzene (*vide infra*). This contrasts markedly with previous related works[2,9-11] in which further oxidation products occurred extensively with toluene or benzene. Presumably in these other cases the much greater susceptibility of phenols compared to aromatic hydrocarbons toward electrophilic substitution leads to more highly substituted or oxidized products.[10] Vesely and Schmerling[11] demonstrated the ready conversion of phe-

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(2) H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964).

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(10) D. H. Derbyshire and W. A. Waters, *Nature*, **165**, 401 (1950).

(11) J. A. Vesely and L. Schmerling, *J. Org. Chem.*, **35**, 4028 (1970).

nols to hydroquinones and catechols with their HF–H_2O_2 method. Evidently further hydroxylation of the initial phenolic product from simple aromatics occurred extensively in their system as evidenced by the high amounts of dihydroxybenzenes and uncharacterized high boilers obtained. Possible factors in our procedure protecting the initial phenolic product from subsequent oxidation might have been the heterogeneous nature of the reaction and deactivation of the phenol by coordination of the aluminum salt on oxygen.

To test the actual susceptibility of cresols to further reaction by peroxide–aluminum chloride, a series of competition reactions were run (Table II). Inclusion of cresols along with *o*-xylene under typical hydroxylation reaction conditions indicated the cresols to be about twice as reactive as *o*-xylene toward oxidation. Since the relative reactivity of *o*-xylene:toluene was 3.05 (Table II) the approximate cresol:toluene reactivity was only about 6. A similar approach using the relative rates of hydroxylation of cresols:benzene and toluene:benzene indicated a cresol:toluene reactivity of about 5.

TABLE II

RELATIVE RATES IN AROMATIC HYDROXYLATION WITH HYDROGEN PEROXIDE–ALUMINUM CHLORIDE[a]

ArH′:ArH	Molar ratio	ArOH′:ArOH	Molar ratio	k'_{ArH}: k_{ArH}
Cresol:benzene	0.018	Reacted cresols[b]: phenol	1.58	87[c]
Cresol:*o*-xylene	0.130	Reacted cresols[b]: xylenols	0.25	1.92
Cresol:*o*-xylene	0.045	Reacted cresols[b]: xylenols	0.10	2.16[d]
o-Xylene:toluene	0.830	Xylenols:cresols	2.53	3.05
Toluene:benzene	0.845	Cresols:phenol	16.4	19.4[e]
Toluene:benzene	0.282	Cresols:phenol	5.3	18.7[e]

[a] Total aromatic:$AlCl_3$:H_2O = 16–30:1.5–2.0:1, 0–5°, 2 hr. [b] Not actually characterized; determined as the amount of cresol reacted by subtracting the amount of recovered cresol from that of starting cresol. [c] $k_{cresol}:k_{benzene}$ calculated from other three relative rates = 119. [d] Average $k_{cresol}:k_{o\text{-xylene}}$ = 2.04. [e] Average of triplicate runs in good agreement; overall average $k_{toluene}/k_{benzene}$ = 19.1.

Since the typical starting aromatic:peroxide ratio was generally about 15:1 (Table I), the statistical preponderance of aromatic:phenol at any given time favored monohydroxylation despite the small preference of the hydroxylating species for the phenol.[12]

The more readily accessible 30% hydrogen peroxide could be substituted for the high-strength peroxide without harmful effects provided at least a 2:1 molar ratio of aluminum chloride:hydrogen peroxide was used. With lesser amounts of catalyst, the hydroxylation yield at least with toluene fell off, quite possibly due to increased hydrolysis of the catalyst by the water present (Table III).

Anisole treated with a 1.5:1 ratio of aluminum chloride:30% hydrogen peroxide showed a dropoff in methoxyphenol yield to 50% compared to 70% at the same ratio with high strength peroxide.

The isomer distributions, particularly with toluene and anisole, were predominantly ortho–para, indicating a fair amount of intramolecular selectivity in the attacking species. Benzene–toluene competition experiments (Table II) also demonstrated intermolecular selectivity. Despite the heterogeneous nature of the reaction and the 2–3% further oxidation, rather consistent results were obtained in repetitive experiments, lending some credence to the average relative rate, $k_{toluene}/k_{benzene}$ = 19.1 (Table II).

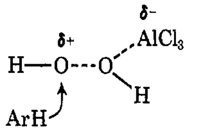
TABLE III

HYDROXYLATION OF TOLUENE WITH 30% HYDROGEN PEROXIDE–ALUMINUM CHLORIDE[a]

Molar ratio, $AlCl_3$:H_2O_2	Cresols, % yield[b]
2	45
1.5	14
1	10

[a] Aromatic:30% H_2O_2 = 14:1, 0–5°, 3 hr. [b] Based on limiting peroxide reagent.

The hydroxylating species in our system shows a much greater selectivity than the hydroxyl radical.[3] This indicates the probable involvement of a hydroxyl cation species which could be formed as shown below.



(2)

A highly polarized peroxide–catalyst complex undergoing nucleophilic attack by the aromatic is more palatable than the intermediacy of the energetically less favorable free hydroxyl cation.

The electrophile in this reaction seems to possess roughly twice the intermolecular selectivity as do the related oxy entities shown in Table IV. A comparison of the aluminum chloride–peroxide systems shows very similar isomer distributions except for the somewhat sterically hindered diisopropylperoxydicarbonate case.[5]

TABLE IV

RELATIVE REACTIVITIES FROM ELECTROPHILIC OXYGENATING SYSTEMS

Oxygenating system	$k_{toluene}/k_{benzene}$	Cresol isomers *o*	*m*	*p*
H_2O_2–$AlCl_3$	19.1	60	8	32
(*i*-$PrOCO_2)_2$–$AlCl_3$[a]	9.6	34	11	55
(*tert*-BuO$)_2$–$AlCl_3$[b]	10.4	59	10	31
tert-BuOOH–$AlCl_3$[c]	13.8	56	8	36
CF_3CO_3H[d]	11.7	78	2	20

[a] Reference 5. [b] Reference 8. [c] Reference 7. [d] Reference 3.

Unexpectedly, aromatic chlorination took place as a competing side reaction in this system (Table I). With high strength peroxide this amounted to 10–30% depending on the aromatic studied. To find out more about the nature of the chlorinating species, the isomeric composition of the chlorotoluenes and chloroanisoles were compared to those of known chlorinating agents (Table V).

The isomer distributions, particularly with anisole, bore a closer similarity to those from positive chlorine systems[13–15] than to those from molecular chlo-

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[12] For example, in a toluene run where cresols were present on the average to the extent of 20% during the reaction there was a 75-fold excess of toluene leading to some 15 times more reaction with toluene than with cresol.

[13] P. Kovacic and M. E. Kurz, *J. Org. Chem.*, **31**, 2459 (1966).

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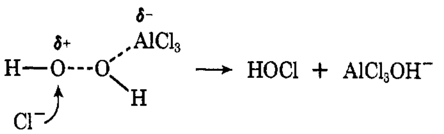
TABLE V

ISOMER DISTRIBUTIONS FROM AROMATIC CHLORINATING SYSTEMS

Aromatic compound	Chlorinating agent	Aryl chlorides		
		o	*m*	*p*
Anisole	H_2O_2–$AlCl_3$	40		60
Anisole	Cl_2–$AlCl_3$[a]	23		77
Anisole	Cl_2–CCl_4[b]	20		80
Anisole	*tert*-BuOCl–$AlCl_3$[a]	37		63
Anisole	$Cl^+(HOCl–H_3O^+)$[b]	35		65
Toluene	H_2O_2–$AlCl_3$	67		33[c]
Toluene	Cl_2–HOAc[d]	60	<1	40
Toluene	Cl^+–HOAc[e]	75	2	23

[a] Reference 13. [b] Reference 14. [c] Includes meta and para (not separated); mostly para by infrared analysis. [d] Reference 15. [e] Reference 16.

rine.[13,14,16] More than likely hypochlorous acid, formed from the peroxide and catalyst, acted as the precursor for the chloronium ion. One could visualize hypochlorous acid formation by attack of chloride on the aluminum chloride–peroxide complex (eq 3). This reaction



$$Cl^- + H\overset{\delta+}{-}O\cdots O(H)\overset{\delta-}{AlCl_3} \longrightarrow HOCl + AlCl_3OH^- \qquad (3)$$

could compete with hydroxylation (2) and would be expected to become more important as the basicity of the aromatic decreases. Somewhat less chlorination was generally noted when 30% hydrogen peroxide was used.

Although phenolic products as formed in the reaction media did not show much tendency toward further hydroxylation, they did exhibit their characteristic propensity towards nuclear chlorination. With toluene some 2% of chlorinated cresols were identified as the major constituents of the higher boiling phenolic products. From the less reactive benzene, phenol chlorination became a more serious problem judging from the 5% chlorophenols appearing along with the larger amount of chlorobenzene.

This method of hydroxylation may prove to be of some value as a laboratory-scale synthesis of certain phenolic products. It offers a simple one-step hydroxylation method converting aromatics directly to phenols, and utilizes readily available starting materials. Unlike the recently reported HF–H_2O_2 system which used a catalyst:peroxide ratio of 27–54:1 and a rather complex apparatus, this employs low catalyst:peroxide ratios and simple laboratory equipment.

Studies are currently underway to examine the scope and more mechanistic details of this reaction. Of particular interest is a comparison of this process to other hydroxylating systems, especially those which have served as models for enzymatic hydroxylation.[4,17] Indeed electrophilic aromatic hydroxylation by trifluoroperacetic acid[4] exhibits the NIH shift, a phenomenon of enzymatic hydroxylation, in which a suitable label initially at the point of substitution undergoes a 1,2 migration to an adjacent position on the aromatic ring.[4,17]

Experimental Section

Materials.—The aromatic reactants of high purity according to glpc were used directly. Aluminum chloride (Baker Analyzed Reagent) was also used without further purification. 90% (Du Pont high strength) and 30% (Mallinckrodt) hydrogen peroxide were analyzed by iodometry before use. We are grateful to the Du Pont Corp. for a generous sample of 90% hydrogen peroxide.

Aromatic Hydroxylation with Hydrogen Peroxide–Aluminum Chloride. General Procedure.—Hydrogen peroxide (0.05 mol of 90 or 30%) was added dropwise to a rapidly stirred solution of aluminum chloride (0.075–0.10 mol) in excess aromatic (0.45–1.0 mol) at 0–5°. Generally a brief induction period was noted before the rather exothermic reaction occurred. Caution should be exercised to prevent excessive buildup of peroxide (especially high test) within the reaction vessel. After stirring for 1–3 hr at this temperature, the reaction mixture was hydrolyzed with dilute hydrochloric acid, and the organic layer was separated, dried and analyzed. The aqueous layer was analyzed by iodometry for peroxide and generally was found to contain 5–15% unreacted H_2O_2. An appropriate marker was added to a portion of the reaction mixture and quantitative glpc analysis was carried out to determine the yields and isomer distributions of the products (glpc, columns A and B).

In many cases the phenolic products were obtained by alkaline extraction of the organic phase followed by preparative glpc purification (column D) of the components. Identity of the products was established by comparison of the ir and, in some cases, nmr spectra with the authentics.

Treatment of toluene with hydrogen peroxide without an added catalyst at 0° for 12 hr and 25° for 8 hr resulted in no reaction. The peroxide was recovered quantitatively by aqueous extraction of the reaction mixture.

Analysis for Further Oxidation Products—Typical reaction runs from the various aromatics were checked carefully for the presence of higher boiling products, both neutral and phenolic. The unreacted aromatic was stripped off on a rotary evaporator and the product residue was analyzed by glpc and then distilled. From anisole about 0.15 g (<2% based on the peroxide) of higher boiling product was found while from toluene 0.2 g (≈3% based on the peroxide) was isolated. In both cases most of this pot residue after distillation was alkali soluble. Glpc analysis (column D) of the anisole pot residue indicated trace amounts of three or four components, none of which were positively identified. Glpc indicated four or five components from toluene, three of which gave identical retention times (columns A and D) with the products resulting from chlorination of *o*- and *p*-cresol respectively.

Stability of Phenols under Simulated Reaction Conditions—Weighed amounts of *o*- and *p*-cresol (0.01–0.05 mol) were dissolved in 100 ml of either *o*-xylene or benzene and treated with hydrogen peroxide (0.05 mol) and aluminum chloride (0.1 mol) under the usual reaction conditions. Glpc analysis was performed on the final reaction mixture to determine the exact amount of unreacted cresols as well as hydroxylated aromatic. Only a small portion of cresol was consumed by oxidation or chlorination in the presence of *o*-xylene, while a greater amount reacted in the benzene case. Of the cresol consumed there was a slight preference for the ortho isomer.

Competitive Reactions.—The general reaction procedure was followed utilizing at least a tenfold molar excess of each aromatic (except the cresols) in comparison to hydrogen peroxide. Phenolic product ratios were determined by glpc (column A).

Analytical Procedures. A. Gas Chromatography.—Glpc was used extensively for separation and purification of products and for quantitative yield determinations. Varian Models 600D, 1400, and 90P were used with the following columns: (A) 10 ft × $^1/_8$ in. 20% SE-30/Chromosorb W AW DMCS; (B) 10 ft × $^1/_8$ in. 10% Apiezon L/Chromosorb W AW DMCS; (C) 5 ft × $^1/_8$ in. 10% Carbowax 20M/Chromosorb W AW DMCS and (D) 5 ft × $^1/_4$ in. 10% Apiezon L/Chromosorb W AW DMCS.

B. For Phenolic Products.—The yields and isomer distributions were determined by adding a marker such as *o*-chlorophenol or *o*-nitrophenol to a portion of the reaction mixture and carrying out a quantitative glpc analysis (column A or B). Separation of the meta from the para isomer was not possible by glpc for the cresols and chlorophenols. Therefore the combined peak was collected by preparative glpc and analyzed by ir. After the appropriate standardization, the bands at 830 and 780

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(16) H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **79**, 5175 (1957).

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cm^{-1} were quantitatively utilized to determine the amounts of *p*- and *m*-cresol, respectively, while bands at 830 and 900 cm^{-1} were used for *p*- and *m*-chlorophenols, respectively. Multiple isomer distribution determinations were done on six cresol mixtures, giving good, reproducible results.

C. **For Chlorinated Products.**—Aryl chloride yields were performed along with phenol yields by glpc (columns A and B). Columns A and C were used to determine the isomeric compositions of the chlorinated hydrocarbons.

D. **For HCl.**—The general procedure was followed except that the reaction flask was continuously purged with nitrogen which was then bubbled through an aqueous sodium hydroxide trap. Titration of aliquots from the trap before and after the reaction gave the amount of acid formed. The yield of HCl produced based on the limiting peroxide reagent was 88% from toluene and 90% from anisole hydroxylations.

Registry No.—Hydrogen peroxide, 7722-84-1; aluminum chloride, 7446-70-0; anisole, 100-66-3; toluene, 108-88-3; chlorobenzene, 108-90-7; *o*-xylene, 95-47-6; mesitylene, 108-67-8; benzene, 71-43-2; nitrobenzene, 98-95-3; cresol, 1319-77-3.

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Cyclization of N-Substituted Diallylamines to Pyrrolidine Derivatives During the Radical Addition of Perfluoroalkyl Iodides

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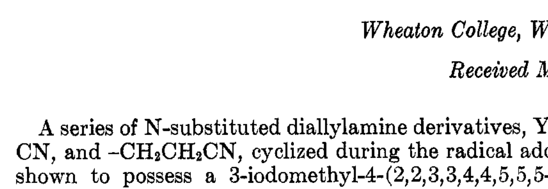
A series of N-substituted diallylamine derivatives, $YN(CH_2CH{=}CH_2)_2$, where Y = CH_3CO, CF_3CO, C_6H_5CO, CN, and $-CH_2CH_2CN$, cyclized during the radical addition of 1-iodoperfluorobutane. The cyclic adducts were shown to possess a 3-iodomethyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)pyrrolidine structure by spectroscopic and chemical methods. Diallylamine (Y = H) and 1-iodoperfluorobutane, in the presence of a radical generating agent only, gave a polymeric salt in quantitative yield, while 3-diallylaminopropionitrile (Y = CH_2CH_2CN) gave both cyclic adduct and a derived polymeric salt. Cyclopolymers of $YN(CH_2CH{=}CH_2)_2$ synthesized under similar radical conditions have been previously thought to contain six-membered ring repeating units.

Free-radical induced reaction of perfluoroalkyl iodides (R_FI) with olefins has given adducts in excellent yield under mild conditions.[1] In many cases structures of the products were readily ascertained by spectroscopic and chemical methods. These reactions also have the merit of producing novel compounds having unusual physical and chemical properties.[2,3] Addition of R_FI to dienes may also involve rearrangement of the intermediate radical both in cyclic and open-chain forms. Thus, norbornadiene and R_FI gave **1a,b**, while certain 1,6-heptadienes gave **2a,b**.[4] By contrast, 1,5-hexadiene and 1,7-octadiene added R_FI entirely without rearrangement, giving monoadducts **3** and **4** without transfer of the radical to an adjacent center of unsaturation, as would have been expected.[5] This is

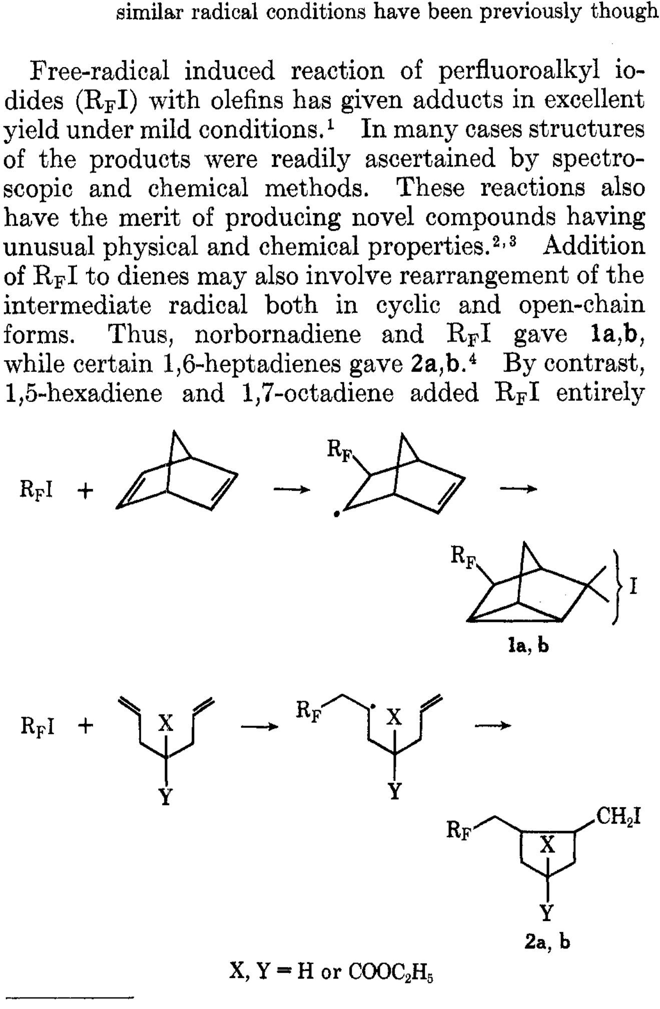
$$R_FI + CH_2{=}CH(CH_2)_nCH{=}CH_2 \longrightarrow R_FCH_2CHI(CH_2)_nCH{=}CH_2$$

3, $n = 2$
4, $n = 4$

surprising in view of the reported[6] cyclization of these dienes during addition of CCl_4.



1a, b



2a, b

X, Y = H or COOC$_2$H$_5$

One of the most intriguing features of the cyclization of 1,6-heptadienes is the preference for five-membered ring formation.[5-7] Other radical cyclizations[8,9] also show this same preference and it has been ascribed to kinetic control and to steric factors. It was recognized that this feature was inconsistent with cyclopolymerization processes, which generally have been thought to give six-membered ring repeating units.[10,11] N-substituted diallylamines, and *N,N*-diallylamides in particular, have been claimed to give cyclopolymers with piperidine ring units,[12-14] based on chemical[12] and infrared evidence.[13,14] Such polymers are important both from the technical and scientific points of view and merit a careful study of their structures. Identification of these structures by the infrared method is a dif-

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