with a variety of orthoformates and hexafluoroacetone at 150°: tri-n-amyl orthoformate yields n-$C_5H_{11}OC$-$(CF_3)_2OH$ and IIIa [57.0%, b.p. 152° (45 mm.), $n^{25}D$

R—C(R')(CF_3)—CF_2R'
|
O—C(CF_3)(CF_2R')—O

IIIa, R = n-C_5H_{11}, R' = F
b, R = CH_2CH=CH_2, R' = F
c, R = CH_2CH_2Cl, R' = F
d, R = C_2H_5, R' = Cl
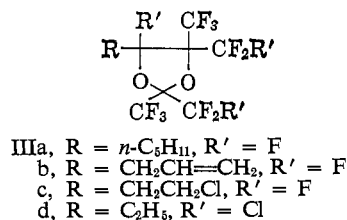
1.3717]; triallyl orthoformate and hexafluoroacetone yields CH_2=$CHCH_2OC(CF_3)_2OH$ and IIIb [64.2%, b.p. 67° (4.3 mm.), $n^{25}D$ 1.3532]; tri-β-chloroethyl orthoformate and hexafluoroacetone yields $ClCH_2$-$CH_2OC(CF_3)_2OH$ and IIIc [28.4%, b.p. 86° (1.5 mm.), $n^{25}D$ 1.3684]. Chloropentafluoroacetone and triethyl orthoformate undergo an analogous reaction, yielding $C_2H_5OC(CF_3)(CF_2Cl)OH$ and IIId [64.7%, b.p. 110° (23 mm.), $n^{25}D$ 1.3728]. On the other hand, perhalo-ketones containing more chlorine undergo a different reaction with orthoformates, which will be the subject of a later communication.

Analogous reactions occur with hexafluoroacetone and cyclic orthoformates such as IV, VI, and VIII to


IV

VI

VII

VIII

IX
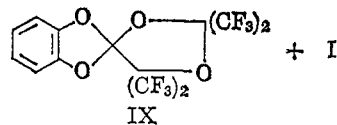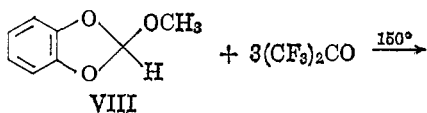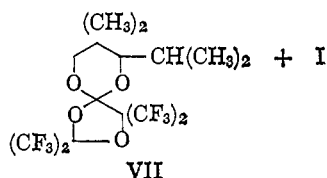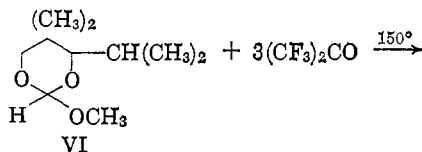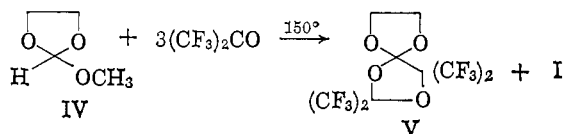
give I in each case and the spiroortho esters V [74.7% b.p. 176° (760 mm.), m.p. 24°], VII (90.0%, m.p. 73–74°], and IX [75.2%, b.p. 207° (760 mm.), m.p. 71–72°].

The first step in these reactions could be the attack on the orthoformate in which hexafluoroacetone acts as a Lewis acid and the orthoformate as a Lewis base. The complex so formed could decompose in the indicated manner, liberating the hemiketal and dialkoxycarbene. Hexafluoroacetone may be an effective trap for the carbene, and steric considerations strongly favor reaction of 2 moles of hexafluoroacetone and formation of the 1,3-dioxolane (II).

$(CH_3O)_3CH + (CF_3)_2C$=$O \rightarrow$
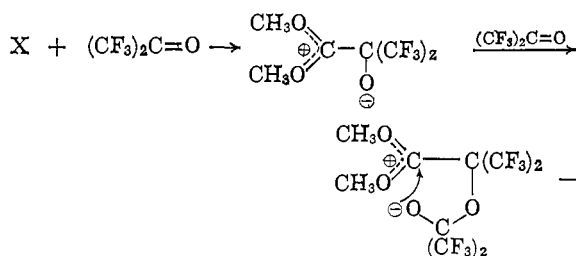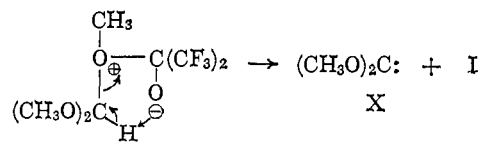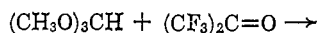
Working from the hypothesis that 2 moles of hexa-fluoroacetone can react with a mole of dialkoxycarbene to give the observed products such as II, III, V, VII, and IX, experiments were devised to observe the reaction of dimethylsilene [$(CH_3)_2Si:$] with hexafluoroacetone. The reaction of dimethyldichlorosilane (1 mole) and hexafluoroacetone (2 moles) in tetrahydrofuran at 10° with lithium metal dispersion (2 moles) gave the analogous product 1,1-dimethyl-3,3,5,5-tetrakis(trifluoromethyl)-2,4-dioxa-1-silacyclopentane (X) (63.5%, b.p. 149–150°, m.p. $-4°$, $n^{25}D$ 1.3342).

$(CH_3)_2SiCl_2 + 2(CF_3)_2C$=$O + 2Li \rightarrow$

X
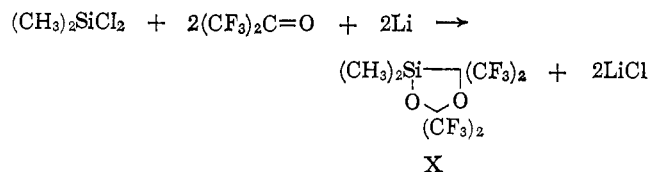
Details of these reactions and the reaction of perhalo-ketones with other ortho esters and acetals will appear in subsequent papers.

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Preferential Formation of the *cis* Olefin in an E2 Elimination

Sir:

We wish to report that the second-order reaction of potassium t-butoxide in t-butyl alcohol with 2-butyl, 2-pentyl, and 3-pentyl arenesulfonates produces the *cis* 2-alkene in considerable excess over the *trans*. All E2 reactions previously reported of alkyl halides and alkyl arenesulfonates produce the more stable *trans* alkene preferentially.[1–3]

For example, 2-butyl tosylate yields 62% 1-, 24% *cis*-2-, and 14% *trans*-2-butene. Similarly, 2-pentyl tosylate yields 74% 1-, 18% *cis*-2-, and 8% *trans*-2-

(1) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Am. Chem. Soc.*, **87**, 3401 (1965).

(2) A. K. Colter and R. D. Johnson, *ibid.*, **84**, 3289 (1962). Very high yields of the *trans* isomer in eliminations involving 3-methyl-2-butyl arenesulfonates have recently been reported: A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43**, 1282 (1965).

(3) High yields of *cis*-4-nonene have been realized in E2 eliminations of 5-nonyl 'onium salts and attributed to an incursion of an E1cb-like process: J. Zavada and J. Sicher, *Proc. Chem. Soc.*, 96 (1963).

Table I. Product Distribution for the Bimolecular Reaction of Secondary Alkyl Derivatives with Alkoxides

Alkyl X	X	Base	Solvent	Olefins produced, % 1	cis-2	trans-2
2-Butyl	Cl	KO-t-Bu	t-BuOH	67	14	18
	Br	KO-t-Bu	t-BuOH	54	19	27
	I	KO-t-Bu	t-BuOH	33	21	46
	Tos	KO-t-Bu	t-BuOH	62	24	14
	Tos	KOEt	EtOH	32	24	44
2-Pentyl	Tos	KO-t-Bu	t-BuOH	74	18	8
3-Pentyl	Tos	KO-t-Bu	t-BuOH		65	35
	Tos	NaOEt	EtOH		30	70
	Tos	NaO-i-Pr	i-PrOH		40	60
	Tos	KO-t-Bu	THF		31	69
	Tos	KO-t-Bu	Diglyme		30	70
trans-2-Methyl-cyclohexyl	Tos	KO-t-Bu	t-BuOH	1[a]	99[b]	
trans-2-Methyl-cyclopentyl	Tos	KO-t-Bu	t-BuOH	1[c]	99[d]	

[a] 1-Methylcyclohexene. [b] 3-Methylcyclohexene. [c] 1-Methyl-cyclopentene. [d] 3-Methylcyclopentene.

pentene. Finally, 3-pentyl tosylate yields 65% cis-2- and 35% trans-2-pentene.

All three components, arenesulfonate as the leaving group, t-butoxide as the base, and t-butyl alcohol as the solvent, appear to be required to achieve this formation of the cis alkene. Thus use of the halide in the elimination gives the usual preferred trans. The use of potassium ethoxide in ethanol on the tosylate yields predominantly trans. Even the use of potassium t-butoxide in tetrahydrofuran or diglyme on the tosylate gives predominant trans. Finally, the treatment of trans-2-methylcyclohexyl tosylate with potassium t-butoxide in t-butyl alcohol yields 99% 3-methylcyclohexene. Thus, this reaction reveals the usual stereochemical preference for trans E2 elimination.

These results are summarized in Table I.

We wish to suggest that the steric model for E2 eliminations[4,5] provides a possible explanation for this unusual formation of cis olefin. According to this interpretation the preferred formation of the cis isomer in the present reaction is a consequence of the fact that the large steric requirements of both the leaving arenesulfonate group and the solvated t-butoxide base cause transition state II to be more favorable energetically than transition state I.

In the usual elimination reaction, the steric interactions between the two alkyl groups (ethyl and methyl in I and II) apparently cause transition state I, with its alkyl groups separated, to be preferred. In the present case, it is our suggestion that the combined presence of two large, sterically demanding groups alters this situation. The geometrical requirements of both groups is such that they must project to the side of the two bonds undergoing rupture.

In a conformation in which the two alkyl groups are to enjoy the separation provided by a trans arrangement, there would appear to be two major possibilities for the attacking t-butoxide and departing arenesulfonate groups. They can either project in opposite directions

(4) H. C. Brown and I. Moritani, J. Am. Chem. Soc., 78, 2203 (1956).
(5) H. C. Brown and R. L. Klimisch, in press.

I

II
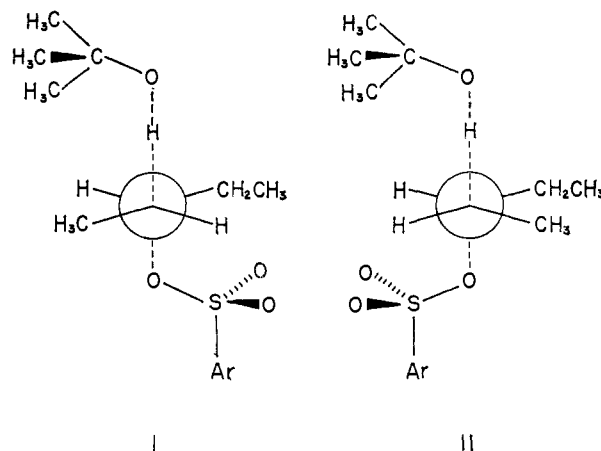
(as shown in I) or they could project in the same direction. In either case there will be significant steric interactions between the alkyl groups and these large, bulky moieties. It is our proposal that the system can reduce the steric interactions by allowing the two alkyl groups their relatively minor interactions in favor of giving the arenesulfonate and t-butoxide groups greater freedom on the opposite side of the assembly (II).

Irrespective of whether this interpretation provides the final explanation for this interesting phenomenon,[6] it is becoming evident that the direction of elimination is subject to a remarkably wide range of control[2] not envisaged in the original interpretation.[7]

(6) It has proven possible to incorporate the interesting results with the onium salts (ref. 3) into the same model. This extended interpretation will be reported shortly.
(7) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, J. Chem. Soc., 2093 (1948).

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The Preparation and Properties of Trimethylenecyclopropane

Sir:

We wish to report the formation of trimethylene-cyclopropane (I). This hydrocarbon has been the subject of much speculation with respect to its stability,[1,2] and a recent report has described the isolation and characterization of the remarkably stable tri-isopropylidenecyclopropane.[3] The parent hydrocarbon, representing an excellent example of a completely cross-conjugated system and having a distinct relationship to benzene (same number of carbon and hydrogen atoms, same degree of unsaturation, and an expected planar structure), has never been prepared.[4]

Compound I was obtained from 2,3-bis(bromo-methyl)-1-methylenecyclopropane (IV) which in turn was prepared from the reduction product[5] of Feist's acid (II). The dibromide, obtained in yields ranging

(1) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, J. Am. Chem. Soc., 74, 4579 (1952).
(2) M. J. S. Dewar and G. J. Gleicher, ibid., 87, 692 (1965).
(3) G. Köbrich and H. Heinemann, Angew. Chem., 77, 590 (1965); Angew Chem. Intern. Ed. Engl., 4, 594 (1965).
(4) (a) A. T. Blomquist and D. T. Longone, J. Am. Chem. Soc., 81, 2012 (1959); (b) I. A. D'Yakonov and E. M. Khoricheva, Zh. Obshch. Khim., 34, 2802 (1964).
(5) W. G. Brown and E. A. Dorko, unpublished results. See E. A. Dorko, Ph.D. Dissertation, University of Chicago, 1964.