[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Rates of Oxidation of Aralkyl Hydrocarbons. Polar Effects in Free Radical Reactions[1,2]

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The rates of reaction of a number of aralkyl hydrocarbons and substituted hydrocarbons with oxygen at 90° in the liquid phase have been measured. In the presence of a free radical initiator and at sufficiently high oxygen pressures the relative rates of oxidation observed are determined by the relative rates of reaction of a peroxy radical with the hydrocarbon (chain propagation) and the relative rates of the chain termination reaction of two peroxy radicals. Termination and propagation rate constants have been at least qualitatively separated by measuring the rates of oxidation of mixtures of hydrocarbons. The results indicate that secondary and primary peroxy radicals terminate more readily than tertiary peroxy radicals and that other structural changes have a rather minor effect on the termination rate constants. The propagation rate constants, in general, increase with increasing stability of the aralkyl radical formed, but also display a polar effect; electron-supplying groups increase and electron-withdrawing groups decrease the rate of the propagation step. The propagation rate constants for *m*- and *p*-substituted cumene and toluene derivatives follow a $\rho\sigma$-relationship with $\rho = -0.4$ and ~ -0.6, respectively. Replacement of an α-hydrogen atom of toluene by various groups also shows the same polar effect on the propagation rate constants but here it is more difficult to separate the polar effect from changes in resonance stabilization of the benzyl-type aralkyl radicals. A table of relative reactivities of aralkyl hydrocarbons toward peroxy radicals has been constructed from the data obtained. This table includes thirty-two hydrocarbons having a one thousand-fold range in reactivity.

The influence of chemical structure on the reactivity of olefinic α-methylene groups toward peroxy radicals has received considerable attention.[3] Some qualitative data are available on the relative ease of oxidation of aralkyl hydrocarbons, but quantitative data are lacking in regard to the over-all rates of oxidation of these hydrocarbons and to the effect of structure on the values of the rate constants that are involved in the over-all rate expressions.

The reaction of a number of aralkyl hydrocarbons with oxygen at 90° in the liquid phase in the presence of a small amount of *t*-butyl perbenzoate has been investigated from the viewpoint of rate, in order to obtain quantitative data on the ease of oxidation of these hydrocarbons. Various mixtures of hydrocarbons have been oxidized in an attempt to separate the effects on the over-all rate of oxidation due to changes in the propagation and termination rate constants.

In Table I are listed the rates of oxygen absorption for the hydrocarbons investigated. The oxidations were performed at 90° in the presence of 0.02 *M* *t*-butylperbenzoate by vigorously shaking the hydrocarbon in the presence of oxygen at a pressure of 760 mm. minus the vapor pressure of the hydrocarbon. Under the conditions employed the amount of oxygen absorbed was linear with time over the first 1–2 mole % oxidation. The agitation was sufficiently vigorous so that an increase or a decrease in the rate of shaking did not effect the rate of oxygen absorption and the reactions were therefore not diffusion controlled. Hydroperoxides formed in the reaction were analyzed by reaction with potassium iodide in acetic acid containing a small amount of phosphoric acid.[4]

TABLE I

RATES OF OXIDATION OF ARALKYL HYDROCARBONS AT 90° IN THE PRESENCE OF 0.02 *M* *t*-BUTYL PERBENZOATE

Hydrocarbon	Concn., mole l.$^{-1}$	Rate, mole l.$^{-1}$ hr.$^{-1}$	Rate/concn., hr.$^{-1}$ × 100	Mole % oxidation	Hydroperoxide, % of oxygen absorbed
α-Methylstyrene	7.28	0.575	7.90	1.5	...
Dibenzyl ether	4.60	.325	7.07	4.9	99.1
Styrene	8.11	.400	4.93	0.8	...
Tetralin	6.91	.210	3.04	8.5	98.5
p-Diisopropylbenzene	4.96	.136	2.74	3.5	99.0
Indan	7.64	.129	1.69	3.1	100.4
p-*t*-Butylcumene	4.60	.055	1.20	2.6	92.2
Phenylcyclopentane	6.11	.071	1.16	2.1	92.5
Cumene	6.65	.067	1.00	2.6	97.5
Allylbenzene	7.10	.057	0.80	3.0	74.2
p-Bromocumene	5.77	.045	.78	2.7	91.0
Methyl *p*-cumate	5.38	.030	.56	2.5	104.0
p-Nitrocumene	6.19	.033	.53	1.6	93.0
p-Cyanocumene	6.18	.031	.50	1.1	100.0
p-Cymene	5.94	.026	.44	1.0	100.0
Fluorene	2.56^a	.010	.39	1.1	69.1
Diphenylmethane	5.65	.020	.35	1.2	85.6
Phenylcyclohexane	5.56	.014	.25	0.3	67.5
Triphenylmethane	2.64^a	.0052	.20	1.2	...
Ethylbenzene	7.58	.014	.18	0.7	83.9
Mesitylene	6.70	.0058	.086	.3	75.4
Methyl phenylacetate	6.67	.0042	.063	.05	75.0
Benzyl benzoate	5.00	.0029	.058	.2	99.8
p-Xylene	7.50	.0039	.052	.2	90.2
Benzyl chloride	8.08	.0037	.046	.3	...
p-*t*-Butyltoluene	5.44	.0015	.028	.1	...
m-Xylene	7.77	.0027	.035	.3	74.4
Phenylacetonitrile	8.17	.0015	.018	.08	...
Toluene	8.68	.0013	.015	.05	62.2
p-Chlorotoluene	7.68	.0010	.013	.2	...
p-Methoxytoluene	6.57	.00063	.0096	.03	...
p-Tolunitrile	7.90	.00060	.0076	.03	...
p-Nitrotoluene	7.96	.00050	.0063	.01	...
Phenyldimethylsilane	$\sim 7^b$	$<.0001$	$<.0015$	..	...

[a] Chlorobenzene solution. [b] Estimated.

Measurements of the rates of oxidation of benzal chloride, benzyl alcohol and phenylacetic acid were attempted, but unreproducible non-linear plots of oxygen absorbed as a function of time were obtained.

The rates of oxidation of various mixtures of hydrocarbons were also measured at constant catalyst concentration. Data on the rate of oxidation of mixtures of tetralin, indan, dibenzyl ether, styrene and α-methylstyrene with cumene have been pre-

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[1] Directive Effects in Aliphatic Substitutions. VII.

[2] Presented before the Division of Organic Chemistry at the Minneapolis Meeting of the American Chemical Society, September, 1955.

[3] J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

[4] A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3408, 3412 (1951).

TABLE II

OXIDATION OF MIXTURES OF ARALKYL HYDROCARBONS AT 90° IN THE PRESENCE OF 0.02 *M* *t*-BUTYL PERBENZOATE

A. Cumene diluted with aromatic hydrocarbons containing an activated tertiary hydrogen atom

Diluent	Concentration, mole l.$^{-1}$ Cumene	Diluent	Rate of oxidn., mole l.$^{-1}$ hr.$^{-1}$
p-Diisopropylbenzene	4.45	1.65	0.0885
p-Diisopropylbenzene	2.81	2.88	.105
p-Diisopropylbenzene	1.35	3.96	.122
p-*t*-Butylcumene	4.07	1.76	.0635
p-*t*-Butylcumene	2.48	2.86	.0610
p-*t*-Butylcumene	1.69	4.48	.0580
p-Bromocumene	4.82	1.70	.0610
p-Bromocumene	3.10	3.25	.0540
p-Bromocumene	1.70	4.56	.0491
p-Nitrocumene	5.09	1.49	.0583
p-Nitrocumene	2.10	4.27	.0429
Phenylcyclopentane	4.87	1.64	.0378
Phenylcyclopentane	3.29	3.11	.0475
Phenylcyclopentane	1.45	4.77	.0595
Phenylcyclohexane	4.79	1.60	.0393
Phenylcyclohexane	3.35	2.80	.0276
Phenylcyclohexane	1.77	4.09	.0191
Triphenylmethane	6.00	0.40	.0016
Triphenylmethane	4.74	1.22	.0018
Phenyldimethylsilane	5.00	1.66	.0470

B. Cumene diluted with aromatic hydrocarbons containing an activated methylene or methyl group

Diluent	Cumene	Diluent	Rate of oxidn.
Allylbenzene	6.33	0.36	0.0198
Allylbenzene	5.11	1.36	.0234
Allylbenzene	2.49	4.37	.0400
Diphenylmethane	6.29	0.28	.0300
Diphenylmethane	5.67	0.84	.0202
Diphenylmethane	3.59	2.64	.01865
Fluorene	6.42	0.19	.0081
Fluorene	5.90	0.73	.0055
Fluorene	4.98	1.62	.0046
Ethylbenzene	5.75	1.06	.0350
Ethylbenzene	3.31	3.81	.0222
Mesitylene	5.02	1.68	.0210
Mesitylene	3.23	3.45	.0093
Toluene	5.25	1.86	.0325
Toluene	3.49	4.14	.0155
p-Methoxytoluene	6.50	0.15	.0185
p-Methoxytoluene	3.35	3.69	.00141

C. Indan diluted with aromatic hydrocarbons containing an activated methylene group

Diluent	Indan	Diluent	Rate of oxidn.
Dibenzyl ether	6.10	1.00	0.170
Dibenzyl ether	2.72	3.03	.255
Tetralin	6.71	0.81	.140
Tetralin	5.50	2.01	.148
Tetralin	2.62	4.62	.184
Diphenylmethane	5.76	1.40	.100
Diphenylmethane	4.07	2.66	.075
Diphenylmethane	2.25	4.03	.049
Fluorene	7.22	0.30	.098
Fluorene	5.80	1.51	.058
Allylbenzene	5.92	1.71	.111
Allylbenzene	2.11	4.85	.080
Ethylbenzene	6.12	1.60	.110
Ethylbenzene	2.60	5.05	.048
Methyl phenylacetate	3.87	3.38	.062

D. Toluene diluted with aromatic hydrocarbons containing an activated methyl group

Diluent	Toluene	Diluent	Rate of oxidn.
Mesitylene	7.01	1.34	0.0021
Mesitylene	3.02	4.33	.0043
p-Xylene	7.10	1.38	.0018
p-Xylene	2.58	4.42	.0027
p-Tolunitrile	6.79	1.72	.0011
p-Tolunitrile	3.51	4.70	.00091
p-Methoxytoluene	7.15	1.18	.00088
p-Methoxytoluene	3.06	4.35	.00068

sented previously.[5] The rates of oxidation of numerous other mixtures of aralkyl hydrocarbons are summarized in Table II.

Discussion

The oxidation of cumene and tetralin at 90° in the presence of *t*-butyl perbenzoate and oxygen at a pressure of about 760 mm. has been shown[5] to involve a reaction sequence similar to that demonstrated for the oxidation of olefins containing activated methylene groups.[6]

$$\text{Catalyst} \xrightarrow{k_i} 2\text{R}\cdot' \xrightarrow[\text{O}_2 + \text{RH}]{\text{RH or}} 2e\text{R}\cdot$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{\text{very fast}} \text{RO}_2\cdot$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_p} \text{RO}_2\text{H} + \text{R}\cdot$$

$$2\text{RO}_2\cdot \xrightarrow{k_t} \text{non-radical products}$$

Under steady state conditions the rate of oxidation is

$$\text{Rate} = \frac{k_p}{k_t^{1/2}}[\text{RH}](2ek_i[\text{Cat.}])^{1/2}$$

where *e* is the efficiency of the catalyst in initiating oxidation chains. When this equation applies, and if the rate of initiation remains constant, the relative rates of oxidation are determined by the relative values of k_p, k_t and the hydrocarbon concentrations. Thus, if it is assumed that a constant catalyst concentration can be taken as evidence of a constant rate of initiation, the values listed in column 4 of Table I represent relative values of $k_p/k_t^{1/2}$.

Bolland, in correlating the rate of oxidation of olefins with structure, has made the assumption that the values of k_t are independent of the structure of the peroxy radical involved.[3] On the other hand, it is known that tetralylperoxy radicals terminate more readily than cumylperoxy radicals.[5] Therefore, it is not feasible to attempt to correlate the values of column 4 of Table I with the relative propagation rate constants for the attack of a peroxy radical on the hydrocarbon without considering changes that may occur in k_t.

Because of the difference in termination rate constants for tetralyl- and cumylperoxy radicals, rather unusual rates of oxidation are observed for mixtures of cumene and tetralin. Small amounts of tetralin, the more reactive hydrocarbon, when added to cumene reduce the rate of oxidation and a minimum rate of oxidation is observed in cumene-tet-

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(5) G. A. Russell, THIS JOURNAL, **77**, 4583 (1955).

(6) (a) J. L. Bolland, *Quart. Revs.* (*London*), **3**, 1 (1949); (b) L. Bateman, *ibid.*, **8**, 147 (1951).

ralin mixtures containing 98 mole % cumene.[5] This type of behavior is not unique for tetralin–cumene mixtures. In Fig. 1 the rates of oxidation as a function of cumene concentration are given for mixtures of cumene with dibenzyl ether, indan, diphenylmethane and ethylbenzene. Fluorene and allylbenzene give similar curves involving a minimum rate of oxidation. Presumably the same effects occur in these systems as in mixtures of cumene and tetralin.

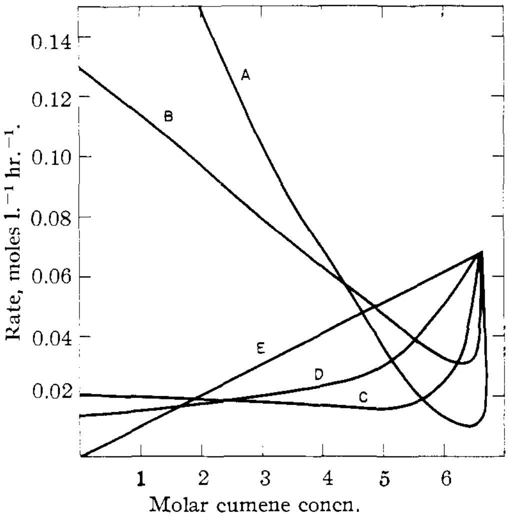

Fig. 1.—Oxidation of mixtures of cumene and aralkyl hydrocarbons at 90°, 0.02 M t-butyl perbenzoate: A, dibenzyl ether; B, indan; C, diphenylmethane; D, ethylbenzene; E, theoretical for an inert diluent.

Our interpretation of these data, based on a thorough study of the oxidation of mixtures of cumene and tetralin,[5] is that the secondary peroxy radicals from these hydrocarbons terminate more readily than cumylperoxy radicals. The dilution of cumene by more reactive hydrocarbon, like tetralin, indan, dibenzyl ether, allylbenzene or fluorene, gives a rate curve that passes through a decided minimum. In these cases the addition of a small amount of the hydrocarbon to cumene causes a relatively high proportion of the total peroxy radicals to be secondary peroxy radicals[7] which terminate more readily than cumylperoxy radicals. Thus, the steady state concentration of peroxy radicals decreases rapidly at first and then more slowly as these hydrocarbons are added to cumene even though the rate of initiation remains constant. As more of the hydrocarbon is added to cumene the rate of oxidation passes through a minimum because of the general increase in the reactivity of the hydrocarbon mixture toward peroxy radicals.

In the case of diphenylmethane this effect is not so pronounced; the minimum is not sharp and is shifted to the left in Fig. 1. This presumably is because diphenylmethylperoxy radicals terminate more readily than cumylperoxy radicals but the hydrocarbon itself is not as reactive as tetralin or indan. With an even less reactive hydrocarbon, like ethylbenzene, this minimum in the rate curve disappears. However, the initial addition of ethylbenzene to cumene suppresses the rate more than would be expected for a completely inert diluent.

Toluene also retards the oxidation of cumene more than would be expected for an inert diluent. Moreover, this effect is observed when the two types of α-hydrogen atoms are in the same molecule. Thus, p-cymene is oxidized at a lower rate than cumene although a p-methyl group should activate the tertiary hydrogen atom of cumene. In fact a solution of toluene and cumene in a 1:1 mole ratio is oxidized at nearly the same rate as p-cymene. The observed rate for a toluene–cumene mixture, 3.85 M in each hydrocarbon, was 0.0160 mole l.$^{-1}$ hr.$^{-1}$ which when corrected to the concentration of pure p-cymene (5.95 M) gives a rate of 0.0246. The observed rate for p-cymene was 0.0256; similarly, a 3:1 mole mixture of cumene and mesitylene gave a corrected rate of 0.0250.

If both peroxy radicals present in a competitive oxidation have the same reactivity, and have the same termination and cross termination rate constants, it can be shown (see equation 3–5, ref. 5) that the rate of oxidation of mixtures of the two hydrocarbons should follow the relationship

$$\text{Rate} = k(k'[\text{RH}'] + k''[\text{RH}''])$$

where k' and k'' are the rate constants for reaction of either of the peroxy radicals with [RH'] and [RH''], respectively. Such relationships have indeed been observed for mixtures of cumene and substituted cumenes (Fig. 2), toluene and substituted toluenes, and for mixtures of indan with dibenzyl ether, tetralin, allylbenzene, diphenylmethane, ethylbenzene or methyl phenylacetate (Fig. 3).

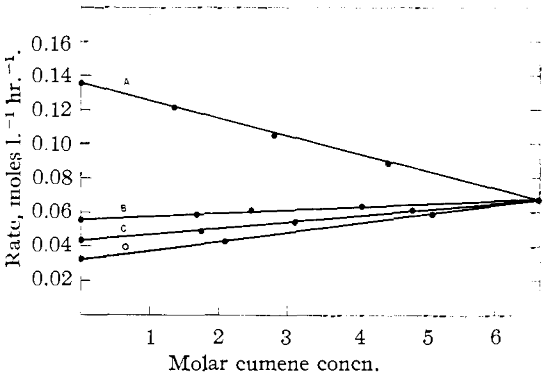

Fig. 2.—Oxidation of mixtures of cumene and substituted cumenes at 90°, 0.02 M t-butyl perbenzoate: A, p-diisopropylbenzene; B, p-t-butylcumene; C, p-bromocumene; D, p-nitrocumene.

Although the above requirements are not the only ones that could satisfy the relationship observed between rate and composition, they are the simplest ones, and, if assumed, lead to some interesting conclusions. Therefore, the rates of oxidation observed for mixtures of cumene and substituted cumenes will be taken as evidence that cumylperoxy radicals and p-substituted cumylperoxy radicals have the same reactivity and terminate at the same rate. Similarly, in the absence of data to the contrary, all secondary peroxy radicals or all primary peroxy radicals will be assumed to have

[7] In the case of allylbenzene the peroxy radical formed is the rearranged cinnamyl peroxy radical.[6b]

TABLE III

RELATIVE REACTIVITIES OF ARALKYL HYDROCARBONS TOWARD PEROXY RADICALS AT 90°

Per tertiary hydrogen atom	Per secondary hydrogen atom	Per primary hydrogen atom
Triphenylmethane (>1.0)	Dibenzyl ether (11)	*p*-Methoxytoluene (>0.075)
Phenylcyclopentane (>1.2)	Fluorene (>2.88)	Mesitylene (0.14)
p-Diisopropylbenzene (1.40)	Tetralin (5.0)	*p*-*t*-Butyltoluene (0.14)
p-*t*-Butylcumene (1.20)	Indan (2.88)	*p*-Xylene (0.12)
p-Cymene (1.19)[a]	Allylbenzene (2.65)	*p*-Cymene (0.11)[a]
Cumene (1.00)	Diphenylmethane (1.13)	*m*-Xylene (0.087)
p-Bromocumene (0.78)	Ethylbenzene (0.59)	Toluene (0.075)
Methyl *p*-cumate (0.56)	Methyl phenylacetate (0.21)	*p*-Chlorotoluene (0.063)
p-Nitrocumene (0.53)	Benzyl benzoate (0.19)	*p*-Tolunitrile (0.028)
p-Cyanocumene (0.50)	Benzyl chloride (0.15)	*p*-Nitrotoluene (0.025)
Phenylcyclohexane (0.25)	Phenylacetonitrile (0.059)	
Phenyldimethylsilane (<0.002)		

[a] From ρσ-plot.

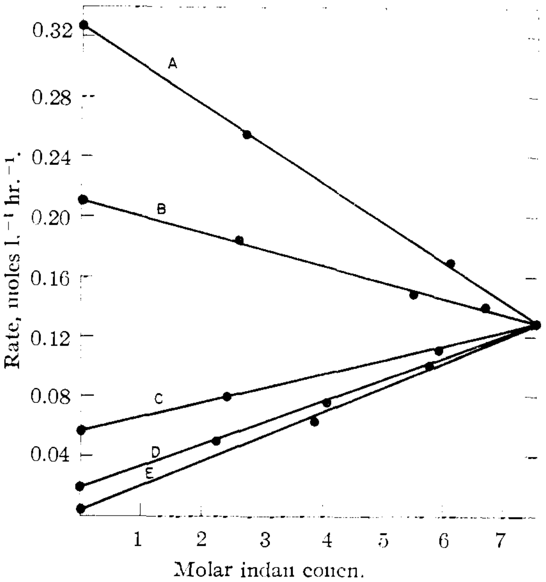

Fig. 3.—Oxidation of mixtures of indan and aralkyl hydrocarbons at 90°, 0.02 *M* *t*-butyl perbenzoate: A, dibenzyl ether; B, tetralin; C, allylbenzene; D, diphenylmethane; E, methyl phenylacetate.

the same reactivity and to terminate at the same rate. The assumption that most peroxy radicals have the same reactivity toward a given hydrocarbon does not appear to be unreasonable since the odd electron in the peroxy radical is separated from the site of any structural changes by at least a carbon and two oxygen atoms and these three atoms should be effective in damping any electrostatic or steric effects created by structural changes. However, Walling and McElhill have reported that *p*-substitution does influence the reactivity of perbenzoate radicals.[8] In addition, co-oxidations of styrene or α-methylstyrene and methyl methacrylate indicate an alternating of hydrocarbon and ester groups in the polymeric peroxide formed.[9] On the other hand, the relative reactivities of tetralin and cumene do not vary significantly when measured by cumyl- or tetralylperoxy radicals.[5]

In Table III the relative reactivities of aralkyl hydrocarbons toward a peroxy radical, as calculated on the basis of the above assumptions, have been summarized. Cumene has been taken as the reference compound and the reactivities of *p*-substituted cumenes have been assigned according to their relative rates of oxidation. Since tetralin was found to be 16–23 times as reactive as cumene toward either the cumyl- or the tetralylperoxy radical,[5] an α-hydrogen atom of tetralin has been given a reactivity of 5.0. The reactivity of the hydrogen atoms of dibenzyl ether, indan, allylbenzene, diphenylmethane, ethylbenzene, methyl phenylacetate, benzyl benzoate, benzyl chloride and phenylacetonitrile have been assigned from the rates of oxidation of these compounds relative to the rate of oxidation of tetralin.

Toluene and its derivatives have been assigned their position in Table III from the relative reactivities of the methyl and isopropyl groups of *p*-cymene. From the ρσ-plot for the reactivity of substituted cumenes (to be discussed later) it can be calculated that the tertiary hydrogen of *p*-cymene should be 1.2 times as reactive as the tertiary hydrogen atom of cumene. From a similar plot for toluene derivatives the methyl group of *p*-cymene is estimated to be 1.5 times as reactive as the methyl group of toluene. The oxidation of *p*-cymene has been investigated carefully at 85° and the products of the reaction found to be 78% tertiary hydroperoxide and 22% primary hydroperoxide.[10] Moreover, the ratio of these products changes only slightly with temperature. Thus from the above data the reactivity of a hydrogen atom of toluene has been assigned a relative reactivity of 0.075. The reactivities of the other toluene derivatives have been assigned from their rates of oxidation relative to the rate of oxidation of toluene.

Triphenylmethane, phenylcyclopentane, fluorene and *p*-methoxytoluene have been assigned speculative positions in Table III. Both phenylcyclopentane and triphenylmethane retard the rate of oxidation of cumene and the rate of oxidation of mixtures passes through a minimum. The shapes of the oxidation curves indicate that both of these compounds are more reactive than cumene. Fluorene retards the oxidation of indan more than would have been expected for an inert diluent and has been assigned a reactivity greater than indan. *p*-Methoxytoluene appears to be considerably more

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[8] C. Walling and E. A. McElhill, THIS JOURNAL, **73**, 2927 (1951).

[9] A. A. Miller, F. R. Mayo and G. A. Russell, unpublished results.

[10] G. S. Serif, C. F. Hunt and A. H. Bourns, *Can. J. Chem.*, **31**, 1229 (1953).

reactive than toluene and to be a good retarder in the oxidation of cumene. This effect is evidently connected with the methoxy group attached to the aromatic nucleus since anisole also shows the same retardation.

Unsaturated materials that react with a peroxy radical by addition to the double bond can also be added to Table III. Thus, styrene is 38 times as reactive as cumene if the polymeric peroxy radical from styrene has the same reactivity and the same termination rate constant as a tetralylperoxy radical. α-Methylstyrene cannot be compared because even at 50° with oxygen at 760 mm. the termination reaction involves alkyl radicals.[9]

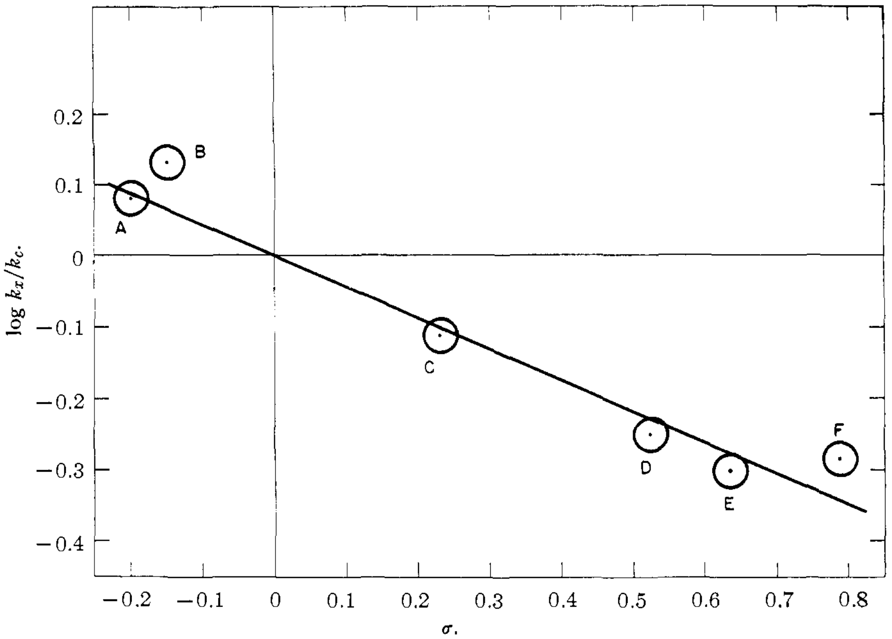

Fig. 4.—$\rho\sigma$-plot for the attack of a peroxy radical on substituted cumenes: A, *p*-*t*-butyl; B, *p*-isopropyl; C, *p*-bromo; D, *p*-carbomethoxy; E, *p*-cyano; F, *p*-nitro, at 90°. k_x and k_c are the rates of reaction of peroxy radicals with a substituted cumene and with cumene, respectively.

In general, the reactivities summarized in Table III may be explained by a consideration of a polar effect and of the stability of the alkyl radical formed in the slow propagation step. The rate of reaction of a peroxy radical with *p*-substituted cumenes or toluenes shows a pronounced polar effect. Electron-withdrawing groups decrease and electron-supplying groups increase the reactivity of the α-hydrogen atoms of cumene or toluene toward a peroxy radical. In Fig. 4 the log of relative rates of oxidation of cumene and substituted cumenes are plotted as a function of Hammett's σ-constants.[11] The experimental points fall on a straight line having a slope (ρ) of −0.43. Treatment of the data obtained in the oxidation of toluene gives a somewhat less satisfactory plot with the best straight line having a slope of −0.6.

The reactivities noted for the various substituted toluene and cumenes cannot be explained from a consideration of the resonance energy of the aralkyl radical formed. Thus, Szwarc[12] has shown that *p*-nitro, *p*-cyano, *p*-chloro or *p*-bromo groups increase the resonance stabilization of benzyl radicals whereas these groups decrease the reactivity of toluene or cumene toward a peroxy radical. Moreover, Szwarc has pointed out that the bond strength observed for substituted benzyl bromides is in no way connected with the Hammett σ-value of the substituent since a *p*-methyl and a *p*-nitro group have nearly the same effect on the carbon–bromine bond dissociation energy.

Polar effects have been recognized to be of importance in free radical polymerizations.[13] Similar polar effects have been observed in hydrogen atom abstraction reactions of perbenzoate radicals,[8] chlorine atoms,[14] bromine atoms[14e] and N-succinimidyl radicals[14e] but not for trichloromethyl radicals.[14e] Kooyman has tried to correlate the magnitude of this polar effect in substitution reactions with the electronegativity of the attacking radical.[14c] On this basis he predicted that the reaction of a peroxy radical with a substituted toluene or cumene should give a value of ρ of −2. Actually the observed ρ is not more than one-third of this value.

We do not think that the electronegativity of the attacking radical is unimportant. However, it is not the only effect that should be considered. We have presented evidence previously that the transition states are actually quite different for substitution reactions involving a low and a high energy of activation, such as photochemical chlorination and bromination[14b,15a]; in the case of a fast exothermic reaction the transition state should resemble the reactants[15b] and the electron density of the carbon–hydrogen bond being attacked may be important in determining reactivity. For reactions involving a higher energy of activation the stabilities of the products, particularly resonance stabilization of the radical, should determine the reactivity; polar effects would be expected to have little importance in determining reactivity.

Stated in another manner, the transition state of a substitution reaction can be considered to consist

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[11] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[12] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948); M. Szwarc and J. S. Roberts, *ibid.*, **16**, 609 (1948); M. Szwarc, C. H. Leigh and A. H. Sehon, *ibid.*, **19**, 657 (1951); C. H. Leigh, A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **209A**, 97 (1951).

[13] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[14] (a) H. C. Brown and A. B. Ash, THIS JOURNAL, **77**, 4019 (1955); (b) G. A. Russell and H. C. Brown, *ibid.*, **77**, 4578 (1955); (c) R. van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954); (d) C. Walling and B. Miller, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York City, 1954, p. 15R; (e) E. C. Kooyman, R. van Helden and A. F. Rickel, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **B56**, 75 (1953).

[15] (a) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4019 (1955); (b) G. S. Hammond, *ibid.*, **77**, 334 (1955).

of the three resonance forms

$$\underset{\text{I}}{\text{R:H}\cdot\text{X}} \longleftrightarrow \underset{\text{II}}{\text{R}^+\cdot\text{H}^-\text{:X}} \longleftrightarrow \underset{\text{III}}{\text{R}\cdot\ \text{H:X}}$$

Polar effects would be expected to be of importance in the order III < I < II. The greater the electronegativity of X· the more will form II be favored and the more important will be the polar effect. On the other hand, a very reactive X· will produce a transition state approaching I and a very unreactive X· will give a transition state that approaches III. That peroxidation is less effected by polar factors (ρ = -0.4 to -0.6) than is bromination (ρ = -1.05) or attack by a N-succimidyl radical (ρ = -1.5) even though oxygen is more electronegative than bromine or nitrogen[16] may mean that the reactivity differences between these radicals are sufficiently great that the transition states have essential differences.

The fact that electron-withdrawing groups decrease the reactivities of toluenes and cumenes toward peroxy radicals indicates that previously certain substituent effects have been misinterpreted in the oxidation of toluene and its derivatives by aqueous potassium permanganate. Thus, it has been suggested that the reaction of toluenes with potassium permanganate to yield benzoic acids involves an ionic rather than a free radical mechanism because the rate of oxidation decreases with electron-withdrawing substituents.[17] Actually this substituent effect is that expected for the attack of a radical with a high electron affinity and cannot be used to exclude a free radical mechanism. It has been suggested that the oxidation of benzaldehydes by potassium permanganate in basic solutions involves a free radical mechanism because electron-withdrawing groups increase the rate of oxidation to the benzoic acid.[18] This also appears to be an erroneous conclusion since electron-withdrawing groups decrease the rate of reaction of not only toluenes and cumenes but also of benzaldehyde[8] with peroxy radicals and a similar effect would be expected for hydroxy radicals.

Most of the reactivity differences in Table III not explained by considering the polar effect can be interpreted in terms of resonance stabilization of the aralkyl radical. The very low reactivity of phenyldimethylsilane relative to cumene is in agreement with the small amount of resonance stabilization expected for a silyl radical because of the high energy requirement of silicon doubly bonded to carbon.[19] Phenylcyclopentane is evidently more reactive than phenylcyclohexane because of the stabilities of the radicals formed. Brown has predicted that cyclopentane should be more reactive than cyclohexane because of the relief in strain (*I*-strain) upon removal of a hydrogen atom from cyclopentane and an increase in strain upon removal of a hydrogen atom from cyclohexane.[20] Another factor that bears consideration in the present example is that a resonance form involving a double bond *exo* to a cyclohexane ring is a relatively high energy structure while a double bond *exo* to a cyclopentane ring is a more stable structure.[21] Phenylcyclopentane has also been observed to be more reactive than phenylcyclohexane toward trichloromethyl radicals and the behavior interpreted in terms of *I*-strain.[22]

The relative reactivities of tetralin and indan are those expected from the *I*-strain concept.[19-21] Models indicate that there is no significant strain in tetralin or the tetralyl radical because the alicyclic ring does not have to be planar. However, in indan the least strained structure involves a planar five-membered ring. Even here there is 27° of strain relative to the preferred 109 and 120° configuration of trigonal and tetrahedral carbon atoms. In the radical the situation is even worse. The sum of the valence angles of three trigonal and two tetrahedral carbon atoms indicates that the radical involves 38° of strain, 11° more than indan itself, thus explaining the lower reactivity noted for indan relative to tetralin.

The reactivities of aromatic hydrocarbons containing an activated methylene group are best correlated by considering them to be derivatives of toluene. Substitution of an α-hydrogen atom of toluene by a cyano group or a chlorine atom causes either a decrease in reactivity or a slight increase in reactivity of the remaining hydrogen atoms. If only resonance stabilization of the radical mattered, a considerable increase in reactivity would have been expected. Since the cyano group is a powerful and the chlorine atom a weak electron-withdrawing group, the polar effect evidently offsets the increase in reactivity expected from resonance stabilization of the radical formed. The carbomethoxy and benzoyloxy groups are both powerful electron-withdrawing groups which would be expected to impart considerable resonance stabilization to the radical. The small increase in reactivity of the hydrogen atoms of methyl phenylacetate or benzyl benzoate relative to toluene indicates that again the two effects nearly cancel each other.

Substitution of an α-hydrogen atom of toluene by a methyl group increases the reactivity of the other hydrogen atoms considerably. Here the polar effect and increased resonance stabilization compliment each other. Substitution of a second methyl group to give cumene increases the reactivity of the remaining hydrogen atom still further. Fluorene, diphenylmethane and allylbenzene also give highly resonance stabilized radicals. The fluorenyl radical is known to have more resonance stabilization than the diphenylmethyl radical.[23] In the case of dibenzyl ether the benzoxy group can stabilize the radical by resonance and is also a powerful electron-supplying group by resonance. Here the two effects compliment each other and dibenzyl ether is observed to be very reactive.

Relative reactivity series, similar to that given in Table III, have been determined by other radicals.

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[16] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1946, p. 58.

[17] C. F. Cullis and J. W. Ladbury, *J. Chem. Soc.*, 1407 (1955).

[18] K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

[19] J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949); H. Gilman and G. E. Dunn, *ibid.*, **72**, 2178 (1950).

[20] H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

[21] H. C. Brown, J. H. Brewster and H. Schechter, *ibid.*, **76**, 467 (1954).

[22] E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 342 (1953).

[23] E. C. Kooyman, *Disc. Faraday Soc.*, **10**, 163 (1951).

In general, the agreements between Table III and these other reactivity assignments are good. Reactivities have been determined toward trichloromethyl radicals,[22,23] chlorine atoms,[14b,c,d] styrene polymer radicals,[24] vinyl acetate polymer radicals,[25] methyl methacrylate polymer radicals,[26] methyl radicals in the vapor phase[27] and methyl and/or acetoxy radicals produced in the decomposition of acetyl peroxide.[28] In Table IV are summarized the relative reactivities of aralkyl hydrocarbons as determined by several of these radicals.

TABLE IV

RELATIVE REACTIVITIES OF ARALKYL HYDROCARBONS TOWARD VARIOUS RADICALS[a]

	Peroxy, 90°	Trichloro-methyl, 91.5°[b]	Styrene, 60°[c]	Acetoxy and/or methyl, 80°[d]
Tetralin	5.0	1.02	..	..
Indan	2.8	0.57	..	..
Allylbenzene	2.7	3.43	..	..
Diphenylmethane	1.2	0.95	1.05	0.67
Cumene	1.00	1.00	1.00	1.00
Ethylbenzene	0.59	0.37	0.41	0.35
Mesitylene	.14	.082	..	..
p-Xylene	.12	.090	..	..
Toluene	.075	.080	0.11	.10

[a] Reactivity per α-hydrogen atom. [b] Ref. 23. [c] Ref. 24a. [d] Ref. 28b.

Tetralin and indan appear to be more reactive, relative to cumene, toward a peroxy radical than toward a trichloromethyl radical. This difference has been discussed previously[5] and may represent a real difference in the reactivity of trichloromethyl and peroxy radicals. For the other compounds listed in Table IV there is fairly good agreement between the relative reactivities determined by peroxy, trichloromethyl, styrene and methyl and/or acetoxy radicals.

Experimental

Oxidation Procedures.—The oxidations were performed by vigorous agitation of the hydrocarbon catalyst in an oxygen atmosphere at a controlled temperature. The oxygen absorption was followed by use of a gas buret with a manually controlled leveling bulb. The procedure has been described previously.[5]

Upon completion of the oxidation, aliquots of the oxidate were added to 50 ml. of glacial acetic acid containing 1 g. of potassium iodide and 1 ml. of phosphoric acid.[4] The solutions were stored in the dark under nitrogen and titrated with 0.1 *N* sodium thiosulfate at 5- to 10-hour intervals. When a constant titer was reached a correction for the *t*-butyl perbenzoate originally present was made in order to determine the yield of hydroperoxide.

Purification of Reagents.—All of the compounds oxidized, with the exception of three solids, were chromatographically filtered over activated silica gel under nitrogen. The filtrates were either immediately oxidized or stored under nitrogen at 5-10°. The hydrocarbons and substituted cumenes used were carefully purified and undoubtedly were purer than 99%. The toluene derivatives were not purified as carefully but had physical constants in close agreement with literature values. Peroxides could not be detected in any of the purified materials. The densities of the compounds oxidized were measured at 90° and can be calculated from the data of Table I.

The cumene, tetralin, styrene, α-methylstyrene, allylbenzene and *t*-butyl perbenzoate used have been described.[5,9] C.P. or research grade mesitylene, ethylbenzene, *p*-xylene, *m*-xylene, toluene and *p*-cymene (terpene free) were rectified in a Podbielniak column (<50 plates) and constant-boiling fractions selected whose boiling points and refractive index checked the best literature values.[29]

p-Diisopropylbenzene was synthesized from purified cumene. The addition of C.P. propylene to 600 g. of cumene and 200 ml. of concentrated sulfuric acid at 0-25° resulted in a weight gain of 200 g. in four hours. The hydrocarbon layer was extracted several times with concentrated sulfuric acid, washed with 10% aqueous sodium hydroxide, and with water, and distilled through a Vigreux column. Rectification in the Podbielniak column gave 89 g. of *p*-diisopropylbenzene, b.p. 121-121.5° at 56 mm., n^{20}_{D} 1.4898, lit.[30] n^{20}_{D} 1.4898.

p-Bromocumene was prepared by the bromination of cumene in the dark. To cumene (720 g.) in 1 l. of a 1-1 mixture of carbon tetrachloride and acetic acid was added 1 g. of iodine and 960 g. of C.P. bromine dissolved in 600 ml. of carbon tetrachloride. The mixture was stirred for eight hours at 0° and then refluxed for 14 hours. The reaction mixture was extracted with 10% aqueous sodium hydroxide, and with water, and distilled through a Vigreux column. Rectification in the Podbielniak column gave 291 g. of *p*-bromocumene, b.p. 123.5° at 53 mm., n^{20}_{D} 1.5363.

p-Nitrocumene was prepared by Dr. J. R. Ladd by nitrating purified cumene by the procedure of Brown and Bonner.[31] The nitration product was rectified in a column packed with glass helices (*ca.* 10 plates) to give *p*-nitrocumene, b.p. 127.5-128.5° at 8 mm., n^{20}_{D} 1.5370; lit.[31] b.p. 134° at 13 mm., n^{20}_{D} 1.5369.

p-*t*-Butylcumene was prepared by Dr. J. R. Ladd by alkylation of purified cumene with *t*-butyl alcohol.[32] Cumene (300 g.) and *t*-butyl alcohol (100 g.) were added to 1 kg. of 92% sulfuric acid at −5°. After 30 minutes the organic layer was separated and washed. Rectification in the Podbielniak column gave 342 g. of *p*-*t*-butylcumene, b.p. 125.5° at 44 mm., n^{20}_{D} 1.4918.

p-Cyano- and *p*-carbomethoxycumene were prepared from *p*-cumic acid by Dr. J. R. Ladd. Eastman Kodak cumic acid was converted to the chloride by thionyl chloride and the chloride was converted to the methyl ester by treatment with methyl alcohol and pyridine.[33] *p*-Cyanocumene was prepared by converting the acid chloride to the amide with ammonium. The amide was then dehydrated by thionyl chloride.[34] The *p*-cyanocumene was rectified through a column packed with glass helices to yield material having a b.p. of 105.5° at 8 mm., n^{20}_{D} 1.5194. The methyl *p*-cumate was rectified in the same column, b.p. 117-119° at 11 mm., n^{20}_{D} 1.5108.

Eastman Kodak phenylcyclohexane was rectified through the Podbielniak column, b.p. 142° at 53 mm., n^{20}_{D} 1.5262; lit.[22] b.p. 112° at 18 mm., n^{20}_{D} 1.5258. Phenylcyclopentane was prepared by the alkylation of benzene by Phillips reagent grade cyclopentene in the presence of sulfuric acid. Rectification in the Podbielniak column gave material boiling at 110-110.5° at 24 mm., n^{20}_{D} 1.5286; lit.[22] b.p. 118° at 25 mm., n^{20}_{D} 1.5285.

Indan was prepared by the Clemmensen reduction of 1-indanone.[35] Eastman Kodak 1-indanone (200 g.) was dissolved in 600 ml. of methyl alcohol to which 1800 ml. of 37% hydrochloric acid and 1200 ml. of water was added. This

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(24) (a) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947); (b) S. L. Kapur, *J. Polymer Sci.*, **11**, 399 (1953).

(25) W. H. Stockmayer, J. T. Clarke and R. O. Howard, Abstracts of Papers, 120th Meeting of the Amer. Chem. Soc., Buffalo, N. Y., March, 1952, p. 2-O; S. L. Kapur and R. M. Joshi, *J. Polymer Sci.*, **14**, 489 (1954).

(26) S. Basu, J. N. Sen and S. R. Palit, *Proc. Roy. Soc.* (*London*), **202A**, 485 (1950).

(27) A. F. Trotman-Dickenson, *Quart. Revs.* (*London*), **7**, 198 (1953).

(28) (a) F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950); (b) W. H. Urry, Abstracts of Papers, 12th National Organic Chemistry Symposium, Denver, Colorado, June, 1950, p. 30.

(29) U. S. National Bureau of Standards Circular 461, "Selected Values of Properties of Hydrocarbons," Washington, D. C., 1947.

(30) A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).

(31) H. C. Brown and W. H. Bonner, THIS JOURNAL, **76**, 605 (1954).

(32) H. Barbier, *Helv. Chim. Acta*, **19**, 1345 (1936).

(33) L. Bert, *Bull. soc. chim. France*, **37**, 1397 (1925).

(34) S. M. McElvain and C. L. Stevens, THIS JOURNAL, **69**, 2663 (1947).

(35) E. Clemmensen, *Ber.*, **47**, 681 (1914).

mixture was added to the amalgamated zinc prepared by the addition of 25 g. of mercuric chloride to 390 g. of 80-mesh zinc metal in the presence of 780 ml. of water and 39 ml. of 37% hydrochloric acid.[36] The mixture was refluxed for three hours and then slowly distilled. By the time 1 l. of water had distilled most of the organic material had been removed from the reaction flask. Separation of the organic layer from the water in the distillate gave 165 g. of material. This was washed with several portions of cold, concentrated sulfuric acid. Apparently a considerable portion of the indan was sulfonated by this procedure. The material left (*ca.* 75 g.) was distilled through a small packed column (*ca.* 5 plates) to give indan, b.p. 81° at 31.5–32 mm., n^{20}_D 1.5382, lit.[22] n^{20}_D 1.5382.

The purest available commercial samples of dibenzyl ether, diphenylmethane, methyl phenylacetate, benzyl benzoate, benzyl chloride, phenylacetonitrile, *p*-chlorotoluene, *p*-methoxytoluene, *p*-tolunitrile and chlorobenzene, were distilled through a Vigreux column under reduced pressure. Fluorene, triphenylmethane and *p*-nitrotoluene were recrystallized from ethyl alcohol. The samples used had m.p.'s of 115–116, 92.5 and 52–53°, respectively.

Phenyldimethylsilane was prepared from the reaction of phenyldimethylchlorosilane with lithium aluminum hydride. To 10 g. of lithium aluminum hydride in 200 ml. of ethyl ether 128 g. of phenyldimethylchlorosilane (b.p. 85.5° at 21 mm.) was added over a 3-hour period. The solution was refluxed for three hours and the excess lithium aluminum hydride destroyed by ethyl acetate. The reaction product was poured over ice, the ether layer separated and the aqueous layer extracted twice with 200 ml. of ether. The ethereal solution was dried over sodium sulfate and distilled until a pot temperature of 85° was reached. The residue did not give a qualitative test for chlorine. The residue upon distillation through a small packed column (*ca.* 5 plates) under nitrogen gave 111 g. of phenyldimethylsilane, b.p. 57° at 20 mm., n^{20}_D 1.4988, d^{20}_4 0.876. The molar refraction, 45.62, was in very good agreement with the value of 45.73 as calculated from the data of Warrick.[37]

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(36) J. H. Brewster, THIS JOURNAL, **76**, 6364 (1954).

(37) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

Some Structural and Geometric Isomers of 1-Cyclohexyl-1,3-butadiene[1]

BY OLIVER GRUMMITT AND ZOLTAN MANDEL[2]

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Four $C_{10}H_{16}$ isomeric conjugated dienes have been prepared and their relative stabilities compared. These are *trans*-1-cyclohexyl-1,3-butadiene (II), 1-cyclohexylidene-2-butene (III), 1-(1-cyclohexenyl)-1-butene (IV) and 1-butylidene-2-cyclohexene (V). *cis*-1-Cyclohexyl-1,3-butadiene (I) could not be obtained. II and III in 4/1 mole ratio are formed by the pyrolysis (475°) of 1-cyclohexyl-3-acetoxy-1-butene (VI). Allylic rearrangement of VI precedes the pyrolysis to III. II does not isomerize to III at 475°. The structure of III (probably the *trans* isomer) was based on oxidative degradation, ultraviolet and infrared absorption, and lack of reactivity with maleic anhydride. II could not be isomerized to I photochemically or thermally, with or without iodine. Thermal isomerization (600°) of II gave III and IV. The structure of IV (probably the *trans* isomer) was elucidated by degradation of the maleic anhydride adduct and by independent synthesis from 1-(1-cyclohexenyl)-1-acetoxybutane (VIII). Pyrolysis of VIII gave IV and V. Calculated heats of hydrogenation indicate the order of increasing stability to be III, I–II and IV. Failure to obtain I by isomerization of II is attributed to hindrance between the ring and side chain which makes the stability difference between the isomers probably greater than 5.5 kcal./mole.

The purpose of this work was to study the preparation and relative stabilities of several $C_{10}H_{16}$ isomeric conjugated dienes: *cis*- and *trans*-1-cyclohexyl-1,3-butadienes (I, II), 1-cyclohexylidene-2-butene (III), 1-(1-cyclohexenyl)-1-butene (IV) and 1-butylidene-2-cyclohexene (V) (Chart 1).

trans-1-Cyclohexyl-1,3-butadiene (II) had been made[3] in 40% yield by the pyrolysis of 1-cyclohexyl-3-acetoxy-1-butene (VI) at 475°. The isomeric 1-cyclohexylidene-2-butene (III) was a coproduct. II does not isomerize to III at 475° under pyrolysis conditions. However, the α-acetoxy group in VI may favor allylic rearrangement to 1-cyclohexyl-1-acetoxy-2-butene (VII) before decomposition. An analogous rearrangement occurs in the conversion of 3-acetoxy-3-cyano-1-butene to 1-acetoxy-3-cyano-3-butene and 2-cyano-1,3-butadiene.[4]

The ease of rearrangement of the isomeric acetates VI and VII was observed at 150, 200 and 240° (Table I). The extent of decomposition was estimated by the acetic acid formed and the extent of isomerization by the refractive index of the recovered reactants.

TABLE I

ALLYLIC REARRANGEMENTS OF ACETATES VI[3] AND VII[5,6]

Temp., °C.	Heat. per., hr.	Frac. decomp., % VI	Frac. decomp., % VII	n^{20}_D of recovd. acetate[a] VI	n^{20}_D of recovd. acetate[a] VII	Frac. (%)[b] of iso. acetate from VI	Frac. (%)[b] of iso. acetate from VII
150	2			....	1.4628	..	0
200	3	0.4	0.3	1.4606	1.4622	12	24
200	4.5	..	..	....	1.4620	..	32
240–241[c]	0.5	8	8	1.4607	1.4614	16	56

[a] 1.4603 for pure VI, 1.4628 for pure VII. [b] Accurate to about ±8%. [c] Five grams was distilled in about 0.5 hour.

While both acetates isomerize at 200 and 240°, the ease of isomerization of VII is much greater—over 50% rearranges at 240°. In an anionotropic mechanism,[7] this signifies that the cyclohexyl group has greater electron-releasing effect than the methyl group. Acetic acid formed in these reactions may have catalyzed the isomerization. Acids catalyze allylic rearrangement of alcohols, but their influence on the isomerization of esters is not clear.[7]

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(5) C. S. Marvel and J. L. R. Williams, *ibid.*, **70**, 3842 (1948).

(6) K. Hess and W. Wustrow, *Ann.*, **437**, 256 (1924).

(7) C. K. Ingold, "Structure and Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y. 1953, pp. 586–601.