When the groups common to these three system, type **7** esters, and the esters in Table II are examined together (Table III), a general correspondence of the orders is evident and the agreement between systems **1** and **8a** is very good.

TABLE III
EFFICIENCIES OF END GROUPS IN PROMOTING NEMATIC MESOMORPHISM IN SYSTEMS **1**, **7**, **8a**, **8b** AND SCHIFF BASE–AZOXYANISOLE MIXTURES

System	Ref	Group efficiencies
1		MeO > NO_2 > Br ~ *n*-PrO ~ Cl > Me > *n*-$C_5H_{11}O$ > F > H
7	6a	MeO > NO_2 > Cl > *n*-$C_5H_{11}O^a$ > F > H
8a	22	MeO > NO_2 > *n*-PrO ~ Cl ~ Br > Me > *n*-$C_5H_{11}O$ > F > H
8b	22	MeO > *n*-PrO > *n*-$C_5H_{11}O$ > Me ~ NO_2^b
Mixtures	21	NO_2 > MeO > Cl = Me > Br ~ H

[a] The $C_5H_{11}O$ ester has not been reported, but this position for it is assured from interpolation between the known C_4H_9O and $C_6H_{13}O$ esters. [b] This position is questionable since the compound decomposed at the N–I transition temperature.

The use of data from a systematic structural modification study of one nematic molecular system as a guide to other systems can be rewarding. Certainly, the discovery of Kelker, *et al.*,[13a] that the *n*-butyl end group lowers the melting points of nematic Schiff bases and the demonstration by Arora, *et al.*,[7] that a methyl substituent on the central phenylene ring of type **1** esters has a similar effect have been applied to other systems with outstanding success.[9,13b,14–19] The correlations presented in this paper are further evidence that this approach is highly worthwhile.

Registry No.—2 (R = H), 2444-19-1; 2 (R = *i*-Pr), 40782-20-5; 2 (R = *t*-Bu), 40782-21-6; 2 (R = cyclohexoxy), 40782-22-7; 2 (R = MeO), 28099-28-7; benzoyl chloride, 98-88-4; *p*-methylbenzoyl chloride, 874-60-2; *p*-methoxybenzoyl chloride, 100-07-2; *p*-isobutoxybenzoyl chloride, 40782-45-4; *p*-hexyloxybenzoyl chloride, 39649-71-3; *p*-(2-ethoxyethoxy)-benzoyl chloride, 40782-47-6; *p*-cyclohexoxybenzoyl chloride, 36823-91-3; *p*-bromobenzoyl chloride, 586-75-4; *p*-cyanobenzoyl chloride, 6068-72-0; *p*-nitrobenzoyl chloride, 122-04-3; *p*-chlorobenzoyl chloride, 122-01-0; *p*-butoxycarbonylbenzoyl chloride, 39853-28-6; *p*-*tert*-butylbenzoyl chloride, 1710-98-1; *p*-isopropylbenzoyl chloride, 21900-62-9; *p*-octyloxybenzoyl chloride, 40782-53-4; *p*-heptyloxybenzoyl chloride, 40782-54-5; *p*-fluorobenzoyl chloride, 403-43-0; *p*-propoxycarbonylbenzoyl chloride, 40782-56-7; *p*-pentyloxybenzoyl chloride, 36823-84-4; *p*-butoxybenzoyl chloride, 33863-86-4; *p*-propoxybenzoyl chloride, 40782-58-9; *p*-ethoxybenzoyl chloride, 16331-46-7; *p*-ethoxycarbonylbenzoyl chloride, 27111-45-1; *p*-methoxycarbonylbenzoyl chloride, 7377-26-6; *p*-isobutoxybenzoic acid, 30762-00-6; *p*-cyclohexoxybenzoic acid, 139-61-7; *p*-(2-ethoxyethoxy)benzoic acid, 40782-64-7; ethyl *p*-hydroxybenzoate, 120-47-8; hydroquinone, 123-31-7.

The Reversible Addition of Hydroxide to Substituted Benzaldehydes

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The equilibrium constants determined for the addition of hydroxide ion to a series of benzaldehydes, mono- and disubstituted in the meta and para positions, can be correlated with $\Sigma\sigma$, with a slope $\rho = 2.24$. From this the stabilization energy of the carbonyl group of benzaldehyde relative to acetaldehyde can be calculated as 2.7 kcal/mol. For benzaldehydes substituted in one ortho position a linear relationship is observed between the equilibrium constants for addition and the pK_a values of the analogous substituted benzoic acids.

Aliphatic aldehydes and some aliphatic ketones undergo a reversible hydration in neutral aqueous solutions to form the *gem*-diol.[1] Aromatic aldehydes are not hydrated to any appreciable extent, owing to the extra resonance stabilization.

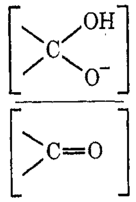
However, in basic solutions, mono- and disubstituted benzaldehydes do undergo a reversible addition of hydroxide ion to form the ionized *gem*-diol. In the present work, equilibrium constants for this addition were measured and are discussed for Scheme I, with correlations proposed for the various substituents.

Experimental Section

The substituted benzaldehydes were pure commercial products, recrystallized before use to a constant melting point. The methiodide of 4-dimethylaminobenzaldehyde, prepared by refluxing the amine with methyl iodide, had mp 158° (lit.[2] mp 156–157°).

Uv spectra were recorded on a Cary 17 spectrophotometer, and the pmr spectra on a Jeol C-60HL instrument at 30°; chemical shifts in parts per million are noted downfield relative to the sodium salt of 3-(trimethylsilyl)propanesulfonate.

The amount of hydroxide addition was followed by uv spectroscopy at 25°, by observing the instant decrease of the aromatic carbonyl band on addition of base. The spectra were recorded at various concentrations of base until the intensity decreased to a constant value, with formation of a new band. For all the benzaldehydes substituted with one or two chlorines only, the final absorption approached or was extrapolated to zero. For the unsubstituted and 2-CH_3 benzaldehydes, only 10–20% hydroxide addition was determined, and the absorption of the *gem*-diol form was taken as zero. The ratio of hydroxide adduct to carbonyl compound is shown in eq 1, where OD_0 is the carbonyl



$$= \frac{OD_0 - OD_{OH}}{OD_{OH} - OD_{final}} \qquad (1)$$

absorption in neutral solution and OD_{OH} is the absorption at some hydroxide concentration. These values were plotted *vs.* the hydroxide ion concentration, the slope of the line being K_{OH}, with intercepts through the origin. As shown, some of the carbonyl compounds are hydrated to a small extent in neutral solution, and OD_0 is the carbonyl absorption in the presence of of the *gem*-diol. However, the same procedure for K_{OH} is valid.

The amount of initial hydration as shown directly by nmr for 4-trimethylammonium benzaldehyde iodide and indirectly for 3-nitrobenzaldehyde (see Results and Discussion) is not more than 10%. As small amounts of *gem*-diol are difficult to deter-

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(1) R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).

(2) G. R. Wiley and S. I. Miller, *J. Org. Chem.*, **37**, 767 (1972).

TABLE I

EQUILIBRIUM CONSTANT DETERMINATIONS

Registry no.	Substituted benzaldehyde	λ_{max}[a] (ϵ)[b]	Range of $[OH^-]$ (*c*)	K_{OH}[d]
100-52-7	3,4-H_2	250 (13,900)	0.36–1.0 (3)	0.18
104-88-1	4-Cl	260 (17,900)	0.20–1.3 (4)	0.47
587-04-2	3-Cl	249 (10,800)	0.13–0.80 (5)	1.13
6287-38-3	3,4-Cl_2	260 (12,800)	0.03–0.90 (7)	2.5
24964-64-5	3-CN	245 (9,900)	0.03–0.50 (6)	4.8
7541-76-6	4-N^+Me_3	230 (22,000)	0.01–0.33 (6)	7.6
10203-08-4	3,5-Cl_2	252 (8,250)	0.03–0.30 (6)	7.7
99-61-6	3-NO_2	233 (19,300)	0.03–0.50 (7)	8.3
555-16-8	4-NO_2	268 (11,450)	0.017–0.30 (6)	13.3
16588-34-4	3-NO_2-4-Cl	245 (19,600)	0.005–0.08 (7)	21
529-20-4	2-CH_3	254 (7,500)	0.65–1.3 (3)	0.095
89-98-5	2-Cl	253 (11,400)	0.067–1.0 (7)	2.6
874-42-0	2,4-Cl_2	264 (12,100)	0.03–0.50 (9)	6.0
83-38-5	2,6-Cl_2	255 (5,800)	0.017–0.50 (7)	10.8
552-89-6	2-NO_2	225 (12,600)	0.01–0.30 (6)	15
6361-22-4	2-Cl-6-NO_2	260[e] (5,250)	0.01–0.06 (5)	36
6361-21-3	2-Cl-5-NO_2	240 (9,800)	0.003–0.03 (4)	62
528-75-6	2,4-$(NO_2)_2$	246 (14,500)	0.0008–0.02 (4)	215

[a] Wavelengths at which absorption was studied. [b] Extinction coefficients are from one sample weighing. [c] Number of points on plot. [d] $K_{OH} = [>C(OH)O^-]/[>C{=}O][OH^-]$ at 25°. [e] Shoulder.

mine accurately by nmr or uv,[3] it can be assumed that other aldehydes with electron-withdrawing substituents have similar small degrees of hydration. For the 2,6-dichloro- and 2-chloro-6-nitrobenzaldehydes, the extinction coefficient is appreciably lower than for the other aldehydes and thus the possibility of hydration arises. It was found, however, that the extinction coefficient of these compounds in organic solvents is even smaller than in water. This served as evidence against hydration in neutral solutions. The extinction coefficients and band shapes for 2,4-dinitrobenzaldehyde were the same in water and the organic solvents acetonitrile, dioxane, and chloroform, and the possibility of some hydration exists.

The addition of base was reversible and by neutralizing the basic solutions, the original spectra were obtained.

Changes in the spectra in basic solutions due to other reactions were checked for, and did not interfere during the time of the experiment.

At base concentrations above 1.5 *M*, the ratio of [ionized *gem*-diol]/[carbonyl] was no longer linear with base, presumably owing to a change in the activity of water in these concentrated solutions, where the proper acidity functions should be used.

The ionic strength was not kept constant in the determination of K_{OH}. In a few cases K_{OH} was measured at μ 1.0 with KCl. The values were 10–15% lower than those presented in Table I. It was therefore assumed that the salt effect on the equilibria would not be of such magnitude as to affect the logarithmic correlations.

Results

In Table I are listed the substituted benzaldehydes studied and the experimental results.

At room temperature and in the range of base concentrations studied (0.01–1.3 *M*), no other reactions, such as the Cannizzaro disproportionation or the cleavage of 2,6-dihalobenzaldehydes to 1,3-dihalobenzenes and formate ion, occur. The latter reaction was studied by Bunnett, *et al.*,[4] who observed the reversible addition of hydroxide.

It has been shown in nmr studies that the aldehydic protons shift to higher fields when the carbonyl group adds water to form the *gem*-diol.[1,5] The difficulty in the present case was the limited solubility of the substituted benzaldehydes in water, usually not sufficient for running the nmr spectra. An exception was the soluble 4-trimethylammoniobenzaldehyde iodide. A 0.50 *M* solution in D_2O showed, in addition to the expected three lines at δ 10.22, 8.24, and 3.84, a small peak at δ 6.2 and a small structured line 0.34 ppm upfield from the aromatic line.[6] These small lines were not observed in DMSO-d_6 as solvent, and were ascribed to the protons of the *gem*-diol compound. Integration and comparison of the aldehydic hydrogen and the hydrogen bound to the *gem*-diol group at δ 10.22 and 6.2, respectively, as well as the two aromatic lines at 8.24 and 7.90 ppm, showed that approximately 10% of the compound was hydrated in D_2O solution. As hydroxide was added to the solution, the aldehyde peak as well as the *gem*-diol hydrogen both shifted and broadened owing to a fast exchange between the species.

In concentrated hydroxide solution the solubilities of the substituted benzaldehydes increased owing to the ionization of the *gem*-diol formed. The nmr spectrum of 2-nitrobenzaldehyde in 1 *M* base had no peak in the range of aldehydic protons. However, a broad line appeared at δ 6.5 ppm, ascribed to the hydrogen bound to the ionized *gem*-diol group.

Discussion

The addition of hydroxide to the substituted benzaldehydes can be viewed as a reversible attack of water which is favored in basic solutions owing to the ionization of the *gem*-diol formed. In Scheme I and eq 2, it is shown that K_{OH} is a composite of K_{H_2O} and K_a, where K_{OH} and K_{H_2O} are defined as association constants and K_a and K_w as dissociation constants of the acids (and include the concentration of water).

Correlation of the Meta- and Para-Substituted Benzaldehydes.—For the series of benzaldehydes, mono- and disubstituted in the 3 and 4 positions, there exists a good correlation with $\Sigma\sigma$, the sum of the aro-

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(3) P. Greenzaid, Z. Rappoport, and D. Samuel, *Trans. Faraday Soc.*, **63**, 2131 (1967).

(4) J. F. Bunnett, J. H. Miles, and K. V. Nahabedian, *J. Amer. Chem. Soc.*, **83**, 2512 (1961).

(5) P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, **89**, 749 (1967).

(6) The aromatic line for this compound had very little structure, as expected for an AA^{1}BB^1 pattern, pointing to similar chemical environments for the aromatic protons.

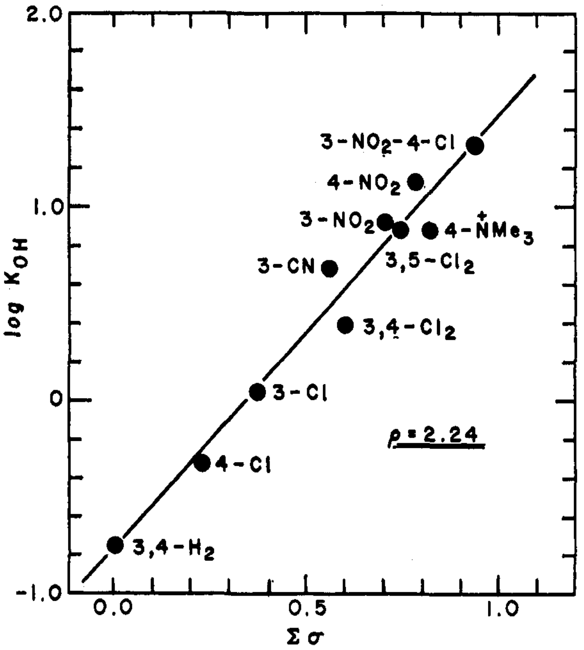
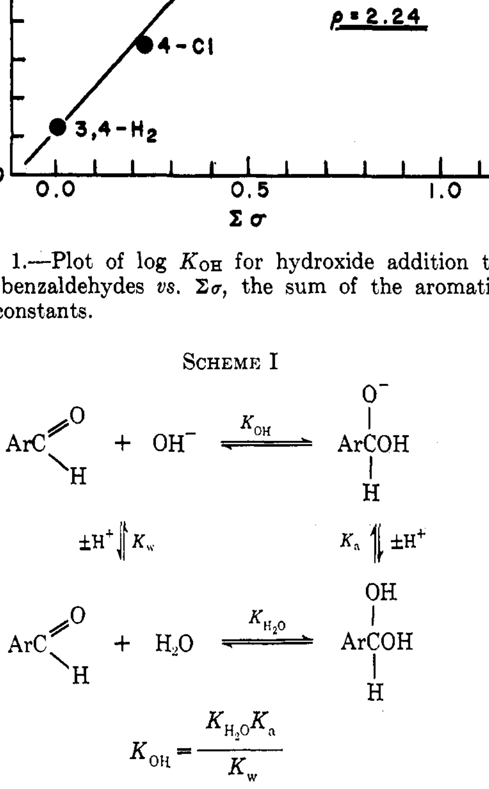


Figure 1.—Plot of log K_{OH} for hydroxide addition to substituted benzaldehydes *vs.* $\Sigma\sigma$, the sum of the aromatic substituent constants.

SCHEME I



$$K_{OH} = \frac{K_{H_2O}K_a}{K_w}$$

(2)

matic substituent constants[7] (Figure 1). The slope of the plot (ρ_{OH}) is 2.24 with a correlation coefficient of 0.982.

From eq 2

$$\rho_{OH} = \rho_{H_2O} + \rho_{K_a} \quad (3)$$

It was shown that the pK_a values of the *gem*-diols of a series of substituted trifluoroacetophenones are correlated with σ values[8] with $\rho = 1.11$. Taking $\rho_{K_a} = 1.1$ for the dissociation of the *gem*-diols of substituted benzaldehydes, from eq 3, $\rho_{H_2O} = 1.1$ for the hydration equilibria. Relative to the dissociation of carboxylic acids ($\rho = 1.0$), these values are similar to those found for aliphatic compounds where $\rho^*_{K_a} = 1.32$,[9] $\rho^*_{H_2O} = 1.70$,[5] and for the acid dissociation[10] $\rho^* = 1.62$.

pK_a and K_{H_2O} Values.—The pK_a values for the substituted benzaldehyde hydrates can be evaluated from those determined for the substituted trifluoroacetophenone hydrates.[8] Of interest here are the reported values of 9.2 for the 3-nitro derivative and 10.0 for the unsubstituted compound. Using $\rho^*_{K_a} = 1.32$ and inserting σ^*_H for $\sigma^*_{CF_3}$, the corresponding pK_a's for the aldehyde hydrates can be derived: for the *gem*-diol of 3-nitrobenzaldehyde, pK_a = 12.0, and for the unsubstituted benzaldehyde hydrate, pK_a = 12.8.

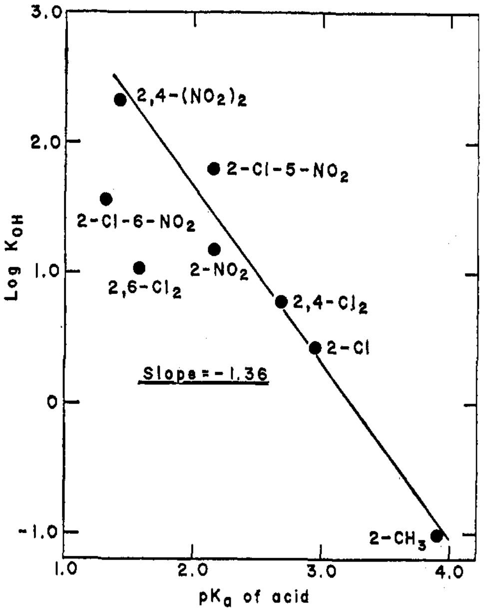


Figure 2.—Plot of log K_{OH} for hydroxide addition to 2-substituted benzaldehydes *vs.* the pK_a values[16] of the analogous benzoic acids.

From eq 2, using the calculated pK_a and the measured K_{OH} values for 3-nitrobenzaldehyde, the value of K_{H_2O} is 0.08. Therefore this compound is slightly hydrated in neutral solution, although less than 10%. For the unsubstituted benzaldehyde K_{H_2O} is calculated to be 1.1×10^{-2}.

Resonance Stabilization of the Aromatic Carbonyl.—From the correlation of K_{H_2O} for the aliphatic compounds,[5] using $\sigma^* = 0.60$ for the phenyl group,[11] the calculated equilibrium constant for hydration of benzaldehyde equals 11.2. This value is higher than that calculated previously, as only the inductive effect of the benzene ring is taken into account without the conjugative interaction with the carbonyl group. In terms of free energy, this means that the additional stabilization of the carbonyl of benzaldehyde is 4.1 kcal/mol, relative to an aliphatic aldehyde with a group of similar inductive effect as the phenyl ring (assuming no extrastabilization of the phenyl ring in the addition product). Relative to acetaldehyde, this stabilization amounts to 2.7 kcal/mol.

In a similar fashion, from the addition of other nucleophiles, Fersht[12] estimated the extra stabilization of the aromatic carbonyl in benzaldehyde compared to acetaldehyde as 4 ± 0.4 kcal/mol. The classical method of evaluating the extra resonance energy of the aromatic carbonyl is from bond dissociation energies and Pauling's calculated value[13] is 4 kcal/mol. However, the relative error in such a treatment is large, as large amounts of energy are subtracted to give a small difference.

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(7) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(8) R. Stewart and R. Van der Linden, *Can. J. Chem.*, **38**, 400 (1960).

(9) J. Hine and G. F. Koser, *J. Org. Chem.*, **36**, 1348 (1971).

(10) G. B. Barlin and D. D. Perrin, *Quart. Rev., Chem. Soc.*, **20**, 75 (1966).

(11) (a) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13; (b) S. Takahashi, L. A. Cohen, H. K. Miller, and E. G. Peake, *J. Org. Chem.*, **36**, 1205 (1971).

(12) A. R. Fersht, *J. Amer. Chem. Soc.*, **93**, 3514 (1971).

(13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 198.

Ortho-Substituted Benzaldehydes.—For benzaldehydes substituted in the ortho position, a similar correlation could not be shown as there is no reliable set of ortho-substituent constants.[14,15] A correlation does exist, however, for values of K_{OH} for six benzaldehydes substituted in only one of the ortho positions, with the pK_a values[16] for the analogous substituted benzoic acids with a slope of -1.36 and correlation coefficient 0.984 (Figure 2). This correlation is limited to compounds with only one ortho position substituted, as the two compounds with substitution at both ortho positions deviate markedly. 2,4,6-Trimethylbenzaldehyde also deviates from the plot, as there was no indication of addition up to 1 *M* base, while the pK_a value for the corresponding acid is 3.44. A similar deviation of diortho substitution was noted when correlating the rate constants for the attack of diphenyldiazomethane on ortho-substituted benzoic acids in ethanol, with the pK_a's of the acids.[17]

Acknowledgment.—Discussions with W. P. Jencks and R. P. Bell are gratefully acknowledged.

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[14] J. Shorter in "Advances in Free Energy Relationships," N. B. Chapman and J. Shorter, Ed., Plenum Press, London, 1972, p 72.

[15] M. Charton, *Progr. Phys. Org. Chem.*, **8**, 235 (1971).

[16] J. F. J. Dippy and S. R. C. Hughes, *Tetrahedron*, **19**, 1527 (1963).

[17] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1824 (1962).

Free-Radical Addition of Iodoperfluoroalkanes to Terminal Alkadienes. Relative Reactivity as a Function of Chain Length and Reaction Conditions[1,2]

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Terminal alkadienes, $CH_2{=}CH(CH_2)_nCH{=}CH_2$ (n = 1–4, **1** to **4**), gave mono- and bisadducts from iodoperfluoroalkanes (R_FI) in high yield. 1,6-Heptadiene (**3**) was unusual in preferentially cyclizing under conditions which favored linear adducts from the other dienes. For **3** the ratio of linear to cyclic adducts was dependent on R_FI concentration, as predicted from kinetic analysis of the reaction scheme. Relative reactivities on an equivalent double-bond basis for alkadienes against either 1-hexene or 1-heptene were the following: **1**, 0.935; **2**, 0.805; **3**, 1.08–1.42, depending on reaction conditions; **4**, 0.945. Thus, only **3** reacted significantly faster than an alkene on the basis of available reaction sites, and this appears to be related to cyclization of **3**. The overall results are interpreted as being dependent on radical intermediate conformations. The absence of significant amounts of cyclization products from **2** or **4**, or of isomeric adducts of the structure $ICH_2CHR_F(CH_2)_nCH{=}CH_2$ (n = 1–4), has been confirmed for azonitrile-initiated reactions.

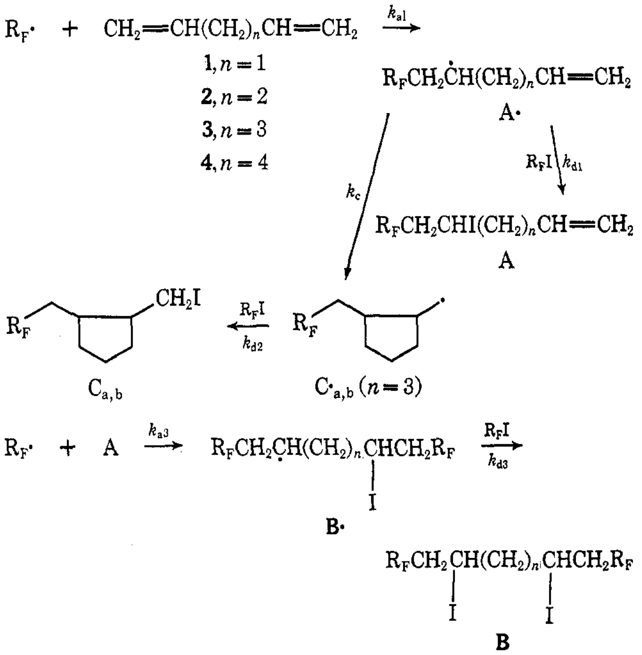
In previous work[3-5] it was found that 1,6-heptadiene (**3**) and substituted 1,6-heptadienes cyclized to *five-membered* ring compounds during the addition of free radicals from perfluoroalkyl iodides (R_FI), carbon tetrachloride, chloroform, and the like. 1,5-Hexadiene (**2**) or 1,7-octadiene (**4**) did not cyclize under free-radical conditions, however, but gave open-chain adducts in excellent yield. By contrast, R_FI and 1,3-butadiene reacted poorly, probably because an unstable product was formed.[6] (Styrene gave an adduct of analogous structure which also was exceedingly sensitive to heat, light, and air.)[7,8] As part of a continuing study of R_FI reactions it seemed worthwhile to determine the relative reactivity of terminal alkadienes, and to look more carefully into the matter of their propensity to cyclize.[9] Quantitative comparison with norbornadiene, which also cyclized with great ease,[10] was desired. It was felt that these data would shed some further light on the nature of these interesting free-radical processes.

Results

Reactions of R_FI with alkadienes **1–4** are outlined in Chart I. The yield of monoadduct A, bisadduct B, or cis and trans cyclic adducts $C_{a,b}$ varied with reaction conditions.

CHART I

REACTION OF R_FI WITH DIENES



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[1] Presented in part at the Fourth European Symposium on Fluorine Chemistry at Ljubljana, Yugoslavia, September 1972.

[2] See paragraph at end of paper regarding supplementary material.

[3] N. O. Brace, *J. Amer. Chem. Soc.*, **86**, 523 (1964).

[4] N. O. Brace, *J. Org. Chem.*, **31**, 2879 (1966).

[5] N. O. Brace, *ibid.*, **32**, 2711 (1967).

[6] N. O. Brace, U. S. Patent 3,145,222, assigned to E. I. du Pont de Nemours and Co., Aug 18, 1964.

[7] N. O. Brace, *J. Org. Chem.*, **27**, 3033 (1962).

[8] N. O. Brace, unpublished observations.

[9] E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, pp 182–185. Cyclizations of 1,7-octadiene and of 1,5-hexadiene during addition of CCl_4 are reported, but neither references to the original literature nor supporting evidence were given.

[10] N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962).