(36) The use of MINDO/3 for acyclic halonium ions was reported during the course of our work; cf. ref 37. Dewar et al. have previously calculated energies of carbocations of various structures with reasonable success; cf. ref 23, 24, and 38.
(37) W. L. Jorgensen, *J. Am. Chem. Soc.*, in press; **99**, 280, 4272 (1977); W. L. Jorgensen and J. E. Monroe, *Tetrahedron Lett*, 581 (1977).
(38) P. K. Bischof and M. J. S. Dewar, *J. Am. Chem. Soc.*, **97**, 2278 (1975), but see ref 36 for corrections; M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *ibid.*, **99**, 377 (1977).
(39) D. G. Graczyk, R. L. Julian, J. W. Taylor, and S. D. Worley, *J. Am. Chem. Soc.*, **97**, 7380 (1975); W. B. Jennings and S. D. Worley, *Tetrahedron Lett.*, 1435 (1977).
(40) W. C. Davidon, *Comput. J.*, **10**, 406 (1968); R. Fletcher, *ibid.*, **8**, 33 (1965); R. Fletcher and M. J. D. Powell, *ibid.*, **6**, 163 (1963).
(41) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974).
(42) J. W. Larsen and A. V. Metzner, *J. Am. Chem. Soc.*, **94**, 1614 (1972).
(43) The **h** and **c** stand for halonium ion and carbocation, respectively.
(44) Our calculated ΔH_f for the 2-butyl cation is 174.5 kcal/mol; ref 24 gives a higher value.
(45) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).
(46) Steric factors are not the probable cause of these errors. For example, the calculated strain energies of ethylcyclopentane (6.81 kcal/mol) and 1,1-dimethylcyclopentane (6.86 kcal/mol) reveal no problem in the hydrocarbon models: S. P. McManus, M. R. Smith, and R. D. Olinger, unpublished results.
(47) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).
(48) G. A. Olah, J. Sommer, and E. Namenworth, *J. Am. Chem. Soc.*, **89**, 3576 (1967).
(49) Obtained by taking the lowest $\Delta\Delta H_f$ from Table I or III and subtracting 6 kcal/mol which was the maximum error between calculated and measured ΔE_s values for alkyl chlorides; see ref 37 and the discussion earlier in this section. These values are not doubly corrected since branching-error corrections do not affect the magnitude of $\Delta\Delta H_f$.
(50) Kebarle (D. K. Sen Sharma and P. Kebarle, *J. Am. Chem. Soc.*, submitted for publication) has just completed the initial experimental studies of the gas-phase equilibria: $R_1^+ + ClR_2 \rightleftharpoons R_1Cl + R_2^+$. His results lend support to our computed $\Delta\Delta H$ values.
(51) B. Capon and S. P. McManus, "Neighboring Group Participation", Plenum Press, New York, N.Y., 1976, pp 43–70.
(52) M. I. Page, *Chem. Soc. Rev.*, **2**, 295 (1973).
(53) One of us has recently found (S. P. McManus and M. R. Smith, *Tetrahedron Lett.*, submitted for publication) that, in general, the errors in calculating enthalpies of formation by MINDO/3 are ca. 2 kcal/mol greater for five-membered rings than for six-membered ones, the error favoring the stabilities of the former over the latter.

Cycloaddition of Diazoalkanes to Penta- and Hexafluoroacetones. Isolation of Δ^3-1,3,4-Oxadiazolines and Their Decomposition via Carbonyl Ylides

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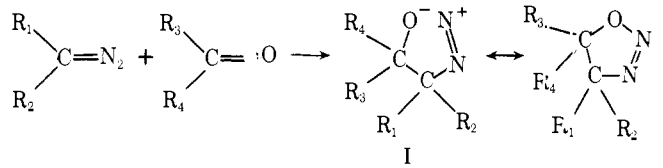
Abstract: Diaryl and arylmethyl diazomethanes add rapidly at −20 °C to hexa- and pentafluoroacetone to yield Δ^3-1,3,4-oxadiazolines (**3** and **4, a–h**). At 25 °C and above in benzene the diaryloxadiazolines lose nitrogen to yield epoxides **5** and **6, a–e** and **h,** accompanied by diaryl ketones in most cases. The phenylmethyloxadiazolines **3f** and **4f,** on nitrogen elimination in benzene, give high yields of the acetophenone enol ethers **7** and **8.** Evidence is presented that the rate-determining step in these decompositions is the concerted formation of a carbonyl ylide which does not entirely retain its configuration. Of various reagents tried, only methanol proved capable of generally intercepting this ylide, yielding as principal product the adduct consisting of the mixed ketal of the aryl ketone. The decompositions of the oxadiazolines were all kinetically of the first order, showing no appreciable polar solvent effect, and responding to the σ^+ parameters of substituents in the benzene ring with a ρ^+ of −0.50. In formation of acetophenone enol ether, the kinetic isotope effect, $k(CH_3)/k(CD_3)$, was only 0.96, confirming that the intramolecular proton transfer occurred within the ylide after the rate-determining step.

Diazoalkanes are well known to react with carbonyl compounds, usually under mild conditions, to give oxiranes and ketones.[2a] Most data on this reaction have been concerned with diazomethane itself. The reaction has been interpreted as a nucleophilic attack of the diazoalkane on the carbonyl group to yield a diazonium betaine (I), or neutral Δ^2-1,2,3-oxadiazoline as a reaction intermediate which is generally too unstable to be isolated.[2b] We have found, however, that aromatic diazo compounds react readily with perfluoroacetones to give unexpected cycloadducts, Δ^3-1,3,4-oxadiazolines, in high yield. Despite the extensive studies on the Δ^3-1,3,4-thiadiazoline,[3a,4-6] little has been reported on the chemistry of oxadiazolines,[3b,7-9] interesting precursors of the carbonyl ylides.[9,10] Hoffmann and Luthardt have succeeded in preparing 2-acetoxy-1,3,4-oxadiazolines by oxidation of benzoyl hydrazones with lead tetraacetate.[8]



I

We report here the results of the cycloaddition reaction of aromatic diazo compounds with hexa- and pentafluoroacetones and show the details of thermal decomposition of isolated 1,3,4-oxadiazolines.

Results

1. Reaction of Aryldiazomethanes with Perfluoroacetones. Dry hexafluoro- or pentafluoroacetone (**1a** or **1b**) was bubbled into a cold pentane solution (ca. −20 °C) of aryldiazomethane (**2a–g**) until the characteristic color of the diazo compound had faded. Usually reaction took place instantly. Solvent was removed by evaporation under vacuum while the solution was kept cool (−20 °C). The residue (solid or liquid) was found to be almost pure cycloadduct (**3** and **4**) by NMR analysis and chemical reactions. All adducts were unstable at room temperature and decomposed smoothly with evolution of nitrogen. The structure of the cycloadducts was confirmed by chemical evidence (see later section) as well as spectral data. Typical NMR spectra of the cycloadduct taken at low temperature are illustrated in Figure 1, and the results are shown in Table I. The reaction of diazoalkanes with acetone or acetophenone was too slow and the adducts could not be detected. It is known that the reaction of diazoalkanes with ketones or

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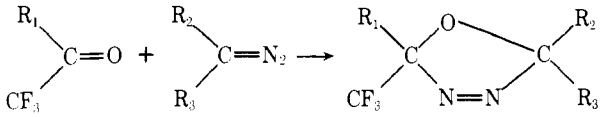
Table I. Cycloaddition Reaction of Aryldiazomethane with Perfluoroacetone

1		2	Cycloadduct (yield, %)	^{1}H NMR (at −25 °C in $CDCl_3$)
R_1	R_2	R_3		
CF_3	Ph	Ph	**3a**, mp 35–36 °C dec (95)	7.24–7.50 (m), 7.48–7.84 (m)[a]
CF_2H	Ph	Ph	**4a**, mp 42–43 °C dec (91)	6.28 (t, J = 52 Hz, 1 H), 7.24–7.50 (m)
CF_3	Ph	*p*-Tolyl	**3b**[b,c]	2.28 (s, 3 H), 7.08 (d, J = 8 Hz, 2 H), 7.22–7.50 (m, 7 H)
CF_2H	Ph	*p*-Tolyl	**4b**[c,c]	2.28 (s, 3 H), 6.24 (t, J = 52 Hz, 1 H), 7.08 (d, J = 8 Hz, 2 H) 7.22–7.50 (m, 7 H)
CF_3	Ph	*p*-Anisyl	**3c**[b,c]	3.72 (s, 3 H), 6.80 (d, J = 8 Hz, 2 H), 7.24–7.44 (m, 7 H)
CF_2H	Ph	*p*-Anisyl	**4c**[b,c]	3.72 (s, 3 H), 6.22 (t, J = 52 Hz) and 6.26 (t, J = 52 Hz) in a ratio of 1:1.1, together 1 H, 6.80 (d, J = 8 Hz, 2 H) 7.24–7.44 (m, 7 H)
CF_3	Ph	*p*-Cl-Ph	**3d**[b,c]	7.20–7.46 (m)
CF_3	*p*-Tolyl	*p*-Tolyl	**3e**[b,c]	2.28 (s, 6 H), 7.18 (d, J = 8 Hz, 4 H), 7.32 (d, J = 8 Hz, 4 H)
CF_2H	*p*-Tolyl	*p*-Tolyl	**4e**[b,c]	2.28 (s, 6 H), 6.22 (t, J = 52 Hz, 1 H), 7.18 (d, J = 8 Hz, 4 H), 7.32 (d, J = 8 Hz, 4 H)
CF_3	Ph	CH_3	**3f**[b,c]	1.98 (s, 3 H), 7.46–7.74 (m, 5 H)[a,d,e]
CF_2H	Ph	CH_3	**4f**[b,c]	1.92 (s, 3 H), 6.12 (t, J = 52 Hz) and 6.36 (t, J = 52 Hz) in a ratio of 1:1.2, together 1 H, 7.28–7.56 (m, 5 H)[d]
CF_2H	CR_2R_3 = 9-fluorenylidene		**4h**, mp 35 °C dec	6.12 (t, J = 52 Hz, 1 H), 7.17–7.64 (m, 8 H)

[a] At 60 MHz. [b] Liquid. [c] Almost quantitative as a crude product. [d] At room temperature. [e] In CCl_4.



1 **2**

R_1 — **3**, $R_1 = CF_3$; **4**, $R_1 = CF_2H$

a, CF_3
b, CF_2H
c, CH_3
d, Ph

a, $R_2 = R_3$ = phenyl
b, R_2 = phenyl; R_3 = *p*-tolyl
c, R_2 = phenyl; R_3 = *p*-anisyl
d, R_2 = phenyl; R_3 = *p*-chlorophenyl
e, $R_2 = R_3$ = *p*-tolyl
f, R_2 = phenyl; $R_3 = CH_3$
g, R_2 = phenyl; $R_3 = CD_3$
h, CR_2R_3 = 9-fluorenylidene

aldehydes can be greatly accelerated by methanol;[2a] however, the reaction was still too slow even in methanol with these unfluorinated ketones.[11] Lewis acids such as boron trifluoride only destroyed aryldiazomethanes. In the cases of **4b,c,f,** two stereoisomers are expected to form. In fact, NMR spectra showed these stereoisomers in the cases of **4c** and **4f.** The NMR spectrum of **4f** showed two triplets at δ 6.16 and 6.36 due to the CF_2H proton of two isomers (in a ratio of 1:1.2). Both signals decreased as the decomposition proceeded and finally were converted to a new triplet at δ 5.92, as shown in Figure 2.

2. Thermal Decomposition of the Cycloadducts. Kinetics. The rates of decomposition of the cycloadducts (**3** and **4**) were determined in benzene solution by measuring nitrogen evolved over a range of temperatures from 25 to 50 °C. The thermal decomposition was found to be of the first order and the rate constants are given in Table II with activation parameters. The rates of decomposition of **4b, 4c,** and **4f** were determined using a mixture of stereoisomers. In the case of **4f,** however, the rate of the decomposition of each isomer could be estimated by NMR analysis. It was found that the initial solution contained two isomers in a ratio of 1:1.2 provisionally assigned to trans and cis isomers, respectively, whereas the isomer ratio was 1.6:1.0 after 56% of decomposition had occurred. This means that the major isomer in the initial solution decomposes more rapidly than the minor one, and the rate ratio of the two isomers was estimated as 2.2.[12] Providing that both isomers decompose in first-order reactions, the first-order rate constants of the isomers could be calculated to be 7.0×10^{-4} and 3.2×10^{-4} s^{-1} at 34.6 °C using 5.25×10^{-4} as the averaged rate constant of the mixture. Table II shows a slight but significant substituent effect. A Hammett correlation with σ^+ gave a

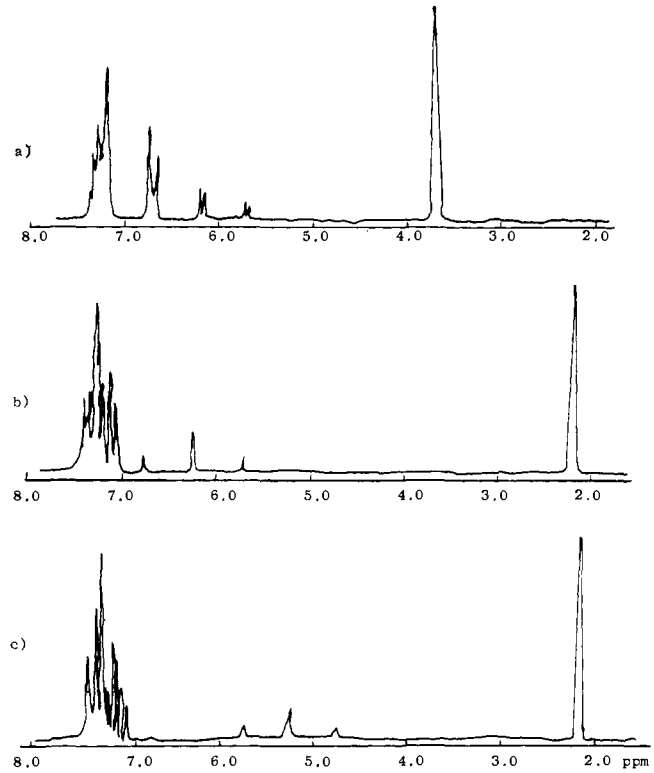
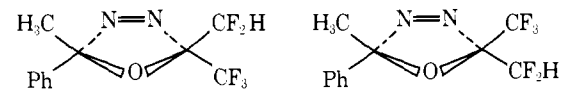


Figure 1. ^{1}H NMR spectra of 1,3,4-oxadiazolines in $CDCl_3$: (a) **4c**; (b) **4b**; (c) products of decomposition of **4b.**



	cis	trans
initial	1.2	1.0
after 56% decomposition	1.0	1.6

Table II. First-Order Rate Constants and Activation Parameters for the Thermal Decomposition of Δ^3-1,3,4-Oxadiazolines

Cycloadduct 3 and 4				$k_1 \times 10^3$, s^{-1}, at 25.6 °C	σ^+	k_{rel}	Log k_{rel}	E_a, kcal/mol	Log A
	R_1	R_2	R_3						
3a	CF_3	Ph	Ph	1.76	0	1.0	0	24.0	14.8
4a	CF_2H	Ph	Ph	1.72		0.98	−0.0088	24.4	15.1
3b	CF_3	Ph	*p*-Tolyl	2.43	−0.256	1.38	0.140	21.9	13.4
4b	CF_2H	Ph	*p*-Tolyl	2.41[a]		1.37	0.137	23.2[a]	14.4[a]
3c	CF_3	Ph	*p*-Anisyl	4.28	−0.648	2.43	0.386	20.1	12.3
3d	CF_3	Ph	*p*-Chlorophenyl	1.50	0.035	0.85	−0.0706	23.8	14.6
3e	CF_3	*p*-Tolyl	*p*-Tolyl	2.96		1.69	0.228	21.4	13.1
3f	CF_3	Ph	CH_3	0.860 (34.6 °C)		0.14[b]	−0.854	24.2	14.1
4f	CF_2H	Ph	CH_3	0.525 (34.6 °C)[c] 0.70 and 0.32[d]				23.0[c]	14.0[c]

[a] Starting material was a mixture of stereoisomers. [b] Relative rate constant at 34.6 °C. [c] Obtained by using a mixture of stereoisomers in a ratio of 1:1.2. [d] Estimated values for each isomer.

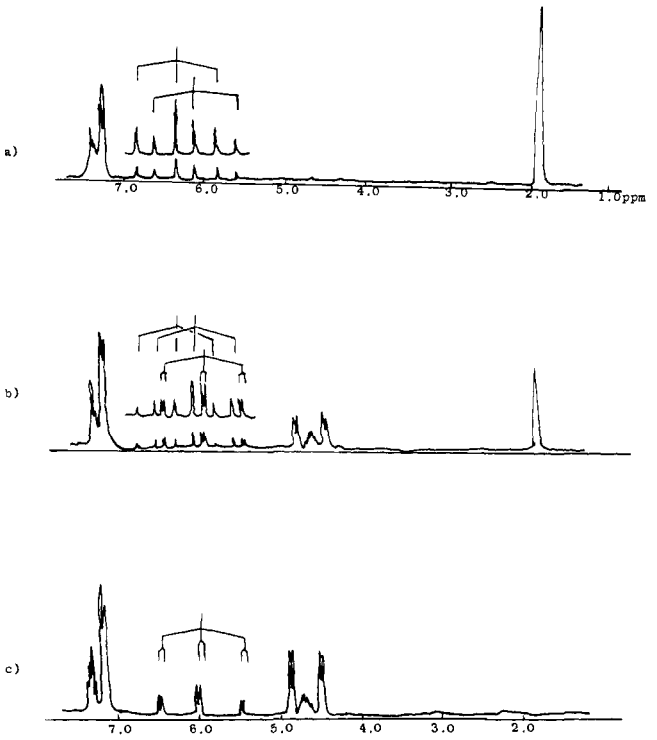


Figure 2. ^1H NMR spectra of oxadiazoline **4f** in $CDCl_3$: (a) initial solution, isomers in ratio 1.2:1.0; (b) during decomposition; (c) after decomposition.

Table III. Decomposition of Oxadiazolines. First-Order Rate Constants in Different Solvents

Solvent	ϵ[a]	$k_1 \times 10^3$, s^{-1}, of **3a** at 25.6 °C	**3f** at 35.0 °C	E_T[b]	Z[c]
Benzene	2.274	1.76	1.05	34.5	54
Methanol	32.7	1.65	1.14	55.5	83.6
N,N-Dimethyl-acetamide	37.8	2.02		43.7	66.9

[a] Dielectric constant. [b] Polarity parameter: C. Reichardt, "Lösungsmittel-Effekte in der Organischen Chemie", Verlag Chemie, Weinheim/Bergstr., Germany, 1969, p 142. [c] Polarity parameter: E. M. Kosower, "Introduction to Physical Organic Chemistry", Wiley, New York, N.Y. 1968, p 301.

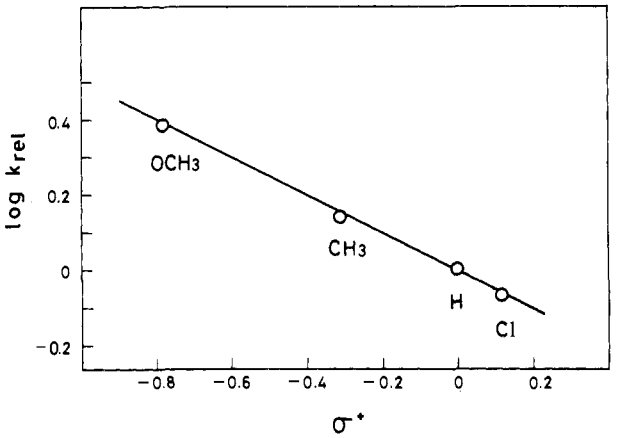
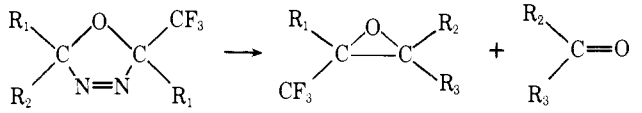


Figure 3. Relative decomposition rates of substituted 1,3,4-oxadiazolines as a function of σ^+. Line corresponds to $\log (k^x/k^H) = -0.50\sigma^+$.

straight line with a small ρ^+ of −0.50, as shown in Figure 3. Solvent polarity did not affect significantly the rate of decomposition of **3a** and **3f**.

Product Analysis. Thermal Decomposition in Benzene. All cycloadducts decomposed smoothly in benzene solution above room temperature. Products were isolated by alumina column chromatography or preparative GLC. In the cases of diaryloxadiazolines, epoxides **5** or **6** were obtained as major products

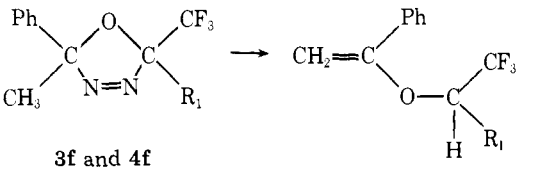


3, $R_1 = CF_3$
4, $R_1 = CF_2H$

5, $R_1 = CF_3$
6, $R_1 = CF_2H$

in 37–95% yields. Another major product was the diaryl ketone. Epoxide formation was more important in **4** than in **3**. Thus **4a** and **4b** gave the epoxides exclusively, whereas **3a** gave **5a** in 72% and **3b** gave **5b** in only 37% yield along with 46% of *p*-methylbenzophenone. When a mixture of two isomers of **4c** in a ratio of 1:1.1 was decomposed in benzene solution at 20 °C, epoxide **6c** was isolated as a mixture of two isomers in a ratio of 1:1.5. The implications of this apparent nonstereospecificity are discussed below.

On the other hand, decomposition of **3f** and **4f** in benzene solution yielded enol ethers, **7** and **8**, almost quantitatively. No

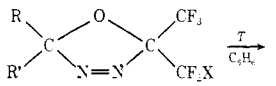
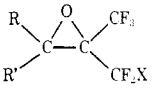


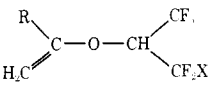
3f and 4f

7, $R_1 = CF_3$
8, $R_1 = CF_2H$

evidence for the formation of epoxide (**6f** or **5f**) could be observed by careful examinations by NMR analysis at low

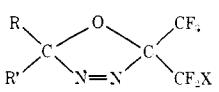
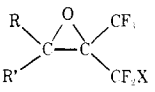
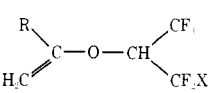
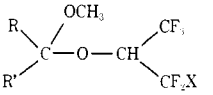
Table IV. Products of Thermal Decomposition of 1,3,4-Oxadiazolines in Benzene

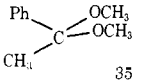





R	R′	X	*T*, °C	% [isomer ratio]	%	%	Other
Phenyl	Phenyl	F	25.6	72			[2 unidentified products]
p-Tolyl	Phenyl	F		37	46		
p-Anisyl	Phenyl	F		38	50		
p-Cl-phenyl	Phenyl	F		56	39		
p-Tolyl	*p*-Tolyl	F		43	38		
Phenyl	Phenyl	H		96			
p-Tolyl	Phenyl	H		97 [1.3]			
p-Anisyl	Phenyl	H		75 [1.5]	20		
Methyl	Phenyl	F	60			92	
Methyl	Phenyl	H	40			97	
9-Fluorenylidene		H		91			

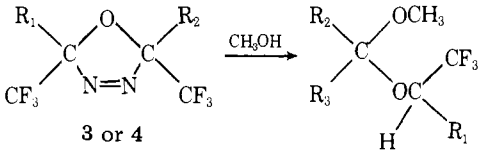
Table V. Products of Thermal Decomposition of 1,3,4-Oxadiazolines in Methanol

R	R′	X				Other
Ph	Ph	F			96	
p-Tol	Ph	F			96	
p-An	Ph	F			95	
(*p*-ClPh	Ph	F)				
p-Tol	*p*-Tol	F			97	
Ph	Ph	H	10		85	
p-Tol	Ph	H	(30 °C) 59		(30 °C) 41	
			(65 °C) 40		(65 °C) 60	
Methyl	Ph	F		23	72	 35
Methyl	Ph	H		27		 26

temperature or GLC analysis during the decomposition. No CIDNP signals could be observed in the thermal decomposition of the cycloadducts carried out in the NMR probe.

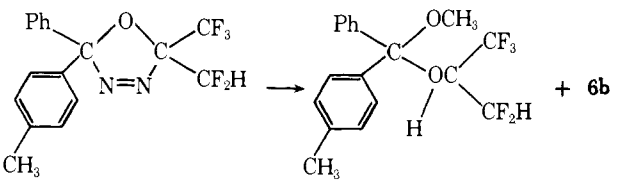
Thermal Decomposition in Methanol. Decomposition of the oxadiazolines in methanol gave quite different products from those obtained in benzene. Thus ketals (**9** and **10**), formally



3 or 4

9, $R_1 = CF_3$
10, $R_1 = CF_2H$

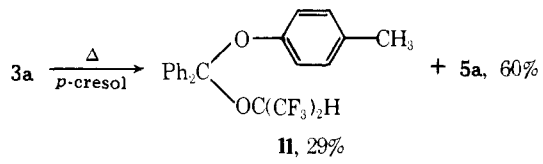
1:1 adducts of the epoxide and methanol, were isolated in all cases. The yield of the ketal was almost quantitative in the case of diaryloxadiazolines with $R_1 = CF_3$. Decomposition of **4**, however, gave both ketal and epoxide. For instance, the decomposition of **4b** in methanol gave **6b** and **10b**. The ketal formation became the more important at the higher temperature. Similar competition between intra- and intermolecular reactions was also found in the case of **3f**: **9f** and **7** were isolated[13] in 72 and 23% yield, respectively. Decomposition of **4f** in methanol, however, gave **8**, acetophenone dimethyl ketal, and acetophenone in 27, 35, and 26% yield.[14] The results are summarized in Table IV. The ketals **9** and **10** are not the



react. temp	rel yield, %	
30°C, 5 h	59	41
65°C, 20 min	40	60

products obtained from methanolysis of the epoxides (**5** or **6**), nor of the olefin (**7** or **8**), since both epoxides and olefins were found to be completely unreactive toward methanol under the conditions listed in Table IV. Beside this, the decomposition in methanol gave only **9** and diaryl ketone formation was totally quenched by methanol.

Thermal Decomposition under Other Conditions. Thermal decomposition of **2** in ether, dichloromethane, chloroform, carbon tetrachloride, *o*-dichlorobenzene, ethanol, and 2-propanol gave the same results as those obtained in benzene solution. When **3a** was decomposed in ether in the presence of 10 mol of excess *p*-cresol at room temperature, ketal **11** was isolated in 29% yield together with the epoxide **5a**. Thermal decomposition of **3a** in benzene solution in the presence of tetracyanoethylene, dimethyl acetylenedicarboxylate, 2,3-dimethyl-2-butene, triphenylphosphine, and triphenyl phos-



phite gave only the same products obtained in the absence of these substrates. However, decomposition of **3a** in 1,4-cyclohexadiene gave a small amount of benzene. In the presence of diethyl azodicarboxylate, **3a** gave a small amount of unidentified product from reaction with this substrate.

Discussion

Reactivity of diazomethane with ketones increases with electron deficiency in the ketone.[2a] In the present case the reaction is extraordinarily sensitive to this structural feature: hexafluoroacetone reacts with the aryldiazomethanes almost instantaneously even at −78 °C, whereas 1,1,1-trifluoroacetone or α,α,α-trifluoroacetophenone does not react at −5 °C even in 2 weeks. This reactivity order alone might have been consistent with the older view of the addition reactions of diazoalkanes proceeding through a two-step, zwitterionic mechanism. It is well established, however, on grounds of stereospecificity, low solvent effect, and absence of competitive reactions of zwitterionic intermediates[15,16] that the addition of diazoalkanes to olefins is a concerted process.

The regiochemistry of the diazoalkane–ketone reaction supports the view that here, too, we are dealing with a concerted process. The most favorable zwitterion, if any, would be a diazonium alkoxide and such a species must close to a 1,2,3-oxadiazoline. On the other hand, a concerted cycloaddition mechanism affords opportunity for the thermodynamic advantages of a 1,3,4-oxadiazoline to contribute to the transition state. Other examples of the favoring of the 1,3,4 structure by strong electron withdrawal in the ketonic component include the reaction of diphenyldiazomethane with diphenylketene[17] and of bis(trifluoromethyl)diazomethane with hexafluorothioacetone.[6a]

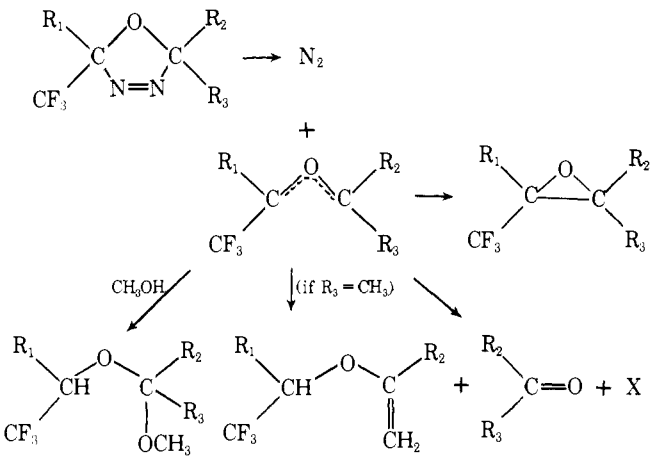
The correlation of the decomposition rates of **3a–d** with the σ^+ parameter, the value of $\rho = -0.5$, and the absence of a polar solvent effect correspond to a concerted elimination of N_2 from the oxadiazoline, with the phenylated carbon atom carrying a small fractional positive charge at the transition state. Any stepwise mechanism involving an energy minimum at an intermediate dipolar ion would necessarily have a larger negative ρ and a large polar solvent effect.

Methanol, when used as solvent for diazoalkane–ketone cycloadditions, does not become involved in product formation, nor does it affect the ratio of epoxides to ketones formed.[2a] Therefore the formation of the ketals **9** and **10** in high yields from the decomposition of **3** and **4** in methanol results from a type of intermediate not present in the cycloadditions. The products seem from decomposition in benzene, namely, epoxide and diaryl ketone, are likewise absent in methanol, which therefore must react with the common intermediate (carbonyl ylide) much faster than the latter can either cyclize or cleave. These findings are consistent with the sequence in Scheme I. In this sequence X may be the carbene R_fCCF_3, which isomerizes into hexa- or pentafluoropropylene, which is not condensed among the products. There was never any evidence for the fluorinated diazomethane as a fission product along with the diaryl ketone.

When $R_3 = CH_3$, 1,4-proton migration occurs exclusively. The small deuterium isotope effect ($k_{CH_3}/k_{CD_3} = 0.96$) indicates that the proton shift, like the other product-forming reactions, occurs after the rate-determining step.

1,3,4-Thiadiazolines are known to give episulfides stereospecifically.[5b,c] However, the stereoisomers of the epoxide **6c** from **4c** were formed in a sufficiently different ratio from those

Scheme I



of the starting material to raise a question of the stereospecificity of this reaction. In a searching investigation of the formation of carbonyl ylides by the thermal and photochemical ring opening of cyanostilbene oxides, Huisgen and collaborators[10d,18] concluded that the ring opening was stereospecific (thermally conrotatory and photochemically disrotatory) but that the barrier to internal rotation of the carbonyl ylide itself was low enough to permit some stereochemical leakage on the way from the cis epoxide to the trapped product on which the configuration was determined. This view is also applicable to the present case.

Experimental Section

Infrared spectra were recorded on a Beckman IR-33 spectrometer. NMR spectra were recorded on a JEOL MH-100 and on a Varian A-60A spectrometer. Mass spectra were recorded on a Finnigan 1015 spectrometer. Hexafluoroacetone and pentafluoroacetone were obtained from commercial sources. The diazomethanes, $R_1R_2C{=}N_2$, $R_1 = R_2$ = phenyl, mp 27–29 °C;[19] R_1 = phenyl, R_2 = *p*-tolyl, mp 54–55 °C ;[20] R_1 = phenyl, R_2 = *p*-anisyl, mp 50–52 °C;[21] R_1 = phenyl, R_2 = *p*-chlorophenyl, mp 32–33 °C;[22] $R_1 = R_2$ = *p*-tolyl, mp 99–100 °C;[20] and 9-diazofluorene, mp 92–93 °C,[23] were prepared by oxidation of the hydrazones with silver oxide in pentane solution.[22]

2,2-Diphenyl-5,5-bis(trifluoromethyl)-1,3,4-oxadiazoline (3a) Preparation. In a 50-mL three-necked flask equipped with a thermometer, a dry ice condenser, and a gas inlet with drying tube was placed diphenyldiazomethane (**2a**, 1.00 g) in 25 mL of pentane and the solution was cooled to −15 to −20 °C by a dry ice–methanol bath. Hexafluoroacetone dried over calcium chloride was bubbled into the stirred solution until the deep color had faded. The reaction mixture was then cooled and allowed to stand at −78 °C for 5 h. Colorless crystals were collected by filtration at low temperature, 1.75 g (95%), mp 35–36 °C dec, which was shown to be oxadiazoline **3a.**

Decomposition in Benzene. 3a (982 mg) was dissolved in 30 mL of benzene and the solution was allowed to stand at room temperature (20 °C) for 1 day. Benzene was removed by a rotary evaporator and the residual oil was chromatographed over alumina. Eluting with pentane gave a colorless solid (646 mg, 72%): mp 57–58 °C (recrystallized from methanol); IR (Nujol) 3100, 3080, 3040, 1600, 1500, 1400, 1325 s, 1235 s, 1180 s, 1145 s, 1035, 995, 970 s, 910, 890 s, 730, 690, 680 cm^{-1}; ^1H NMR ($CDCl_3$) 7.40–7.68 ppm (multiplet); ^{13}C NMR ($CDCl_3$) 62.29 (septet, J = 36 Hz, $C(CF_3)_2$), 71.55 ($C(Ph)_2$), 121.14 (quartet, J = 281 Hz, CF_3), 128.65 (meta and para carbons), 125.88 (ortho carbons), 136.12 ppm (α carbons); mass spectrum *m/e* (rel intensity) 332 (M^+, 100), 313 (10), 263 (13), 166 (63), 106 (18). These data are consistent with the epoxide **5a.** Lithium aluminum hydride reduction of **5a** in ether under reflux for 2 weeks gave benzhydrol in 70% yield and heating with an equimolar amount of triphenylphosphine at 250 °C for 30 min gave 1,1-diphenyl-2,2-bis(trifluoromethyl)ethylene. Eluting with 10% ether in pentane gave a yellow oil (227 mg), which was found to contain at least two other products together with a small amount of benzophenone (4%) by GLC analysis (2 ft 20% Silicon DC-550 on Chromosorb P, at 210 °C). The

mixture of the two unidentified products showed strong IR absorptions at 1665, 1310, 1275, 1220, and 1195 cm^{-1}.

Decomposition in Methanol. Similarly, **3a** (600 mg) was decomposed in methanol (20 mL) at room temperature for 1 day. Removing solvent left a colorless oil, which was crystallized from pentane, mp 19–20 °C (630 mg, 96%), and shown to be **9a:** IR (liquid) 3100, 3075, 3040, 2960, 2850, 1605, 1495, 1450, 1355, 1280 s, 1185 s, 1150 s, 1110 s, 1100 s, 970, 940, 900, 880, 860, 740, 690 cm^{-1}; NMR ($CDCl_3$) 3.19 (s, 3 H), 4.28 (septet, J = 6 Hz, 1 H), 7.18–7.62 ppm (m, 10 H); mass spectrum *m/e* (rel intensity) 364 (M^+, 2), 333 (36), 197 (57), 105 (100).

2,2-Diphenyl-5-difluoromethyl-5-trifluoromethyl-1,3,4-oxadiazoline (4a) Preparation. In a procedure similar to that in the case of hexafluoroacetone, dry pentafluoroacetone was bubbled into a cold (−15 to −20 °C) pentane solution (50 mL) of diphenyldiazomethane (1.40 g) until the color had faded. About half of the solvent was removed by evaporation under vacuum (ca. 0.1 mmHg) while the solution was kept cold (−20 °C). Then the solution was allowed to stand at −78 °C for 5 h. The cycloadduct, **4a,** was obtained as colorless crystals, mp 42–43 °C dec, 2.24 g (91%).

Decomposition in Benzene. 4a (1.47 g) was dissolved in 50 mL of benzene and the solution was allowed to stand at 30 °C for 5 h. Evolution of nitrogen (103 mL) was quantitative. Benzene was removed by evaporation and the residue was chromatographed over alumina. Eluting with pentane gave a white solid, mp 79–80 °C (recrystallized from pentane) (1.23 g, 96%), which was shown to be the epoxide **6a:** IR (Nujol) 1330 s, 1200 s, 1170 s, 1150 s, 1130 s, 1070 s, 980, 885, 730, 680 cm^{-1}; NMR (CCl_4) 5.16 (triplet, J = 52 Hz, each split to quartet with J = 1 Hz, 1 H), 7.16–7.50 ppm (m, 10 H); mass spectrum *m/e* (rel intensity) 314 (M^+, 30), 313 (56), 295 (2), 263 (9), 166 (22), 165 (100), 105 (44). Eluting with ether gave a yellow solid (50 mg) which showed strong absorptions at 1665, 1320, 1275, 1200, and 1180 cm^{-1}.

Decomposition in Methanol. 4a (1.20 g) was decomposed in methanol (50 mL) at 30 °C for 5 h. Solvent was removed by evaporation and the residue was chromatographed over alumina. Eluting with pentane gave first the epoxide (**6a**) and then another product. The latter showed the following spectral properties: IR (liquid) 3080, 3040, 2950, 2850, 1455, 1350, 1320, 1265 s, 1190 s, 1150 s, 1100, 1065 s, 980, 955, 745, 685 cm^{-1}; NMR (CCl_4) 3.10 (s, 3 H), 4.00 (septet, J = 6 Hz, 1 H), 5.48 (triplet, J = 52 Hz, 1 H), 7.16–7.40 ppm (m, 10 H); mass spectrum *m/e* (rel intensity) 346 (M^+, 0.5), 315 (14), 269 (4), 197 (100), 165 (22), 105 (100), 77 (80). These data are consistent with **10a.** The yields of **6a** and **10a** were 10 and 85%, respectively.

2-Phenyl-2-*p*-tolyl-5,5-bis(trifluoromethyl)-1,3,4-oxadiazoline (3b) Preparation. Hexafluoroacetone was bubbled into a cold (−20 °C) pentane solution of *p*-tolylphenyldiazomethane, **2b** (1.45 g), until the color had faded. Solvent was removed by evaporation under vacuum while the solution was kept cool (−20 °C). The residue, a colorless oil, was found to be almost pure adduct, **3b,** by NMR analysis. The oil decomposed rapidly at room temperature.

Decomposition in Benzene. 3b (1.13 g) was dissolved in 50 mL of benzene and the solution was allowed to stand at room temperature for 1 day. Solvent was removed by evaporation and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil (390 mg, 37%) which was shown to be **5b:** IR (liquid) 3080, 3050, 2940, 1610, 1600, 1450, 1400 s, 1320 s, 1230 s, 1190 s, 1140 s, 1100, 1070, 890, 810, 720, 700, 680 cm^{-1}; NMR ($CDCl_3$) 2.32 (s, 3 H), 7.24 (d, J = 8 Hz, 2 H), 7.38–7.68 ppm (m, 7 H); mass spectrum (rel intensity) 346 (M^+, 35) 345 (68), 331 (100), 165 (58). Elution with 5% ether in pentane gave *p*-methylbenzophenone (272 mg, 46%). From GLC analysis, the crude reaction mixture was found to contain other minor products (below 5% yield) than **5b** and *p*-methylbenzophenone. One of them was isolated by preparative GLC and showed the following spectral properties: IR (liquid) 1620, 1450, 1355 s, 1280 s, 1220 s, 1185 s, 1100 s, 960, 870, 810, 760, 690, 670 cm^{-1}; NMR ($CDCl_3$) 2.42 (s, 3 H), 4.10 (broad s, 2 H), 7.36 (s, 4 H), 7.55 ppm (s, 5 H); mass spectrum *m/e* (rel intensity) 348 (22), 347 (90), 119 (100).

Decomposition in Methanol. 3b (1.35 g) was dissolved in 20 mL of methanol and the solution was allowed to stand at room temperature for 1 day. Solvent was removed and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil, **9b** (1.30 g, 96%): IR (liquid) 3100, 3090, 2960, 2860, 1530, 1490, 1455, 1360 s, 1280 s, 1220 s, 1180 s, 1090 s, 1075 s, 1020, 980, 930, 865, 810, 760, 690, 675 cm^{-1}; NMR ($CDCl_3$) 2.36 (s, 3 H), 3.22 (s, 3 H), 4.30 (septet, J = 6 Hz, 1 H), 7.24 (d, J = 8 Hz, 2 H), 7.38–7.60 ppm (m, 7 H); mass spectrum *m/e* (rel intensity) 378 (M^+, 1), 347 (13), 211 (100), 119 (25).

2-Phenyl-2-*p*-tolyl-5-difluoromethyl-5-trifluoromethyl-1,3,4-oxadiazoline (4b) Preparation. Pentafluoroacetone was bubbled into a cold (−30 °C) pentane solution (50 mL) of *p*-tolyphenyldiazomethane (2.00 g) until the color had faded. Solvent was evaporated under vacuum while the solution was kept at −30 °C. The residue was shown to be almost pure **4b** by NMR analysis. The oil was unstable at room temperature with evolution of nitrogen.

Decomposition in Benzene. 4b (1.28 g) was dissolved in 20 mL of benzene and the solution was kept at 30 °C for 5 h, during which period 92 mL of nitrogen was generated. Benzene was removed and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil (1.13 g, 97%), which was shown to be a mixture of isomeric epoxides, **6b,** in a ratio of 1:1.3: IR (liquid) 3080, 3040, 2940, 2880, 1455, 1435, 1325 s, 1205 s, 1175 s, 1155 s, 1135 s, 1075 s, 990, 895, 810, 765, 730, 685 cm^{-1}; NMR (CCl_4) 2.26 (s, 3 H), 5.20 (t, J = 52 Hz, each split to multiplet with J = 1 Hz, 1 H), 7.02 (d, J = 8 Hz) and 7.06 (d, J = 8 Hz) together 2 H, 7.20–7.44 ppm (m, 7 H); mass spectrum *m/e* (rel intensity) 328 (M^+, 34), 327 (59), 313 (100), 165 (86).

Decomposition in Methanol. 4b (1.30 g) was dissolved in 50 mL of methanol and the solution was kept at 30 °C for 5 h. Methanol was evaporated and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil which was shown to be a mixture of **6b** and **10b.** The latter was isolated by preparative GLC using a column packed with 20% Silicone DC-550 on Chromosorb P (2-ft column at 160 °C, retention times were 8.8 and 11.2 min for **6b** and **10b,** respectively): IR (liquid) 3080, 3040, 2960, 2845, 1455, 1410, 1350, 1320, 1265 s, 1190 s, 1155 s, 1105 s, 1070 s, 985, 960, 810, 755, 690 cm^{-1}; NMR ($CDCl_3$) 2.28 (s, 3 H), 3.12 (s, 3 H), 4.10 (septet, J = 7 Hz, 1 H), 5.54 (t, J = 52 Hz, each split to multiplet, 1 H), 7.04 (d, J = 8 Hz, 2 H), 7.20–7.48 ppm (m, 7 H); mass spectrum *m/e* (rel intensity) 360 (M^+, 0.2), 329 (4), 314 (12), 312 (12), 269 (5), 211 (95), 197 (90), 165 (29), 119 (48), 105 (100), 77 (70). The yields of **6b** and **10b** were 59 and 41%. Similarly **4b** was decomposed in methanol by heating at 65 °C for 20 min. **6b** and **10b** were obtained in 40 and 60% yield, respectively.

2-Phenyl-2-*p*-anisyl-5,5-bis(trifluoromethyl)-1,3,4-oxadiazoline (3c) Preparation. Hexafluoroacetone was bubbled into a cold (−30 °C) pentane–ether (1:1) solution of **2c** (1.2 g) until the color had faded. The solvent was removed by evaporation under vacuum while the solution was kept at −20 °C. The residue was found to be almost pure **3c.**

Decomposition in Benzene. 3c (1.05 g) was dissolved in 20 mL of benzene and the solution was allowed to stand at room temperature for 1 day. Benzene was evaporated and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil (370 mg, 38%) which was shown to be the epoxide, **5c:** IR (liquid) 3080, 3040, 3020, 2960, 3840, 1620, 1515, 1450, 1400, 1320 s, 1300, 1235 s, 1190 s, 1040 s, 1020, 1000, 970, 890, 820, 720, 685 cm^{-1}; NMR ($CDCl_3$) 3.80 (s, 3 H), 6.96 (d, J = 9 Hz, 2 H), 7.30–7.56 ppm (m, 7 H); mass spectrum *m/e* (rel intensity) 362 (50), 361 (100), 331 (41), 292 (23), 152 (60), 135 (50).

Decomposition in Methanol. 3c (1.10 g) was dissolved in methanol (20 mL) and the solution was allowed to stand at room temperature for 1 day. Methanol was removed by a rotary evaporator and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil, **9c** (1.05 g, 95%): IR (liquid) 3080, 3020, 2920, 2850, 1615, 1510, 1455, 1360, 1280 s, 1250 s, 1230 s, 1190 s, 1170 s, 1100 s, 1030, 980, 950, 910, 820, 690 cm^{-1}; NMR ($CDCl_3$) 3.18 (s, 3 H), 3.82 (s, 3 H), 4.28 (septet, J = 6 Hz, 1 H), 6.94 (d, J = 9 Hz, 2 H), 7.38–7.60 ppm (m, 7 H).

2-Phenyl-2-*p*-anisyl-5-difluoromethyl-5-trifluoromethyl-1,3,4-oxadiazoline (4c) Preparation. Pentafluoroacetone was bubbled into a cold (−15 to −20 °C) pentane–ether (4:1) (30 mL) solution of **2c** (1.50 g) until the color had faded. Removing the solvent by evaporation under vacuum left an oil, which was shown to be a mixture of isomeric oxadiazolines, **4c,** in a ratio of 1:1.1 from NMR analysis at low temperature ($CDCl_3$, at −25 °C): 3.72 (s, 3 H), 6.22 (t, J = 52 Hz), and 6.26 (t, J = 52 Hz) together 1 H, 6.80 (d, J = 9 Hz, 2 H), 7.24–7.44 ppm (m, 7 H).

Decomposition in Benzene. 4c (1.20 g) was dissolved in 20 mL of benzene and the solution was allowed to stand at room temperature for 5 h. Solvent was removed by evaporation and the residue was chromatographed over alumina. Eluting with pentane gave a colorless

oil (830 mg, 75%), which was found to be a mixture of isomeric epoxides, **6c**, in a ratio of 1:1.5: IR (liquid) 3080, 3040, 3020, 2970, 2950, 2920, 2850, 1615, 1510, 1450, 1430, 1320 s, 1250 s, 1200 s, 1175 s, 1130 s, 1070 s, 1025, 890, 820, 775, 760, 730, 685 cm^{-1}; NMR ($CDCl_3$) (signals due to the minor isomer, where resolvable, are shown in italics) 3.60 (s, 3 H), *5.16* (t, J = 52 Hz, each split to quartet with J = 1 Hz), and 5.22 (t, J = 52 Hz, each split to quartet with J = 1 Hz), together 1 H, *6.68* (d, J = 9 Hz) and 6.71 (d, J = 9 Hz) together 2 H, 7.08–7.40 ppm (m, 7 H). Eluting with ether gave a yellow solid. Recrystallization from methanol gave colorless crystals of *p*-methoxybenzophenone (135 mg, 20%).

Reaction of Hexafluoroacetone with *p*-Chlorophenylphenyldiazomethane and Decomposition of the Product in Benzene. Hexafluoroacetone was bubbled into a cold (−15 °C) pentane solution (50 mL) of **2d** (0.82 g) until the color had faded. Solvent was removed by evaporation under vacuum while the solution was kept at −15 °C.

The residue (1.18 g) was dissolved in 20 mL of benzene and the solution was heated at 50 °C for 5 h. Benzene was removed by a rotary evaporator and the residue was chromatographed over alumina. Eluting with pentane gave a colorless oil which was shown to be epoxide **5c** (600 mg, 56%): IR (liquid) 3100, 3080, 3045, 1605, 1500, 1370, 1330 s, 1300 s, 1240 s, 1190 s, 1145 s, 1100 s, 1090 s, 1000, 990, 970 s, 820, 845, 700, 685 cm^{-1}; NMR (CCl_4) 7.30–7.65 ppm (multiplet); mass spectrum *m/e* (rel intensity) 368 (15), 367 (15), 366 (60), 331 (65), 165 (100). Eluting with 10% ether in pentane gave *p*-chlorobenzophenone (250 mg, 39%).

2,2-Di-*p*-tolyl-5,5-bis(trifluoromethyl)-1,3,4-oxadiazoline (3e) Preparation. Hexafluoroacetone was bubbled into a cold (−20 °C) pentane–ether (1:1) (50 mL) solution of **2e** (1.5 g) until the color had faded. The solvent was evaporated under vacuum. The residual oil was found to be almost pure adduct, **3e**, by NMR analysis. This oil was rapidly decomposed at room temperature.

Decomposition in Benzene. 3e (1.12 g) was dissolved in benzene (20 mL) and the solution was allowed to stand at room temperature for 1 day. Benzene was removed by a rotary evaporator and the residue was chromatographed over alumina. Eluting with pentane gave a colorless solid (450 mg, 43%), which was shown to be epoxide **5e:** mp 70–71 °C (recrystallized from methanol); IR (Nujol) 1620, 1360, 1325 s, 1290 a, 1230 s, 1185 s, 1140 s, 1100 s, 970, 895, 810, 760, 730, 700, 670 cm^{-1}; NMR ($CDCl_3$) 2.32 (s, 6 H), 7.20 (d, J = 8 Hz, 4 H), 7.44 ppm (d, J = 8 Hz, 4 H); mass spectrum *m/e* (rel intensity) 360 (M^+, 7), 345 (100), 178 (44), 179 (44), 165 (14). Eluting with 10% ether in pentane gave *p,p'*-dimethylbenzophenone (230 mg, 38%).

Decomposition in Methanol. 3e (1.05 g) was dissolved in 20 mL of methanol and the solution was allowed to stand at room temperature for 1 day. Methanol was evaporated and the residue was chromatographed over alumina eluting with pentane. Removing the solvent left a colorless oil (1.02 g, 97%), which was shown to be **9e:** IR (liquid) 3050, 3000, 2950, 2840, 1620, 1515, 1360 s, 1280 s, 1230 s, 1185 s, 1110 s, 1090 s, 1080 s, 920, 865, 805, 670 cm^{-1}; NMR ($CDCl_3$) 3.18 (s, 3 H), 2.36 (s, 6 H), 4.26 (septet, J = 6 Hz, 1 H), 7.22 (d, J = 8 Hz, 4 H), 7.40 ppm (d, J = 8 Hz, 4 H); mass spectrum (rel intensity) 392 (M^+, 2), 361 (10), 225 (100), 119 (65).

2-Methyl-2-phenyl-5,5-bis(trifluoromethyl)-1,3,4-oxadiazoline (3f) Preparation. In a 50-mL round flask were placed 4.0 g of silver oxide and 50 mL of pentane. The solution was cooled to −30 °C by a dry ice–methanol bath. Into the well-stirred solution was added 2.0 g of acetophenone hydrazone and the solution was stirred at −30 °C for 5 h. The solution was dried over sodium sulfate and filtered. In a procedure similar to that for diphenyldizaomethane, hexafluoroacetone was bubbled into the cold red solution (−20 °C) thus obtained until the color had faded. Solvent was evaporated under vacuum while the solution was kept cool (−15 to −20 °C). The resulting oil was shown to be almost pure oxadiazoline **3f:** IR (liquid) 3100, 3080, 3000, 2955, 1500, 1450, 1320 s, 1270 s, 1220 s, 1150 s, 1100 s, 1060, 970 s, 745, 680 cm^{-1}; NMR (CCl_4) 1.98 (s, 3 H), 7.48–7.74 ppm (m, 5 H).

Decomposition in Benzene. 3f (1.10 g) was dissolved in 20 mL of benzene and the solution was heated to 50 °C for 5 h. Solvent was removed and the residue was chromatographed over alumina eluting with pentane. Removing solvent left a colorless oil which was shown to be the olefin **7** (930 mg, 92%): IR (liquid) 3100, 3080, 2990, 1640 s, 1500, 1455, 1365 s, 1270 s, 1220 s, 1190 s, 1130 s, 1100 s, 940, 890, 865, 820, 760, 675 cm^{-1}; NMR (CCl_4) 4.62 (d, J = 4 Hz, 1 H), 4.90 (septet, J = 6 Hz, 1 H), 5.06 (d, J = Hz, 1 H), 7.42–7.76 ppm (m, 5 H); mass spectrum *m/e* (rel intensity) (M^+, 90), 269 (100), 103 (46), 91 (46).

Decomposition in Methanol. 3f (1.35 g) was dissolved in 20 mL of methanol and the solution was heated at 60 °C for 2 h. Methanol was evaporated and the residue was chromatographed over alumina cooled by dry ice–methanol.[24] Eluting with pentane gave the olefin **7** (280 mg, 23%) and another colorless oil (985 mg, 72%) in order of elution. The latter was found to be **9f:** IR (liquid) 3090, 3015, 2970, 2860, 1455, 1360 s, 1280 s, 1225 s, 1190 s, 1095 s, 1030 s, 880, 755, 680 cm^{-1}; NMR (CCl_4) 1.72 (s, 3 H), 3.22 (s, 3 H), 4.60 (septet, J = 6 Hz, 1 H), 7.42–7.72 ppm (m, 5 H): mass spectrum *m/e* (rel intensity) 302 (1), 287 (6), 271 (19), 135 (72), 119 (100), 117 (100), 105 (42).

2-Methyl-2-phenyl-5-difluoromethyl-5-trifluoromethyl-1,3,4-oxadiazoline (4f) Preparation. Diazoacetophenone was prepared in the same way as described above. Pentafluoroacetone was bubbled into a cold (−20 °C) pentane (50 mL) solution of diazoacetophenone prepared from 2 g of hydrazone until the deep red color had faded. Solvent was evaporated under vacuum. The residual oil was shown to be a mixture of isomeric oxadiazolines **4f** in a ratio of 1:1.2 from NMR analysis: IR (liquid) 3080, 3050, 3010, 1500, 1455, 1385, 1365, 1315, 1265, 1195 s, 1100 s, 1070, 1060, 1000 s, 950, 920, 895, 830, 790, 750, 725, 685 cm^{-1}; NMR ($CDCl_3$) 1.92 (s, 3 H), 6.12 (t, J = 52 Hz) and 6.36 (t, J = 52 Hz) in a ratio of 1:1.2 (together 1 H), 7.28–7.56 ppm (m, 5 H).

Decomposition in Benzene. 4f (1.21 g) was dissolved in benzene (20 mL) and the solution was heated at 40 °C for 2 h. Benzene was removed. The residue was chromatographed over alumina eluting with pentane. Removing the solvent gave a colorless oil which was shown to be the olefin **8** (1.06 g, 97%): IR (liquid) 3100, 3080, 3055, 1640 m, 1270 s, 1200 s, 1160 s, 1120, 1085 s, 1060 s, 930, 865, 815, 760, 690, 670 cm^{-1}; NMR (CCl_4) 4.40 (d, J = 4 Hz, 1 H), 4.56 (m, 1 H), 4.82 (d, J = 4 Hz, 1 H), 5.92 (t, J = 52 Hz, each split to doublet with J = 4 Hz, 1 H), 7.16–7.50 ppm (m, 5 H); mass spectrum *m/e* (rel intensity) 252 (M^+, 18), 251 (18), 105 (100), 103 (50).

Decomposition in Methanol. 4f (1.05 g) was dissolved in 20 mL of methanol and the solution was allowed to stand at room temperature for 1 day. Solvent was removed. The residue was chromatographed over alumina at −78 °C. Eluting with pentane gave a colorless oil which was shown to be a mixture of **8** and acetophenone dimethyl ketal by NMR and GLC analysis. The yields of **8**, acetophenone, and its dimethyl ketal were 27, 26, and 35%, respectively.

It was found that the major isomer of oxadiazoline **4f** decomposed more rapidly than the minor one did. Thus when **4f** (a mixture of isomers) was decomposed in chloroform-*d* at 30 °C, the initial isomer ratio 1:1.2 changed into 1.6:1.0 after 56% decomposition.

Reaction of Pentafluoroacetone with 9-Diazofluorene and Decomposition of the Product in Benzene. Pentafluoroacetone was bubbled into a cold (−30 °C) ether solution (30 mL) of 9-diazofluorene (1.40 g) for 30 min. The orange solution was evaporated under vacuum while the solution was kept at −20 °C. The residual orange solid after decomposition at 35 °C was dissolved in 50 mL of benzene and the solution was allowed to stand at room temperature for 1 day. Benzene was removed and the residue was chromatographed over alumina. Eluting with pentane gave a light orange solid (1.8 g) which was shown to be epoxide **6h:** mp 76–77 °C (recrystallized from methanol); IR (Nujol) 1620, 1600, 1310 s, 1295 s, 1185 s, 1130 s, 1070 s, 970, 900, 735 cm^{-1}; NMR ($CDCL_3$) 6.36 (t, J = 52 Hz, 1 H), 7.18–7.70 ppm (m, 8 Hz); mass spectrum *m/e* (rel intensity) 312 (M^+, 30), 311 (50), 261 (7), 165 (100). Elution with 5% ether in pentane gave 250 mg of unreacted 9-diazofluorene. The yield of **6h** was 91%.

Similarly hexafluoroacetone was bubbled into a cold ether solution of **2h** (1.00 g) for 15 min. Removing the solvent under vacuum left an orange solid. Recrystallization from 2-propanol gave colorless crystals of **5h:** mp 94–95 °C (1.42 g, 92%); IR (Nujol) 1310 s, 1230 s, 1210 s, 1180 s, 1160 s, 1090, 970 s, 730, 705 cm^{-1}; NMR ($CDCl_3$) 7.08–7.80 (multiplet); mass spectrum *m/e* (rel intensity) 330 (M^+, 61), 311 (9), 261 (66), 165 (100).

Thermal Decomposition of 3a in the Presence of *p*-Cresol and of Diethyl Azodicarboxylate. 3a (217 mg) was dissolved in 10 mL of benzene including 650 mg of *p*-cresol. The solution was allowed to stand at room temperature for 1 day. Benzene was removed by a rotary evaporator and the residue was chromatographed over alumina eluting with pentane. Removing solvent left a colorless oil which was rechromatographed over alumina at 0 °C. Eluting with pentane gave colorless crystals, **5a** (120 mg, 60%), and a colorless oil in order of

elution. The latter was shown to be **11** (77 mg, 27%): IR (liquid) 3080, 3040, 2950, 1510, 1460, 1360, 1280 s, 1220 s, 1190 s, 1100 s, 1015, 970, 950, 770, 750, 675 cm^{-1}; NMR ($CDCl_3$) 2.22 (s, 3 H), 4.48 (septet, J = 6 Hz, 1 H), 7.09 (s, 4 H), 7.35–7.90 ppm (m, 10 H); mass spectrum m/e (rel intensity) (M^+, p-methylphenoxy, 100), 273 ($M^+ - OC(CF_3)_2H$, 2), 165 (10), 105 (60).

A mixture of **3a** (500 mg), diethyl azodicarboxylate (500 mg), and 10 mL of benzene was kept at 35 °C for 2 h. Solvent was evaporated and excess diethyl azodicarboxylate was removed by distillation under vacuum. The yellow residue was chromatographed over alumina. Eluting with pentane gave a colorless solid, **4a** (275 mg, 60%). Eluting with 10% ether in pentane gave a white solid. Recrystallization from pentane gave colorless crystals (20 mg) which showed the following properties: IR (Nujol) 3320, 1775, 1725, 1525, 1350, 1320, 1260, 1245 vs, 1200 vs, 1120, 1055, 1000, 965, 890, 760, 700 cm^{-1}; NMR ($CDCl_3$) 0.92 (t, J = 6 Hz, 3 H), 1.22 (t, J = 6 Hz, 3 H), 3.98–4.36 (m, 4 H), 6.30 (broad, 1 H), 7.48–8.28 ppm (m, 10 H).

Kinetics. All oxadiazolines were found to decompose with first-order kinetics. The rate of decomposition was determined in benzene solution (0.2 m) by measuring gas evolution at at least three different temperatures in a range from 20.5 to 47.4 °C. The first-order rate constant for the decomposition of **3a** and **4a** did not depend on the initial concentration of the oxadiazoline in a range of 0.1–0.5 m solution.

Preparation of 2,2-Bis(trifluoromethyl)-5-methyl-d_3-5-phenyl-Δ^3-1,3,4-oxadiazoline. A pentane solution of diazoacetophenone-α,α,α-d_3 was prepared in the same way as diazoacetophenone using acetophenone-d_3 hydrazone prepared from acetophenone-d_3 and hydrazine hydrate. Into a cold pentane solution of diazoacetophenone-d_3 (30 °C) was bubbled hexafluoroacetone until the characteristic color had faded. Solvent was removed by evaporation under vacuum while the solution was kept at −20 °C. The isotopic purity of the resulting oxadiazoline was found to be 88% by NMR measurement. The first-order rate constant of the thermal decomposition of this oxadiazoline in benzene solution at 34.6 °C was 8.92×10^{-4} s^{-1}, $k(CH_3)/k(CD_3)$ = 8.60/8.92 = 0.96.

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References and Notes

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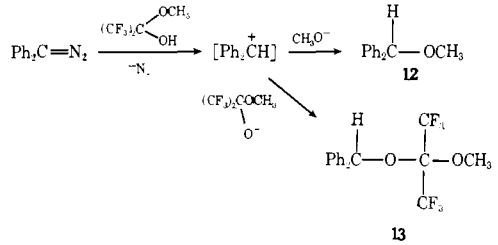
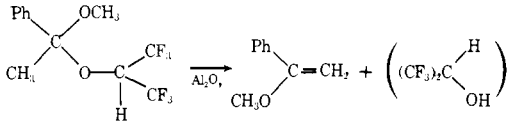
(2) (a) C. D. Gutsche, *Org. React.*, **8**, 364 (1954); H. Zollinger, "Azo and Diazo Chemistry. Aliphatic and Aromatic Compounds", Interscience, New York, N.Y., 1961; (b) F. Schlotterbeck, *Ber.*, **42**, 2559 (1909); F. Arndt, B. Eistert, and W. Ender, *ibid.*, **62**, 44 (1929); H. Meerwein, T. Bersin, and W. Burneleit, *ibid.*, **62**, 999 (9129).
(3) (a) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920); (b) H. Staudinger and T. Reber, *ibid.*, **4**, 3 (1921).
(4) D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Commun.*, 1226 (1970).
(5) (a) R. M. Kellogg, *J. Org. Chem.*, **38**, 844 (1973); (b) J. Buter, S. Wassenaar, and R. M. Kellogg, *ibid.*, **37**, 4045 (1972); (c) R. M. Kellogg, S. Wassenaar, and J. Buter, *Tetrahedron Lett.*, 4689 (1970); (d) R. M. Kellogg and S. Wassenaar, *ibid.*, 1987 (1970).
(6) (a) W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969); (b) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *ibid.*, **30**, 1375 (1965); (c) W. J. Middleton and W. H. Sharkey, *ibid.*, **30**, 1384 (1965).
(7) (a) L. I. Smith and W. B. Pings, *J. Org. Chem.*, **2**, 95 (1937); but see (b) B. Eistert, *Angew. Chem.*, **54**, 99 (1941).
(8) R. W. Hoffmann and H. J. Luthardt, *Tetrahedron Lett.*, 411 (1966).
(9) P. Rajagopalan and B. G. Advani, *Tetrahedron Lett.*, 2689 (1967).
(10) (a) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); (b) T. DoMinh, A. M. Trozzolo, and G. W. Griffin, *J. Am. Chem. Soc.*, **92**, 1402 (1970); (c) D. R. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970); (d) A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *Chem. Commun.*, 1192 (1971); (e) C. W. Martin, J. A. Landgrebe, and E. Rapp, *ibid.*, 1438 (1971). (f) For a different type of route to carbonyl ylides by intramolecular interaction, see M. Hamaguchi and T. Ibata, *Tetrahedron Lett.*, 4475 (1974); *Chem. Lett.*, 499 (1975).
(11) Reaction of hexafluoroacetone and diphenyldiazomethane in methanol gave two ethers, **12** and **13**, in 60 and 30% yield, respectively. This may



12

13

be the result of acid-catalyzed decomposition of **2a** because hexafluoroacetone is known to react with methanol to give a hemiketal which must be acidic.
(12) The rate ratio between the two isomers is expressed as k_A/k_B = log (A_0/A)/log (B_0/B), where A_0 and B_0 are the initial intensities of the triplets due to CF_2H proton measured by using acetophenone as an internal standard and A and B are those after decomposition.
(13) **9f** could be isolated from the reaction mixture by alumina column chromatography eluting with pentane at low temperature (−78 °C). When **9f** was chromatographed over alumina at room temperature, only α-methoxystyrene was isolated.



(14) **10f** seems to be reactive toward methanol forming acetophenone dimethyl ketal, which is partly hydrolyzed to give acetophenone during the isolation process by chromatography.
(15) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964, Chapter 11, p 739.
(16) J. P. Anselme, "The Chemistry of the Carbon Nitrogen Double Bond", Interscience, New York, N.Y., 1970, Chapter 7, p 299.
(17) (a) H. Staudinger and T. Reber, *Helv. Chim. Acta*, **4**, 1 (1921); (b) W. Kirmse, *Chem. Ber.*, **93**, 2357 (1960).
(18) (a) R. Huisgen. *Angew. Chem., Int. Ed. Engl.*, **16**, 572 (1977); (b) see also I. J. Lev, K. Ishikawa, N. S. Bhacca, and G. W. Griffin, *J. Org. Chem.*, **41**, 2654 (1976).
(19) H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, **49**, 1928 (1916).
(20) H. Staudinger and J. Goldstein, *Ber.*, **49**, 1923 (1916).
(21) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Am. Chem. Soc.*, **95**, 826 (1973).
(22) W. Schroeder and L. Katz, *J. Org. Chem.*, **19** 718 (1954).
(23) H. Staudinger and O. Kupfer, *Ber.*, **44**, 2197 (1911).
(24) **9f** was unstable under chromatography over alumina at room temperature, and α-methoxystyrene was isolated instead of **9f** when the crude mixture was chromatographed over alumina at room temperature.