2-Benzoyl-2-deuterio-5-phenyl-1,3-oxathiole 3,3-Dioxide (10-*2-d*). A mixture of 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10,** 0.5 g) in chloroform-d_1 (3 ml), methanol-*O-d* (1 ml) and pyridine (0.1 g) was stirred at room temperature for 20 min. On addition of light petroleum the deuterated product **10**-*2-d* crystallized: mp 139–140°; yield 0.4 g; R_f (benzene) 0.14; nmr (acetone-d_6) δ 7.17 (s, 1, =CH), 7.5–8.0 (m, 10, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 301 (0.40), 300 (0.10), 238 (0.50), 237 (2.90), 236 (0.90), 107 (0.45), 106 (7.00), 105 (100), 104 (0.65), 103 (1.25), 102 (6.00), 92 (0.25), 91 (0.30), 90 (0.70), 89 (0.75), 78 (2.20), 77 (23.5).

2-Benzoyl-4-deuterio-5-phenyl-1,3-oxathiole 3,3-Dioxide (10-*4-d*). 2-Benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5,** 70.9 mg) was added to a solution of acetone-d_6 (0.4 ml) and methanol-*O-d* (0.1 ml). The nmr of the mixture showed peaks at δ 7.20 (s, 1, CH), and 7.6–8.05 (m, 10, aromatic). Triphenylphosphine (70 mg) was added and the reduction reaction was followed by nmr at about 40°. The peak at δ 7.2 (CH in **5**) disappeared almost instantly and a peak developed at δ 7.0 (CH in **11**-*4-d*) reaching a maximum in about 20 min. No deuterium scrambling, *e.g.*, the formation of compound **11**-*2-d* (δ 7.17, =CH), was detected under the conditions used.

Acknowledgment. Financial support from The Swedish Natural Science Research Council is gratefully acknowledged. We thank Professor Roald Hoffmann for communicating results concerning the bonding in three-membered rings containing sulfur prior to their publication.

Registry No.—**2,** 51911-54-7; **5,** 51911-55-8; **10**-*2-d*, 51911-56-9; **11,** 51911-57-0; **13,** 51911-58-1; **16,** 51911-59-2; bis(phenacyl) sulfone, 3708-08-5; bis(phenacyl) sulfide, 2461-80-5.

References and Notes

(1) (a) D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30,** 636 (1965); (b) D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Amer. Chem. Soc.*, **91,** 2097 (1969).

(2) For recent reviews on the Ramberg–Bäcklund rearrangement, see L. A. Paquette, *Accounts Chem. Res.*, **1,** 209 (1968); F. G. Bordwell, *ibid.*, **3,** 281 (1970).

(3) K. Dickoré, *Justus Liebigs Ann. Chem.*, **671,** 135 (1964).

(4) (a) D. C. Dittmer, G. E. Kuhlmann, and G. C. Levy, *J. Org. Chem.*, **35,** 3676 (1970); (b) D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Amer. Chem. Soc.*, **89,** 2793 (1967).

(5) A. Padwa, D. Crumrine, and A. Shubber, *J. Amer. Chem. Soc.*, **88,** 3064 (1966); A. Padwa and D. Crumrine, *Chem. Commun.*, 506 (1965).

(6) J. Tafel and A. Mauritz, *Ber.*, **23,** 3474 (1890).

(7) E. Fromm and W. Schömer, *Justus Liebigs Ann. Chem.*, **399,** 353 (1913).

(8) L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, **93,** 476 (1971).

(9) F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **92,** 2581 (1970).

(10) D. Diller and F. Bergmann, *J. Org. Chem.*, **37,** 2147 (1972).

(11) H. Nozaki, M. Takaku, Y. Hayasi, and K. Kondô, *Tetrahedron*, **24,** 6563 (1968).

(12) R. Hoffmann, H. Fujimoto, J. R. Swenson, and C.-C. Wan, *J. Amer. Chem. Soc.*, **95,** 7644 (1973).

(13) H. Klocsterziel and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **71,** 1235 (1952).

(14) G. E. Kuhlmann and D. C. Dittmer, *J. Org. Chem.*, **34,** 2006 (1969).

(15) The authors have been in direct personal communication with Professor Dittmer regarding the mass spectrum of the oxathiole. On the basis of all available data an unpublished spectrum of Dittmer gives the appearance of being that of dibenzoylstilbene, perhaps arising because of thermal desulfurization in the inlet. The authentic mass spectrum of the oxathiole **14** is detailed in the Experimental Section.

(16) D. R. Berger and R. K. Summerbell, *J. Org. Chem.*, **24,** 1881 (1959).

(17) W. Küsters and P. de Mayo, *J. Amer. Chem. Soc.*, **95,** 2383 (1973).

(18) A. Robert and B. Moisan, *J. Chem. Soc., Chem. Commun.*, 337 (1972).

(19) D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.*, **82,** 4736 (1960).

(20) C. J. Ireland and J. S. Pizey, *J. Chem. Soc., Chem. Commun.*, 4 (1972).

(21) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6,** 149 (1967).

(22) H. J. Backer and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **54,** 170 (1935).

Sulfonylation of Alkylidene- and Arylidenephosphoranes. An Unexpected Rearrangement

B. A. Reith, J. Strating, and A. M. van Leusen*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

Received January 15, 1974

Sulfonyl-stabilized alkylidene- and arylidenetriphenylphosphoranes have been synthesized from alkyl- and aralkylsulfonyl fluorides and phosphoranes. A number of these reactions have been interpreted by [2 + 2] cycloadditions of sulfenes and phosphoranes to form four-membered ring intermediates, which will ring open in one or two possible directions, depending on the size of the substituents. This frequently leads to phosphonium ylides of rearranged structure. Relatively large substituents at the ylide carbon are sterically unfavorable.

In a previous paper[1] we have reported a useful method for the synthesis of sulfonyl-stabilized methylenetriphenylphosphoranes. These ylides (**3,** R^2 = H) were obtained in yields of 60–80% according to eq 1 for R^1 = aryl or alkyl.

$$\underset{\mathbf{1}}{R^1SO_2F} + \underset{\mathbf{2}}{2R^2CH{=}PPh_3} \xrightarrow[20°]{THF} \underset{\mathbf{3}}{R^1SO_2CR^2{=}PPh_3} + R^2CH_2\overset{+}{P}Ph_3\overset{-}{F} \qquad (1)$$

For other studies we needed derivatives of the sulfonylmethylenephosphoranes **3** with R^2 = alkyl or aryl, insted of H. However, the results of reaction 1 were unsatisfactory when the less reactive benzylidenetriphenylphosphorane (**2,** R^2 = phenyl) was used. Even under more severe reaction conditions compounds **3** (R^1 = aryl; R^2 = phenyl) were obtained only in 12–15% yields.[1]

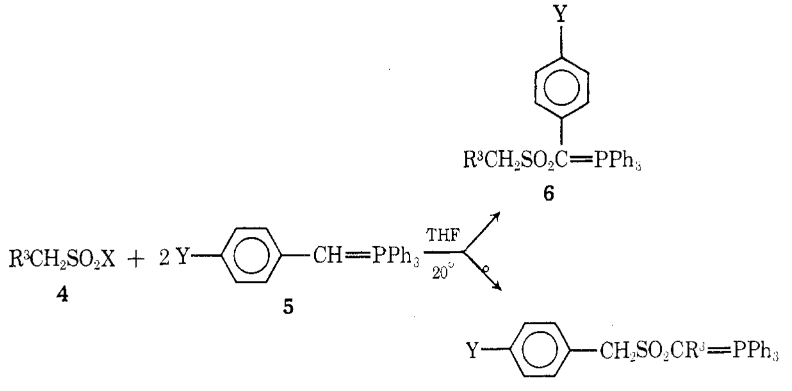
In an attempt to improve these results, we investigated the utility of more reactive sulfonylating agents (*i.e.*, sulfonic anhydrides and alkanesulfonyl fluorides) in the reaction with arylidenetriphenylphosphoranes. During these investigations an unexpected and intriguing rearrangement was discovered, the scope of which is evaluated in the present paper.

Two separate examples of compounds of type **3** with R^2 = phenyl[2a] and benzyl[2b] have been reported previously by other groups.

α-Sulfonylarylidenetriphenylphosphoranes.

The sulfonylation of benzylidenetriphenylphosphorane (**2,** R^2 = phenyl, prepared in the usual way from benzyltriphenylphosphonium bromide and butyllithium) was not improved by using, in reaction 1, *p*-toluenesulfonic anhy-

Table I
Reactions of Arylidenephosphorane and Alkanesulfonyl Fluoride (Anhydride)



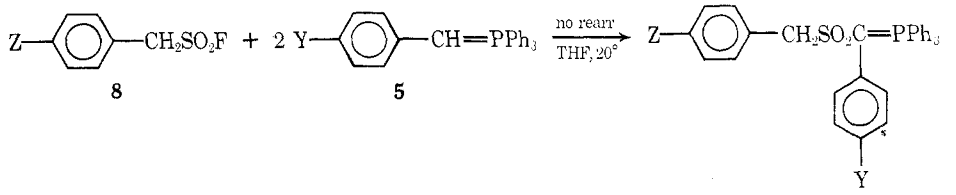
4 5 6 7

(2)[a]

Expt	R^3	X	Y	Product	Registry no.	Yield, %	Reaction time, hr
1	H	F	H	**7a**[b]	36196-00-6	95	0.5
2	H	OSO_2Me	H	**7a**[b]		54	0.5
3	H	OSO_2Me	MeO	**7b**	51848-88-5	61	0.5
4	Me	F	H	**7c**	51848-89-6	94	0.5
5	*t*-Bu	F	H	**6d**	51848-90-9	77	2

[a] Reference 3. [b] Compound reported previously; see ref 1.

Table II
Reactions of Arylidenephosphorane and Aralkanesulfonyl Fluoride



8 5 9

(3)

Expt	Y	Z	Product	Registry no.	Yield, %	Reaction time, hr	Mass spectra[a,b] $M\cdot^{+}$	F_1	F_2	F_3	Metastables
6	H	H	**9a**	51848-91-0	91	0.5	506	415	367	351	340.4 (506 → 415), 324.6 (415 → 367), 296.9 (415 → 351)
7	MeO	H	**9b**	51848-93-2	88	1	536	445	397	381	369.4 (536 → 445), 294.0 (536 → 397), 326.2 (445 → 381)
8	H	NO_2	**9c**	51848-92-1	48	1.5	551	415	367	351	312.6 (551 → 415), 324.6 (415 → 367), 296.9 (415 → 351)
9	NO_2	H	**9d**	51848-94-3	82	3	551	460	412	396	384.0 (551 → 460), 308.1 (551 → 412), 369.0 (460 → 412), 340.9 (460 → 396)

[a] Further details of these spectra are given in the Experimental Section. [b] $F_1 = M\cdot^{+} - p\text{-}ZC_6H_4CH_2$, $F_2 = M\cdot^{+} - p\text{-}ZC_6H_4CH_2SO$, $F_3 = M\cdot^{+} - p\text{-}ZC_6H_4CH_2SO_2$.

dride instead of tosyl fluoride. The yield of **3a** (R^1 = *p*-tolyl; R^2 = phenyl) was the same in both cases (12%). Much better results, however, were obtained when benzylidenetriphenylphosphorane (**5a,** Y = H, eq 2) was sulfonylated with *methane*sulfonyl fluoride (**4**, R^3 = H; X = F). Surprisingly, the product of this smoothly occurring reaction was not the expected compound **6** (R^3 = Y = H). Instead, the isomeric ylide **7a,** in which an apparent migration of the phenyl group has occurred, was formed in 95% yield. The same product (**7a**) was obtained with methanesulfonic anhydride (4, R^3 = H; X = OSO_2Me).

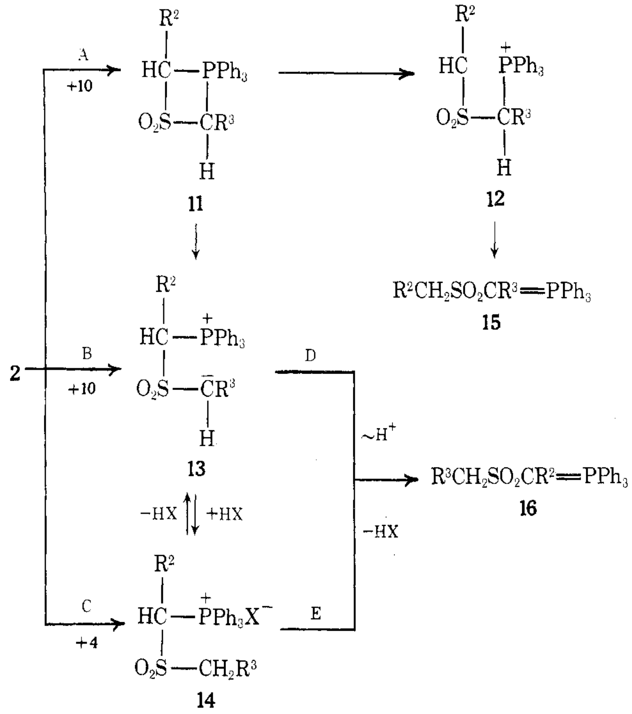
The structure of compound **7a** is supported by its pmr spectrum (see Table V), which shows an one-proton doublet at δ 2.60 with a J_{P-H} of 13 Hz. Further, the same compound was prepared[1] previously according to eq 1, with $R^1 = C_6H_5CH_2$; R^2 = H.

An analogous rearrangement was observed in the reaction of benzylidenephosphorane and ethanesulfonyl fluoride, providing ylide **7c** (eq 21), which means that phenyl can be interchanged with a methyl group also. Rearrangement fails to occur, however, when R^3 becomes the bulky *tert*-butyl group. Here, the only observed product is the unrearranged ylide **6d** (77% yield). These results, summarized in Table I (expt 1–5), demonstrate that steric effects strongly influence the course of the reaction.

The rearranged structure of **7c** (which is identical with ylide **16j**, Table III) follows from the presence of a three-proton doublet for R^3 = Me at δ 1.60 with J_{P-H} = 13 Hz. Compound **7c** shares this feature with a number of similar ylides (**15d, 16e, 16g,** and **17**, Table V), and in particular with α-tosylethylidenetriphenylphosphorane (**3b**), which has been prepared by a reaction occurring without rearrangement (*vide infra*). Futhermore, **7c** shows a benzylic methylene singlet at δ 4.00 (comparable to that of **7a** at δ 3.89), which differs clearly from the neopentyl methylene singlet at δ 2.70 of (unrearranged) **6d.** Also, the singlets of

Scheme I

$$\underset{\mathbf{4}}{R^3CH_2SO_2X} + \underset{\mathbf{2}}{2R^2CH{=}PPh_3} \longrightarrow \underset{\mathbf{10}}{R^3CH{=}SO_2} + R^2CH_2\overset{+}{P}Ph_3X^- \quad (4)$$



[a][2 + 2] cycloaddition.

6d at δ 0.91 (9 H) and 2.70 (2 H) are compatible with the neopentylsulfonyl group by comparison with compounds **15c, 15d,** and **16h** (Table V).

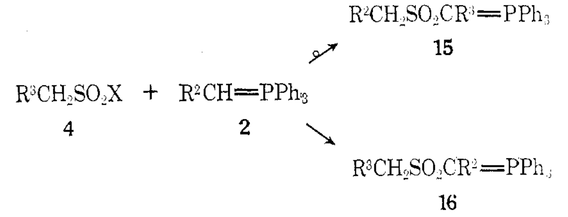
In a subsequent series of reactions the influence of steric effects was elaborated. With substituents of approximately the same size in both reaction partners (*i.e.*, differently para-substituted aryl groups) rearrangement was not observed at all (eq 3, expt 6–9 in Table II).

Although the benzylic protons of **9c** (δ 4.06, Z = NO_2) are found at somewhat lower field than those of **9a,b,d** (δ 3.88–3.98, Z = H; see Table V), the small difference hardly provides a basis for structural assignment. More convincing evidence, however, comes from the mass spectral data given in Table II. All compounds **9** evidently lose the uncharged fragments $p\text{-}ZC_6H_4CH_2$, $p\text{-}ZC_6H_4CH_2SO$, and $p\text{-}ZC_6H_4CH_2SO_2$ from the parent ion ($M\cdot^+$) to give the peaks F_1, F_2, and F_3, respectively. Several of these fragmentations are supported by metastables.

Discussion. The formation of rearranged product (expt 1–4, products **7a–c**, Table I) can be explained by invoking a four-membered ring intermediate **11** (Scheme I). At least three different routes (A, B, and C) to **11** are conceivable, and these will be commented on below. Ring opening of intermediate **11** could lead to **12** and/or **13**. When R^2 = aryl and R^3 = H or CH, relief of steric strain will lead to preferential formation of **12**. Moreover, a phenyl group at R^2 will stabilize the negative charge in **12**, as compared to **13**. Even with a donating methoxy substituent attached to phenyl (*i.e.*, **11**, $R^2 = p\text{-}CH_3OC_6H_4$; R^3 = H) only rearranged product **15** (*i.e.*, **7b** in eq 2) was obtained.

However, a bulky *tert*-butyl group at R^3 will outweigh any electronic factors. Assuming that a four-membered ring intermediate is reached at all, maximum relief of steric strain is obtained now by going from **11** to **13**. Thus, ylide **16** (*i.e.*, **6d** in eq 2) is formed without rearrangement (expt 5), a product which alternatively can be explained through reactions B–D or C–E (Scheme I).

Table III
Reactions of Alkylidenephosphorane and (Ar)alkanesulfonyl Fluoride (Anhydride)

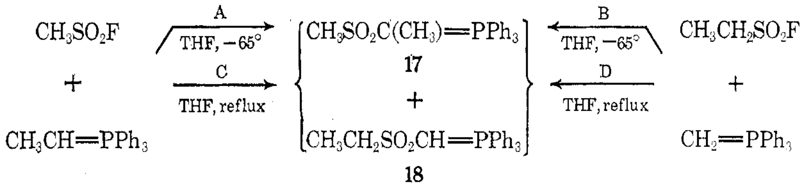


$$\underset{\mathbf{4}}{R^3CH_2SO_2X} + \underset{\mathbf{2}}{R^2CH{=}PPh_3} \begin{array}{l} \nearrow \underset{\mathbf{15}}{R^2CH_2SO_2CR^3{=}PPh_3} \\ \searrow \underset{\mathbf{16}}{R^3CH_2SO_2CR^2{=}PPh_3} \end{array} \quad (5)$$

Expt	R^3	X	R^2	Product	Registry no.	Yield, %	Reaction conditions Time, hr	Reaction conditions Temp, °C
10	H	F	H	**16a**[a,b]	5554-83-6	70	1	Room
11	H	OSO_2Me	H	**16a**[a,b]		73	1	Room
12	H	OSO_2Me	1-Adamantyl	**15b**	51848-95-4	51	0.5	Room
13	H	OSO_2Me	*t*-Bu	**15c**	51848-96-5	58	0.5	Room
14	H	F	*t*-Bu	**15c**		69	0.5	Room
15	H	F	*t*-Bu	**15c**[c]		65	1	−90
16	Me	F	*t*-Bu	**15d**	51848-97-6	65	1	Room
17	Me	F	*t*-Bu	**15d**[d]		76	4	−90
18	*t*-Bu	F	Me	**16e**[e]		50	1	Room
19	*i*-Pr	F	H	**16f**	51848-98-7	63	1	−95
20	Me	F	Me	**16g**[a]	51848-99-8	75	0.5	Room
21	*t*-Bu	F	*t*-Bu	**16h**[a]	51849-00-4	3	0.5	Room
22	Ph	F	H	**16i**[b,f]		63	1	Room
23	Ph	F	Me	**16j**[g,h]		30	1	Room
24	Ph	F	*t*-Bu	*i*			1	Room

[a] In those cases where $R^2 = R^3$, no distinction can be made between rearranged and unrearranged products. [b] Compound reported previously, ref 1. [c] In addition to the rearranged product **15c**, the unrearranged ylide $CH_3SO_2C(t\text{-}Bu){=}PPh_3$ (**16c**) was obtained in low yield (1.3%). [d] In addition to the rearranged product **15d**, the unrearranged ylide $C_2H_5SO_2C(t\text{-}Bu){=}PPh_3$ (**16d**) was obtained in 7% yield. [e] Compound **16e** is identical with **15d**. [f] Identical with compound **7a** (Table I). [g] In addition to the compound listed (**16j**), a bis-sulfonylated ylide, still containing an unrearranged ethylidenephosphorane moiety, $PhCH_2SO_2CH(Ph)SO_2C(CH_3){=}PPh_3$ (**23**), was obtained in 33% yield (see Experimental Section). [h] Identical with compound **7c** (Table I). [i] In contrast to expt 23, here we isolated only bis-sulfonylated ylide, with a rearranged neopentylidenephosphorane moiety, $t\text{-}BuCH_2SO_2CH(Ph)SO_2C(Ph){=}PPh_3$ (**24**) in 31% yield (see Experimental Section).

Table IV
Reaction of Methanesulfonyl Fluoride with Ethylidenephosphorane and Ethanesulfonyl Fluoride with Methylenephosphorane



$$\begin{Bmatrix} CH_3SO_2F \\ + \\ CH_3CH{=}PPh_3 \end{Bmatrix} \xrightarrow[\text{C: THF, reflux}]{\text{A: THF, }-65^\circ} \begin{bmatrix} CH_3SO_2C(CH_3){=}PPh_3 \ \mathbf{17} \\ + \\ CH_3CH_2SO_2CH{=}PPh_3 \ \mathbf{18} \end{bmatrix} \xleftarrow[\text{D: THF, reflux}]{\text{B: THF, }-65^\circ} \begin{Bmatrix} CH_3CH_2SO_2F \\ + \\ CH_2{=}PPh_3 \end{Bmatrix} \qquad (6)$$

Expt	Path	Product	Yield, %	Product	Yield, %	Reaction conditions Time, min	Reaction conditions Temp, °C
25	C	**17**	30[a]	**18**	50[a]	15	Reflux
26	A	**17**	62			15	−65
27	D	**17**	32[a]	**18**	64[a]	15	Reflux
28	B	**17**	83			15	−65

[a] Yields of **17** (registry no., 51849-01-5) and **18** (51849-02-6) were determined by pmr analysis of the mixture of isomers.

When R^2 and R^3 are both aryl groups, rearrangement was not observed (expt 6–9, Table II). Since steric factors must be of minor importance here, electronic factors could in principle determine the sense of ring opening in intermediate **11**. Thus, especially when R^2 = *p*-nitrophenyl and R^3 = phenyl (expt 9) at least partial rearrangement *via* **12** to **15** could have occurred; however, such a reaction was not observed. We therefore tend to conclude that for R^2 and R^3 = aryl intermediate **11** is not formed, but that reaction rather occurs through the reaction sequences B–D or C–E (Scheme I). This view is supported by the failure to isomerize ylide **9d** to **9c** by refluxing **9d** with, or without, butyllithium for 15 hr in tetrahydrofuran. Compound **9d** was recovered unchanged.

α-Sulfonylalkylidenetriphenylphosphoranes

Extension of the previously reported[1] reaction of tosyl fluoride and methylenetriphenylphosphorane (**2**, R^2 = H, eq 1) was possible to the homologous ethylidenetriphenylphosphorane, providing **3b** (R^1 = *p*-tolyl; R^2 = CH_3) in 50% yield. When, however, the size of the substituent R^2 in ylide **2** was increased to *tert*-butyl or 1-adamantyl, sulfonylation with either tosyl fluoride or *p*-toluenesulfonic anhydride was no longer possible.

The same bulky substituents in **2** did not prevent, on the other hand, sulfonylation by *aliphatic* sulfonyl fluorides or *aliphatic* sulfonic anhydrides. In general, alkylidenephosphoranes react smoothly according to eq 5.

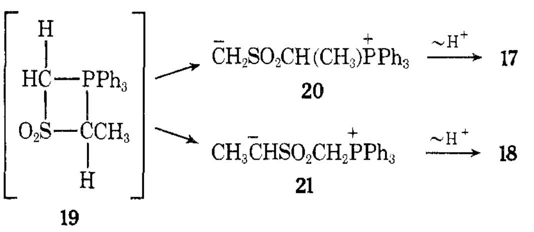
The majority of the compounds listed in Table III belong either to the category of ylides with an α-methine proton, showing a one-proton doublet at δ 2.6–2.9, J_{P-H} = 13–14 Hz (compounds **15b**, **15c**, **16a**, **16f**, **16i**), or to the group of ylides with an α-methyl group characterized by a three-proton doublet at δ 1.6–1.8, J_{P-H} = 13 Hz (compounds **15d**, **16e**, **16g**, **16j**, **23**, see Table V). A third group of ylides (**16c**, **16d**, **16h**, with an α-*tert*-butyl substituent, was obtained in low yield in addition to the more abundant isomers **15c** and **15d** (in expt 15 and 17, respectively), or as the sole product in expt 21. The structures of **16c**, **16d**, and **16h** follow from comparison of the pmr spectra of the isomers (Table V), and by the great similarity of the mass spectra after loss of the $R^2CH_2SO_2$ fragments, *i. e.*, by the fragmentation pattern of the *t*-BuC=PPH$_3$ (315) segment (see Experimental Section).

Discussion. Whether rearranged product (**15**) is formed or not depends primarily on the difference in size between R^2 and R^3, and also to some extent on the reaction temperature. For example, the reaction of neopentylidenetriphenylphosphorane (**2**, R^2 = *t*-Bu) with methane- or ethanesulfonyl fluoride led to rearranged product **15** (R^2 = *t*-Bu; R^3 = H or Me, respectively; expt 14 and 16, Table III). At low temperature (−90°) minor quantities of unrearranged product **16** were obtained as well (1.3 and 7%, respectively; expt 15 and 17). Rearrangement also was observed with 1-adamantylmethylenephosphorane (**2**, R^2 = 1-Ad) and methanesulfonic anhydride (expt 12). Conversely, only unrearranged ylides **16** were obtained when a buky substituent was present in the sulfonyl fluoride **4** (R^3 = *t*-Bu or *i*-Pr) against a small substituent in the phosphorane **2** (R^2 = Me or H, respectively; expt 18 and 19). These results can be explained by assuming a cyclic four-membered ring intermediate **11** (see Scheme I). The direction of ring opening (to give **12** or **13**) will be determined by maximum relief of steric strain, in agreement with the main products in expt 12–19.

The unrearranged products in expt 18 and 19 need not necessarily be formed through **11**, but can be explained alternatively by the routes B–D or C–E (Scheme I). The same holds, of course, for the reactions where R^2 equals R^3 (expt 10, 11, 20, and 21). In expt 21, with R^2 = R^3 = *t*-Bu, only a very low yield (3%) of ylide **16** is obtained, which obviously reflects steric problems.

Intermediates 11 and 19. The results of expt 25–28 (Table IV and eq 6) deserve special consideration. The following observations were made. (1) At −65° methanesulfonyl fluoride and ethylidenetriphenylphosphorane gave exclusively ylide **17** (62% yield), which constitutes a reaction *without* rearrangement (reaction 6A; expt 26). (2) On the other hand, ethanesulfonyl fluoride and methylenetriphenylphosphorane gave at the same temperature only the same product **17** (83% yield), which means a reaction occurring exclusively *with* rearrangement (reaction 6B; expt 28). (3) In refluxing tetrahydrofuran after 15 min these two reactions (expt 25 and 27) gave a mixture of the ylides **17** and **18** in nearly the same ratio **17**/**18** = 0.6 and 0.5, respectively. This means a preference for rearranged product in reaction 6C (expt 25), against a comparable preference for unrearranged product in reaction 6D (expt 27). (4) When the reaction mixture, prepared at −65° according to 2 and containing **17** only, was refluxed afterwards for 3.5 hr no **18** was formed at all. Ylide **17** was isolated in a yield of 89%. (5) Pure **17** was recovered unchanged after 19 hr of reflux in tetrahydrofuran in the presence of 0.1 equiv of methylenetriphenylphosphorane.

We feel that these results are explained satisfactorily, in accordance with Scheme I, by eq 7. The four-membered ring structure **19** (analogous to **11** in Scheme I) is the common intermediate in all reactions indicated in eq 6. Without the bulky substituents discussed above, **19** will now, at reflux temperature, ring open in either of two directions to give **20** and **21**, which will lead to the kinetically controlled products **17** and **18**, respectively. The (small) preponderance of **18** in the ylide mixture, irrespective of the starting materials, indicates that ring opening to **21** is still sterically favored to some extent. Since pure **17** could not be isomerized to **18**, the ring opening and/or the proton shift must be an irreversible process under the conditions studied.



(7)

At −65°, the ring opening of **19** apparently goes in a single direction (to **20**). We tentatively assume that at this low temperature the selectivity is controlled by the greater stability of the carbanion segment in betaine **20** than in **21**.

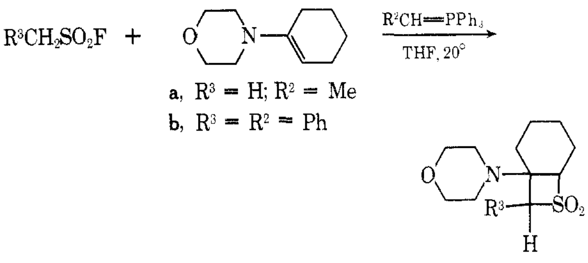
Reaction of ^{13}C-enriched methanesulfonyl fluoride with benzylidenetriphenylphosphorane, as an initial probe into a more detailed mechanistic study, gives rearranged ylide **7a** with the label exclusively at the methine carbon, in agreement with the proposed mechanisms *via* **11**. Furthermore, in a similar reaction with methylenetriphenylphosphorane the label is completely scrambled over the methine carbon and the methyl carbon of the resulting methylsulfonylmethylenetriphenylphosphorane (**16a**). This is consistent with, but not conclusive for, a [2 + 2] cycloaddition leading to a trigonal bipyramidal structure[11] of the intermediate **11** ($R^2 = R^3 = H$). Pseudo-rotation[11] then could distribute the label over the apical and equatorial methylene positions before ring opening occurs.

A four-membered ring transition state, comparable to the intermediate **11** (and **19**), was assumed previously by Ito, *et al.*,[2b] to explain the rearrangement observed in the reaction of α-carboalkoxyethylidenetriphenylphosphorane and sulfene to give α′-carboalkoxyethylsulfonylmethylenetriphenylphosphorane. Furthermore, Bestmann[4] has described a four-membered ring transition state to explain a similar rearrangement in the reaction of isopropylidenetriphenylphosphorane and ketene. In these two instances, substitution at C_α of the already *di*substituted methylenephosphorane derivatives was no longer possible. We now have shown the possibility of rearrangement in phosphorus ylide reactions, even though substitution without rearrangement could have occurred as an alternative.

Intermediacy of Sulfenes. The different reactions observed with arylsulfonyl fluorides on the one hand, and alkyl- or aralkylsulfonyl fluorides on the other, are suggestive of a sulfene intermediate **10**, generated by elimination of hydrogen fluoride from the latter type of sulfonyl fluorides[5] (reaction 4 in Scheme I). Similarly, sulfene may be generated from methanesulfonic anhydride[6] in expt 2, 3, 12, and 13.

$$EtSO_2Cl + CH_2{=}PPh_3 \xrightarrow[20^\circ]{THF} ClCH_2\overset{+}{P}Ph_3EtSO_2^- \qquad (8)$$

Support for such a sulfene intermediate was obtained by the following observations. (1) Ethanesulfonyl *chloride* and methylenetriphenylphosphorane reacted by nucleophilic attack on the chlorine atom,[1] without the formation of sulfonylated ylide (reaction 8). (2) When the same reaction was carried out in the presence of an excess of triethylamine, which is known to generate sulfenes,[7] a 1:1 mixture of the ylides **17** and **18** was obtained in a total yield of 33% (compare reaction 6D, with Cl instead of F). (3) When reaction 6C was repeated (at room temperature) in the presence of an excess of the sulfene-trapping reagent *N*-(1-cyclohexenyl)morpholine,[8] thietane *S,S*-dioxide **22a** indeed was formed in 60% yield (reaction 9). (4) The same reaction without the addition of ethylidenetriphenylphosphorane did not give **22a**.[8b,9] (5) Analogous to the formation of **22a**, phenylmethanesulfonyl fluoride gave thietane dioxide **22b**.[10]



(9)

22

This evidence supports the existence of sulfene intermediates in the reactions of alkyl- and aralkylsulfonyl fluorides with phosphoranes. Therefore path C in Scheme I seems unlikely. It now follows that for the reactions of arylidenephosphoranes with aralkylsulfonyl fluorides (expt 6–9, occurring without rearrangement, see Table II) path B–D is most likely, since path A was already rejected in a previous section of this paper. On the other hand, the failure to isomerize **17** to **18** and the nearly constant ratio **17**/**18** in reactions 6C and 6D (see previous section) are in favor of a [2 + 2] cycloaddition to **19**, followed by an irreversible ring opening to **20** and **21** (eq 7). By extrapolation we propose this mechanism for all other reactions of Tables I, III, and IV that occur with rearrangement, following path A in Scheme I.

Concluding Remarks

The present work offers the opportunity to design a practical synthesis for almost any sulfonylmethylenephosphorane substituted with alkyl or aryl at the ylide carbon. An exception must be made, however, for very large substituents such as *tert*-butyl and adamantyl. The mechanistic interpretation is at this stage unavoidably speculative.

Experimental Section

The ir spectra were run on a Perkin-Elmer 257 grating spectrometer from samples in Nujol, unless stated otherwise. Pmr spectra were taken on Varian A-60 or A-60D apparatus; they were recorded in δ values (parts per million) downfield from TMS used as an internal standard. Mass spectra were determined by Mr. A. Kiewiet with an AEI ms 902 apparatus operating at 70 eV and using a direct inlet system.

Melting points were determined on a Mettler FP 2 apparatus equipped with a Mettler FP 52 microscope attachment.

The elemental microanalyses of all new compounds were carried out in the Analytical Department of this laboratory under the supervision of Mr. W. M. Hazenberg by Mr. H. Draaijer, Mr. J. Ebels, and Mr. J. Vos, and found within 0.4% of the calculated values.

Starting Materials. Literature references to the starting materials follow: $R^3CH_2SO_2F$[12] (R^3 = H, Me, *i*-Pr, Ph); $(MeSO_2)_2O$;[13] $R^2CH{=}PPh_3$ (R^2 = H,[14] Me,[15] Ph,[16] *p*-$CH_3OC_6H_4$,[17] *p*-$O_2NC_6H_4$[18]).

***p*-Nitrophenylmethanesulfonyl Fluoride.** According to Davies and Dick [12] *p*-nitrophenylmethanesulfonyl chloride[19] (10.0 g, 42.5 mmol) was converted into the corresponding fluoride by heating with 70% aqueous potassium fluoride (6 ml) for 1.5 hr at 100 °. The yield, after crystallization from dichloromethane–hexane, was 1.5 g (6.8 mmol, 16%) of *p*-nitrophenylmethanesulfonyl fluoride: mp 127–128°; pmr ($CDCl_3$) δ 4.71 (2 H, d, J_{F-H} = 3 Hz), AB quartet at 7.65 (2 H) and 8.32 (2 H) (*J* = 8.5 Hz); ir (Nujol) 1530 and 1355 (NO_2), 1400 and 1210–1220 cm^{-1} (SO_2).

Neopentanesulfonyl Chloride. Neopentanesulfonyl chloride, prepared previously by two unattractive methods,[20] was obtained in good yield *via* an alternate route by chlorination[19a] of neopentanethiol[21] in aqueous medium.

Pieces of sodium (19.0 g, 0.83 g-atom) were added all at once, without cooling, to diethyleneglycol monomethyl ether (250 ml) under nitrogen. After 2 hr of vigorous stirring the resulting homogeneous solution was chilled to 0° and saturated with hydrogen sulfide. Neopentyl *p*-toluenesulfonate[22] (130 g, 0.54 mol) was added, after which the mixture was refluxed for 2.5 hr and subsequently cooled to room temperature. Dilution with ice-water (500 ml) was followed by treatment with concentrated hydrochloric acid to pH 3–4. The resulting oil was separated and the water was extracted with diethyl ether (2 × 250 ml). The combined organic layers were dried over anhydrous sodium sulfate and concentrated at atmospheric pressure (bath temperature not exceeding 45°).

A vigorously stirred mixture of the crude neopentanethiol and 500 ml of ice-water was saturated with chlorine as fast as possible at a temperature not exceeding 10°. The reaction mixture was extracted with diethyl ether (3 × 200 ml), and the ethereal solution was washed with 5% sodium hydrogen sulfite solution and then with water and dried over anhydrous sodium sulfate. The ether was removed at atmospheric pressure (bath temperature not exceeding 45°). The crude neopentanesulfonyl chloride was distilled at reduced pressure under nitrogen from solid potassium carbonate.[23] Thus, 66.0 g (0.39 mol, 72% based on neopentyl *p*-toluenesulfonate) of neopentanesulfonyl chloride was obtained: bp 35–36° (0.5 mm); $n^{19}\mathrm{D}$ 1.4585 (lit.[20] $n^{25}\mathrm{D}$ 1.4556); pmr ($CDCl_3$) δ 1.26 (9 H, s), 3.80 (2 H, s); ir (neat) 1370 and 1170 cm^{-1} (SO_2).

Neopentanesulfonyl Fluoride. A 70% aqueous solution of potassium fluoride (42.0 g, 0.72 mol) was heated to 80°. After addition of neopentanesulfonyl chloride (34.0 g, 0.2 mol) the temperature was raised in 5 min to 100° under vigorously stirring. Additional stirring at 100° over a period of 10 min (a longer reaction time lowered the yield) was followed by rapid cooling to room temperature. The reaction mixture was diluted with ice-water (150 ml) and extracted with diethyl ether (3 × 100 ml). The organic layer was washed with water (50 ml), dried over anhydrous sodium sulfate, and concentrated at atmospheric pressure (bath temperature not exceeding 45°). The residual oil was distilled from solid potassium carbonate, providing 14.3 g (0.093 mol, 46%) of neopentanesulfonyl fluoride: bp 23° (0.4 mm); $n^{23}\mathrm{D}$ 1.4121; pmr ($CDCl_3$) δ 1.23 (9 H, d, $J = 1$ Hz), 3.33 (2 H, d, $J_{\mathrm{F-H}} = 3$ Hz); ir (neat) 1410 and 1206 cm^{-1} (SO_2); mass spectrum (70 eV, 60°, cold inlet system) *m/e* (rel abundance) 139 (55), 138 (26), 75 (40), 71 (42), 70 (100), 64 (11), 57 (100), 56 (49), 55 (100), 43 (64), 41 (96), 39 (57), 29 (82), 27 (49) (no molecular ion present). Sufficiently pure material for elemental analysis could not be obtained even after repeated distillation.

Neopentyltriphenylphosphonium Iodide. The procedure of Seyferth and Singh[24] was modified to avoid the use of an excess of neopentyl iodide. A stirred solution of neopentyl iodide[25] (36.0 g, 0.182 mol) and triphenylphosphine (48.0 g, 0.182 mol) in sulfolane (25 ml) was heated at 160° in a nitrogen atmosphere for 24 hr. Sulfolane was removed at reduced pressure. After work-up as described by Seyferth, *et al.*, 77 g (0.167 mol, 91%) of neopentyltriphenylphosphonium iodide was obtained, decomposing at *ca.* 197° (melting point not reported by Seyferth[24]).

1-Iodomethyladamantane. The starting material 1-hydroxymethyladamantane was obtained by reduction of 1-adamantylcarboxylic acid[26] with $LiAlH_4$ in refluxing diethyl ether over a period of 24 hr, according to the procedure for the reduction of *tert*-butylcarboxylic acid.[27] The yield was 98%, mp 115–117° (lit.[28] mp 115°).

According to the procedure of Stone and Shechter[29] 1-iodomethyladamantane was prepared as follows. Orthophosphoric acid (200 g, 85%, Merck) was added, with stirring, to 52 g of phosphoric anhydride. After cooling of the resulting 95% orthophosphoric acid to room temperature, sodium iodide (34.0 g, 0.226 mol) and 1-hydroxymethyladamantane (24.0 g, 0.145 mol) were added. The mixture was stirred and heated at 105° for 3 hr under nitrogen, and then poured into water (4 l.) under vigorously stirring. The crude product was collected, washed with water, and dissolved in diethyl ether (500 ml). The ethereal solution was washed with 0.2 *N* sodium thiosulfate to remove the color, washed with water (2 × 150 ml), and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was crystallized from hexane (30 ml), providing 32.3 g (0.117 mol, 81%) of 1-iodomethyladamantane: mp 53.5–54.0°; pmr ($CDCl_3$) δ 1.4–1.7 (12 H, m), 1.95 (3 H, br), 3.01 (2 H, s).

1-Adamantylmethyltriphenylphosphonium Iodide. A solution of 1-iodomethyladamantane (12.0 g, 43.5 mmol) and triphenylphosphine (11.4 g, 43.5 mmol) in sulfolane (125 ml) was heated, with stirring, at 205° for 22 hr in a nitrogen atmosphere. Sulfolane was removed at 85° (0.2 mm). The resulting solid was washed intensively with ethyl acetate (200 ml) and, next, crystallized from chloroform (150 ml) and diethyl ether (400 ml), providing 21.7 g (40.3 mmol, 93%) of 1-adamantyltriphenylphosphonium iodide: decomposing at 291–293° (melting block); pmr ($CDCl_3$) δ 1.3–2.0 (15 H, m), 3.63 (2 H, d, $J_{\mathrm{P-H}} = 13$ Hz), 7.5–8.3 (15 H, m). Crystallization from dichloromethane–acetone furnished an analytically pure sample, decomposing at the same temperature.

***α*-Tosylbenzylidenetriphenylphosphorane (3a, Eq 1).** The sulfonylation of benzylidenetriphenylphosphorane with *p*-toluenesulfonic anhydride[30] was performed by the same procedure reported[1] for the sulfonylation of benzylidenetriphenylphosphorane with tosyl fluoride. With both sulfonylating agents the same yield of **3a** (12%) was obtained, identical by mixture melting point, pmr, and ir.

***α*-Tosylethylidenetriphenylphosphorane (3b, Eq 1) and Hydrolysis.** According to the general procedure for the preparation of monosulfonyl-substituted methylenetriphenylphosphoranes,[1] ethylidenetriphenylphosphorane (prepared form 7.42 g, 20 mmol, of the corresponding phosphonium bromide[15]) was tosylated with tosyl fluoride (1.74 g, 10 mmol), affording 2.22 g (5.0 mmol, 50%) of **3b**, mp 185–187°. Analytically pure material with the same melting point was obtained by crystallization from dichloromethane–diethyl ether. Spectral data are compiled in Table V.

Hydrolysis of **3b** (0.60 g, 1.35 mmol) with 0.5 g of sodium hydroxide in 30 ml of refluxing water–dioxane (1:1, 1 hr) provided 0.20 g (81%) of ethyl *p*-tolyl sulfone, mp 54–56° (Beilstein **6**, 417, mp 55–56°).

***α*-Sulfonylarylidenetriphenylphosphoranes and *α*-Sulfonylalkylidenetriphenylphosphoranes (Tables I–IV, Expt 1–28).** ***α*-Benzylsulfonylbenzylidenetriphenylphosphorane (9a, Expt 6).** At room temperature, under nitrogen, a solution of butyllithium in hexane (10 ml, 2.0 *M*, 20 mmol), was added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide[16] (8.66 g, 20 mmol) in tetrahydrofuran (250 ml). After stirring for 30 min, a solution of benzylsulfonyl fluoride[12] (1.74 g, 10 mmol) in tetrahydrofuran (30 ml) was added dropwise in *ca.* 15 min. A white precipitate formed immediately. Stirring was continued for 30 min. The precipitate was removed and the filtrate was concentrated *in vacuo*. The residue was dissolved in chlorobenzene (250 ml) and washed with water (3 × 100 ml). After drying over anhydrous sodium sulfate, the chlorobenzene was removed *in vacuo* and the residue was triturated with ether (50 ml). The white solid was collected and washed with a little ether, providing 4.61 g (9.1 mmol, 91%) of **9a**, mp 209–210.5°. After crystallization from dichloromethane–diethyl ether, material sufficiently pure for elemental analysis was obtained: mass spectrum (70 eV, 200°, direct inlet system) *m/e* (rel abundance >35) 506 (36), 415 (71), 367 (35), 351 (100), 183 (54), 165 (92), 105 (95), 91 (35).

The procedure given for **9a** (expt 6) is typical for most of the experiments 1–28. Experiments, 9, 15, 17, 21, 23, and 24, however, are described separately below.

In some of the experiments, carried out on the same molar scale as **9a**, minor but essential differences have to be considered as follows (number of experiments, milliliters of THF, milliliters of chlorobenzene): 8, 400, 250; 18, 250, 500; 25–28, 500, 250. After the crude product was triturated with the appropriate solvent (*i.e.*, ethyl acetate for expt 2, 3, and 7; ether–pentane for expt 1, 5, 14, 16, 18, and 25–28; and ether for all others), the solid was found to be isomerically pure sulfonylphosphorane by pmr (except, of course, in expt 25 and 27). The concentrated mother liquid was discarded, after the absence of isomeric sulfonylphosphorane had been established by pmr. Also, the precipitated phosphonium salts were dissolved in water to demonstrate the absence of any water-insoluble ylide in these fractions.

Melting points and ir and pmr data of the products are compiled in Table V. Mass spectral data of the products of expt 9, 15, 17, 21, and 23 are described below. The mass spectral data of compounds **9b** and **9c** follow: **9b** (70 eV, 135°, direct inlet system) *m/e* (rel abundance >23) 536 (31), 381 (45), 278 (55), 277 (100), 262 (23), 231 (23), 183 (31), 152 (25), 135 (56), 121 (58), 91 (44), 77 (28); **9c** (70 eV, 180°, direct inlet system) *m/e* (rel abundance > 25) 551 (43), 415 (86), 367 (43), 352 (32), 351 (100), 183 (25), 165 (45), 105 (75).

***α*-Benzylsulfonyl-*p*-nitrobenzylidenetriphenylphosphorane (9d, Expt 9).** Contrary to the procedure given above for **9a**, an excess of solid benzylsulfonyl fluoride[12] (3.48 g, 20 mmol) was added all at once to a solution of *p*-nitrobenzylidenetriphenylphosphorane (prepared from 8.67 g, 20 mmol, of *p*-nitrobenzyltri-

Table V
Melting Points and Spectral Data of the Sulfonyl-Stabilized Phosphonium Ylides

Compd	Mp, °C (from)	Ir (Nujol), cm^{-1} ν_{SO_2} (asym)	Ir (Nujol), cm^{-1} ν_{SO_2} (sym)	Pmr ($CDCl_3$), δ ppm nonaromatic protons[a]
3b	185–187[g]	1260	1120 1100	1.70 (d, 3 H, J_{P-H} = 13 Hz), 2.33 (s, 3 H)
7a = **16i**[b]	172–174	1280	1114 1104	2.60 (d, 1 H, J_{P-H} = 13 Hz), 3.89 (s, 2 H)
7b	214–215 (CH_2Cl_2–Et_2O)	1270 1252	1105	2.53 (d, 1 H, J_{P-H} = 14 Hz), 3.78 (s, 3 H), 3.81 (s, 2 H)
7c = **16j**	171.5–172.5 (CH_2Cl_2–Et_2O)	1275 1252	1111	1.60 (d, 3 H, J_{P-H} = 13 Hz), 4.00 (s, 2 H)
6d	163.5–164.5 (Et_2O)	1271	1115 1110	0.91 (s, 9 H), 2.70 (s, 2 H)
9a	210–211 (CH_2Cl_2–Et_2O)	1270 1250	1110	3.96 (s, 2 H)
9b	194–195 (CH_2Cl_2–Et_2O)	1247	1100 1097	3.70 (s, 3 H), 3.98 (s, 2 H)
9c[c]	214.5–215 (EtOAc)	1253	1110	4.06 (s, 2 H)
9d[d]	275–276[g]	1285 1263	1106	3.88 (s, 2 H)
16a[b]	202–204	1267	1118 1107	2.75 (s, 3 H), 2.83 (d, 1 H, J_{P-H} = 14 Hz)
15b	140–141 ($CHCl_3$–Et_2O)	1272	1111	1.4–2.1 (br, 15 H), 2.57 (s, 2 H), 2.87 (d, 1 H, J_{P-H} = 14 Hz)
15c	146–147 (CH_2Cl_2–hexane)	1266	1114 1110 1102	1.03 (s, 9 H), 2.70 (s, 2 H), 2.88 (d, 1 H, J_{P-H} = 14 Hz)
16c	222–223.5[g]	1253 1245	1103	1.15 (s, 9 H), 2.76 (s, 3 H)
15d = **16e**	*g*	1260	1105	0.98 (s, 9 H), 1.72 (d, 3 H, J_{P-H} = 13 Hz), 2.69 (s, 2 H)
16d	183–184[g] (Et_2O)	1258	1110 1098	1.12 (s, 9 H), 1.02 (t, 3 H, J = 7 Hz), 2.87 (q, 2 H, J = 7 Hz)
16f	125–126 (EtOAc)	1275 1250	1112 1100	0.92 (d, 6 H, J = 6.5 Hz), 2.17 (m, 1 H, J = 6.5 Hz), 2.58 (d, 2 H, J = 6.5 Hz), 2.80 (d, 1 H, J_{P-H} = 14 Hz)
16g	162–163 (EtOAc–$CHCl_3$–Et_2O)	1262	1105	1.17 (t, 3 H, J = 7 Hz), 1.76 (d, 3 H J_{P-H} = 13 Hz), 2.80 (q, 2 H, J = 7 Hz)
16h	219–220 dec[g]	1250	1100	0.85 (s, 9 H), 1.14 (s, 9 H), 2.8 (br, 2 H)
17	200–201 ($CHCl_3$–Et_2O)	1256	1104	2.74 (s, 3 H), 1.72 (d, 3 H, J_{P-H} = 13 Hz)
18		1250	1113 1098	1.18 (t, 3 H, J = 7.5 Hz), 2.68 (q, 2 H, J = 7.5 Hz)
23[e]	191–192[g]	1287	1128 1115 1108	1.60 (d, 3 H, J_{P-H} = 13 Hz), AB quartet consisting of two doublets at 4.40 and 4.70 (2 H, J = 15 Hz), 4.61 (s, 1 H)
24[f]	201–202[g]	1292	1120 1110	1.06 (s, 9 H), 3.30 (q, 2 H, J = 14 Hz), 4.80 (s, 1 H)

[a] All spectra showed the expected aromatic protons. [b] Compound reported previously, ref 1. [c] Ir 1520 and 1354 cm^{-1} (NO_2). [d] Ir 1580 and 1336 cm^{-1} (NO_2). [e] Ir 1326 and 1170–1160 cm^{-1} (SO_2). [f] Ir 1323 and 1142 cm^{-1} (SO_2). [g] See Experimental Section.

phenylphosphonium chloride[18]) in tetrahydrofuran (250 ml). The reaction mixture was stirred for 3 hr. The yellow precipitate was collected and washed by intensively stirring with water (1 l.). The crude material was dissolved in dichloromethane (250 ml), washed with water (3 × 100 ml), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The yellow material was washed with ether (50 ml), affording 3.70 g of **9d** (6.7 mmol, 67% calculated on the theoretically convertible amount of benzylsulfonyl fluoride), mp 269–271°. After crystallization from dichloromethane–diethyl ether, dichloromethane–acetone, and dichloromethane–diethyl ether, respectively, analytically pure material was obtained: mp 275–276°; mass spectrum (70 eV, 225°, direct inlet system) *m/e* (rel abundance >23) 551 (14), 461 (34), 460 (100), 412 (45), 396 (47), 183 (23).

The tetrahydrofuran filtrate was concentrated. The residual oil was dissolved in chlorobenzene (250 ml) and washed with water (3 × 100 ml). During the washings a pH of 7 was maintained by addition of 2 *N* hydrochloric acid to prevent contamination of the chlorobenzene layer with *p*-nitrobenzylidenetriphenylphosphorane, which would have been liberated from its salt under basic conditions. After drying over anhydrous sodium sulfate, the chlorobenzene was removed *in vacuo*. The resulting yellow oil was treated with ether (50 ml), affording an additional fraction (0.83 g, 1.5 mmol, 15%) of **9d**, mp 269–271°.

Neopentylsulfonylmethylenetriphenylphosphorane (15c) and α-Methylsulfonylneopentylidenetriphenylphosphorane (16c, Expt 15). A solution of neopentylidenetriphenylphosphorane (prepared from 8.19 g, 17.8 mmol, of neopentyltriphenylphosphonium iodide, see above) in tetrahydrofuran (500 ml) under nitrogen was cooled to −90°. Methanesulfonyl fluoride[12] (0.88 g, 9.0 mmol) in tetrahydrofuran (5 ml) was added all at once. After additional stirring for 1 hr at −90° the temperature was raised to room temperature in 30 min. The precipitate was separated and extracted with tetrahydrofuran. The combined organic layers were concentrated *in vacuo*. The residual oil was dissolved in chlorobenzene (250 ml), washed with water (3 × 100 ml), and dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was dissolved in diethyl ether (100 ml). After stirring for 4 hr, 1.75 g 14.27 mmol, 48%) of **15c** was collected. The mother liquid was concentrated to a volume of 10 ml. Addition of pentane (100 ml) furnished an additional amount of **15c** (0.61 g, 1.49 mmol, 17%): mass spectrum (70 eV, 150°, direct inlet system) *m/e* (relative abundance >9) 410 (19), 395 (12), 354 (21), 353 (28), 339 (33), 289 (9), 277 (23), 276 (60), 275 (91), 200 (16), 199 (100), 185 (21), 183 (30), 165 (19), 152 (9), 121(9), 91 (9), 77 (9).

The volume of the mother liquid was then reduced to 50 ml and the liquid was cooled to −30°. A fraction of 0.26 g of **16c** was obtained (contaminated with some **15c**). Recrystallization from chloroform–ether yielded 47 mg (0.12 mmol, 1.3%) of pure **16c**: mp 222–223.5°; mass spectrum (70 eV, 180°, direct inlet system) *m/e* (rel abundance >5) 410 (9), 395 (100), 316 (9), 315 (28), 301 (20), 261 (5), 201 (5), 185 (5), 183 (16), 108 (9), 91 (5), 57 (5), 43 (5), 41 (10).

α-Neopentylsulfonylethylidenetriphenylphosphorane (15d)

and α-Ethylsulfonylneopentylidenetriphenylphosphorane (16d, Expt 17). A solution of neopentylidenetriphenylphosphorane (prepared from 9.20 g, 20 mmol, of the corresponding phosphonium iodide, see above) in tetrahydrofuran (500 ml) under nitrogen was cooled to −90°. Ethanesulfonyl fluoride[12] (1.12 g, 10 mmol) in tetrahydrofuran (30 ml) was added dropwise in 1 hr. After additional stirring for 4 hr at −90° the temperature was raised to room temperature. The work-up was carried out as above for expt 15. Chlorobenzene was removed *in vacuo*. The resulting viscous oil was dissolved in diethyl ether (150 ml) and pentane (100 ml) was added. After stirring for 1.5 hr 2.28 g (5.4 mmol, 54%) of **15d** was collected. The solid softened at different temperatures (>120°), strongly depending on the initial temperature of the melting block. Ylide **15d** was identical by pmr and ir with **16e** (expt 18): mass spectrum (70 eV, 190°, direct inlet system) *m/e* (rel abundance >5) 424 (5), 353 (6), 289 (41), 278 (49), 277 (100), 263 (9), 262 (10), 213 (10), 202 (16), 201 (29), 199 (14), 185 (13), 183 (27), 152 (10), 133 (5), 108 (9), 77 (29), 71 (18), 57 (10), 55 (8), 51 (18), 47 (10), 43 (22), 41 (11), 39 (7).

After addition of pentane (100 ml) to the mother liquid, followed by concentration of the solution to *ca.* 100 ml, an additional crop of **15d** (0.93 g, 2.2 mmol, 22%) was obtained. After the mother liquid was concentrated further, the resulting viscous oil was dissolved in diethyl ether (10 ml). Crystallization at −30° afforded 300 mg (0.7 mmol, 7%) of **16d**, mp 183–184°. After four recrystallizations from diethyl ether, a still unsatisfactory elemental analysis was obtained for carbon. Therefore, the absolute mass of **16d** was determined, relative to the standard ^{12}C = 12.000000: calcd 424.162578; found 424.164 ± 0.003. **16d** had mass spectrum (70 eV, 150°, direct inlet system) *m/e* (rel abundance >5) 424 (14), 409 (100), 395 (7), 331 (5), 315 (25), 301 (16), 289 (11), 262 (7), 261 (9), 201 (6), 185 (7), 183 (20), 108 (9), 91 (5), 57 (7), 43 (5), 41 (8).

α-Neopentylsulfonylneopentylidenetriphenylphosphorane (16h, Expt 21). To a solution of neopentylidenetriphenylphosphorane (prepared from 9.20 g, 20 mmol, of the corresponding phosphonium iodide, see above) in tetrahydrofuran (250 ml) under nitrogen was added dropwise at room temperature a solution of neopentanesulfonyl fluoride (1.54 g, 10 mmol, see above) in tetrahydrofuran (30 ml). After additional stirring for 0.5 hr the white suspension was filtered. Water (*ca.* 6 drops) was added to the filtrate (to decompose unreacted neopentylidenetriphenylphosphorane). After filtration and evaporation *in vacuo*, the resulting viscous oil was dissolved in diethyl ether (250 ml), washed with water (3 × 50 ml), and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was crystallized from carbon tetrachloride (3 ml) at −30°, providing 137 mg (0.29 mmol, 3%) of **16h**, decomposing at *ca.* 210°. After recrystallization from diethyl ether–pentane, 47 mg (0.1 mmol, 1%) of **16h** sufficiently pure for elemental analysis was obtained: mp 219–220° dec; mass spectrum (70 eV, 180°, direct inlet system) *m/e* (rel abundance >5) 466 (11), 451 (100), 437 (24), 395 (9), 331 (8), 316 (10), 315 (28), 301 (20), 262 (5), 202 (5), 185 (5), 183 (13), 108 (8), 57 (8), 41 (9).

α-Benzylsulfonylethylidenetriphenylphosphorane (16j) and α′-Benzylsulfonyl-α-benzylsulfonylethylidenetriphenylphosphorane (23, Expt 23). To a solution of ethylidenetriphenylphosphorane (prepared from 7.42 g, 20 mmol, of the corresponding phosphonium bromide[15]) in terahydrofuran (250 ml) under nitrogen was added dropwise at room temperature, until the yellow color disappeared, a solution of benzylsulfonyl fluoride[12] (*ca.* 2.1 g, 12 mmol) in tetrahydrofuran (30 ml). Stirring was continued for 1 hr. The precipitate was removed and the filtrate was concentrated *in vacuo*. The residue was dissolved in chlorobenzene (250 ml) and washed with water (3 × 100 ml). After drying over anhydrous sodium sulfate the chlorobenzene was removed *in vacuo*. To the resulting oil was added, consecutively, dichloromethane (5 ml) and diethyl ether (100 ml). After stirring for 16 hr the suspension was filtered, providing 1.29 g (2.2 mmol, 33%) of crude **23**. Crystallization from dichloromethane–ethyl acetate (two times) and dichloromethane–diethyl ether, respectively, furnished analytically pure material, mp 191–192°.

Addition of pentane (200 ml) to the mother liquid provided 1.21 g (3.0 mmol, 30%) of **16j**, identical by pmr, ir, and mixture melting point with **7c** (expt 4): mass spectrum (70 eV, 150°, direct inlet system) *m/e* (rel abundance >5) 444 (9), 353 (100), 305 (9), 289 (33), 262 (19), 261 (7), 185 (5), 183 (19), 133 (5), 108 (12), 77 (5), 43 (7).

α′-Neopentylsulfonyl-α-benzylsulfonylbenzylidenetriphenylphosphorane (24, Expt 24). To a solution of neopentylidenetriphenylphosphorane (prepared from 9.20 g, 20 mmol, of the corresponding phosphonium iodide, see above) in tetrahydrofuran (250 ml) under nitrogen was added dropwise at room temperature, until the yellow color disappeared, a solution of benzylsulfonyl fluoride[12] (*ca.* 2.3 g, 13.3 mmol) in tetrahydrofuran (25 ml). After additional stirring for 1 hr the white suspension was filtered off. The filtrate was concentrated *in vacuo* to a viscous oil (*ca.* 5 g). Chromatography over silica gel with chloroform–diethyl ether (1:4) provided 1.3 g (2.05 mmol, 31%) of crude **24**. Crystallization from ethyl acetate–diethyl ether (two times) furnished an analytically pure sample, mp 201–202°.

Reaction of Ethanesulfonyl Chloride with Methylenetriphenylphosphorane in the Presence of Triethylamine. To a solution of methylenetriphenylphosphorane (prepared from 7.14 g, 20 mmol, of the corresponding phosphonium bromide[14]) in tetrahydrofuran (250 ml) under nitrogen was added at room temperature triethylamine (50 g, 0.5 mol), immediately followed by dropwise addition of *ca.* 25 ml of a solution of ethanesulfonyl chloride[19a] (2.57 g, 20 mmol) in tetrahydrofuran until the yellow color of methylenetriphenylphosphorane disappeared. Work-up according to the general procedure given above for **9a** afforded 1.21 g (3.3 mmol, 33%) of a mixture of **17** and **18** in a ratio of 1:1.

Reaction of Methanesulfonyl Fluoride with Ethylidenetriphenylphosphorane in the Presence of *N*-(1-Cyclohexenyl)morpholine. A solution of ethylidenetriphenylphosphorane (prepared from 3.71 g, 10 mmol, of the corresponding phosphonium bromide[15]) in tetrahydrofuran (250 ml) was added dropwise in 70 min to *N*-(1-cyclohexenyl)morpholine[31] (16.7 g, 0.1 mol) and methanesulfonyl fluoride[12] (0.98 g, 10 mmol) in tetrahydrofuran (100 ml) under nitrogen at room temperature. After additional stirring for 15 min the white precipitate was collected and identified as ethyltriphenylphosphonium bromide (3.42 g, 9.2 mmol, 92%) by comparison of the ir and pmr spectra with those of authentic material.[15] (The THF solution of ethylidenetriphenylphosphorane contains lithium bromide generated from ethyltriphenylphosphonium bromide with butyllithium. Dehydrofluorination of methanesulfonyl fluoride to the corresponding sulfene with ethylidenetriphenylphosphorane yields ethyltriphenylphosphonium fluoride, which apparently exchanges a fluoride ion against the bromide ion of lithium bromide.)

The tetrahydrofuran layer was concentrated *in vacuo*. The residual oil was dissolved in dichloromethane (250 ml), washed with water (3 × 100 ml), and dried over anhydrous sodium sulfate. After removal of dichloromethane, the yellow oil was vigorously stirred with pentane (250 ml). The pale yellow precipitate was collected and washed with pentane, affording crude thietane dioxide **22a** (2.41 g). The ylides **17** and **18** could not be detected by pmr. Crystallization from methanol (25 ml) yielded **22a** (1.48 g, 6.0 mmol, 60%) mp 137–138.5°, identical by pmr, ir, and mixture melting point with an authentic sample.[8]

Reaction of Benzylsulfonyl Fluoride with Benzylidenetriphenylphosphorane in the Presence of *N*-(1-Cyclohexenyl)morpholine. Under the same conditions as described above, we obtained benzyltriphenylphosphonium bromide (3.57 g, 8.2 mmol, 82%) and thietane dioxide **22b** (2.28 g, 7.1 mmol, 71%, crystallized from methanol), mp 135–136° (lit.[10] mp 136°).

Acknowledgment. The authors are indebted to Dr. R. M. Kellogg for stimulating discussions during this work, and to Mr. O. Possel for carrying out the ^{13}C experiments.

Registry No.—**2,** R^2 = H, 3487-44-3; **2,** R^2 = 1-adamantyl, 51849-03-7; **2,** R^2 = *t*-Bu, 3739-96-6; **2,** R^2 = Me, 1754-88-7; **3a,** 36196-01-7; **3b,** 51849-04-8; **4,** R^3 = H; X = F, 558-26-8; **4,** R^3 = H; X = OSO_2Me, 7143-01-3; **4,** R^3 = Me; X = F, 754-03-0; **4,** R^3 = *t*-Bu; X = F, 51849-05-9; **4,** R^3 = *i*-Pr; X = F, 659-90-5; **4,** R^3 = Ph; X = F, 329-98-6; **4,** R^3 = Me; X = Cl, 594-44-5; **5,** Y = H, 16721-45-2; **5,** Y = MeO, 21960-26-9; **5,** Y = NO_2, 6933-17-1; **8,** Z = H, 368-43-4; **8,** Z = NO_2, 349-96-2; **16c,** 51849-06-0; **16d,** 51849-07-1; **23,** 51849-08-2; **24,** 51849-09-3; 1-iodomethyladamantane, 51849-10-6; 1-hydroxymethyladamantane,770-71-8; 1-adamantyltriphenylphosphonium iodide, 51849-11-7.

References and Notes

(1) A. M. van Leusen, B. A. Reith, A. J. W. Iedema, and J. Strating, *Recl. Trav. Chim. Pays-Bas,* **91,** 37 (1972).

(2) (a) H. Hoffmann and H. Förster, *Tetrahedron Lett.,* 1547 (1963); (b) Y. Ito, M. Okano, and R. Oda, *Tetrahedron,* **23,** 2137 (1967).

(3) Unlike in eq 1, the phosphonium salt formed from the second equivalent of starting ylide and HX is no longer indicated in eq 2 and the following equations.

(4) H. J. Bestmann and R. Zimmermann, *Fortschr. Chem. Forsch.*, **20**, 38 (1971).
(5) *Cf.* Y. Shirota, T. Nagai, and N. Tokura, *Tetrahedron*, **23**, 639 (1967).
(6) *Cf.* J. F. King, E. G. Lewars, and L. J. Danks, *Can. J. Chem.*, **50**, 866 (1972).
(7) For a review, see G. Opitz, *Angew. Chem.*, **79**, 161 (1967); see also ref 2b.
(8) (a) G. Opitz, H. Schempp, and H. Adolph, *Justus Liebigs Ann. Chem.*, **684**, 92 (1965); (b) I. J. Borowitz, *J. Amer. Chem. Soc.*, **86**, 1146 (1964).
(9) G. Opitz and K. Fischer, *Z. Naturforsch. B*, **18**, 775 (1963).
(10) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (*Milan*), **44**, 873 (1962); *Chem. Abstr.* **60**, 13240*c* (1964).
(11) *Cf.* F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).
(12) W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931); 483 (1932).
(13) M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 528 (1971); L. N. Owen and S. P. Whitelaw, *J. Chem. Soc.*, 3723 (1953).
(14) G. Wittig and U. Schöllkopf, *Org. Syn.*, **40**, 66 (1960).
(15) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961).
(16) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).
(17) H. Hoffmann, *Justus Liebigs Ann. Chem.*, **634**, 1 (1960).
(18) R. Ketcham, D. Jambotkar, and L. Martinelli, *J. Org. Chem.*, **27**, 4666 (1962).
(19) (a) C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **16**, 621 (1951); (b) J. F. King and D. J. H. Smith, *Can. J. Chem.*, **43**, 1870 (1965).
(20) R. B. Scott and H. L. McLeod, *J. Org. Chem.*, **21**, 388 (1956).
(21) F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Amer. Chem. Soc.*, **73**, 5004 (1951).
(22) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944); S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).
(23) R. B. Scott and R. E. Lutz, *J. Org. Chem.*, **19**, 830 (1954).
(24) D. Seyferth and G. Singh, *J. Amer. Chem. Soc.*, **87**, 4156 (1965).
(25) S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).
(26) H. Koch and W. Haaf, *Org. Syn.*, **44**, 1 (1964).
(27) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 2548 (1947).
(28) H. Stetter, M. Schwartz, and A. Hirschhorn, *Chem. Ber.*, **92**, 1629 (1959).
(29) H. Stone and H. Schechter, *J. Org. Chem.*, **15**, 491 (1950).
(30) L. Field and J. W. McFarland, *Org. Syn.*, **36**, 91 (1956).
(31) G. Opitz, H. Hellmann, and H. W. Schubert, *Justus Liebigs Ann. Chem.*, **623**, 112 (1959).

Alkyl Metal Asymmetric Reduction. VI. Alkyl Phenyl Ketone Reductions by Dialkylzinc Compounds. Some Dynamic and Stereochemical Aspects

Giampaolo Giacomelli, Luciano Lardicci,* and Roberto Santi

Istituto di Chimica Organica, Facoltà di Scienze M.F.N., Università di Pisa, 56100, Pisa, Italy

Received January 8, 1974

The reactivity of organozinc compounds having β-branched alkyl groups toward alkyl phenyl ketones has been investigated; at 86° the dialkylzinc compounds are shown to reduce the carbonyl substrate to the corresponding carbinol, which is the only product formed. On the basis of the results obtained, the reduction process is assumed to involve the formation of a coordinative bond between the ketone and the dialkylzinc compound, followed by a β-hydride transfer from the alkyl group of the organozinc compound to the carbonyl carbon atom in a six-membered cyclic transition state. The eventual occurrence of side reduction processes, like the Meerwein–Ponndorf–Verley reaction, in the experimental conditions was tested too. Finally, the reduction of alkyl phenyl ketones by (+)-bis[(*S*)-2-methylbutyl]zinc affords (*S*)-alkylphenylcarbinols. The stereoselectivity of the process is discussed and compared with that encountered in other alkyl metal reductions.

Although the reactivity of the organozinc compounds should correspond in principle to that of their Grignard counterparts, it is generally accepted that organozinc compounds, isolated by distillation, are scarcely reactive toward carbonyl substrates.[1,2] On the contrary, *in situ* organozinc reagents react rapidly and efficiently with simple carbonyl compounds to give mainly addition products.[2,3] Concerning the reactivity of *isolated* dialkylzinc compounds, diethylzinc was observed to eliminate ethylene quantitatively in the reaction with benzophenone at 110°, giving ethylzinc diphenyl methoxide.[4]

Therefore, in the course of studies on the reactions of organometallic compounds with functional substrates[5] and on the alkyl metal asymmetric reductions,[6,7] we have investigated the actual reactivity of dialkylzinc compounds toward alkyl phenyl ketones and, in this connection, the stereochemistry of their reduction by optically active organozinc compounds.[7]

Results

At relatively high temperatures, dialkylzinc compounds having branched alkyl groups[7] react with alkyl phenyl ketones; the reactions have been carried out mainly in the absence of solvents at 86.5°. In the experimental conditions adopted, after hydrolysis of the reaction mixtures, secondary carbinols corresponding to the reduction of the carbonyl group are recovered together with the unreacted ketone. No addition product was detected in the reaction of alkyl phenyl ketones with $\text{Zn}(i\text{-Bu})_2$ or with bis(2-methylbutyl)zinc, while γ- or δ-branched alkylzinc compounds were observed to yield also tertiary carbinols, although to a low extent.[7] The main results we have obtained are summarized in Tables I and II, from inspection of which several general observations can be noted.

(1) The reaction rate seems to be dependent on the structure and on the nature of the carbonyl substrate; while trifluoromethyl phenyl ketone reacts completely within 20 min at room temperature (runs 11 and 12), the reduction of the alkyl phenyl ketones occurs with conversions higher than 50% only after heating at 86.5° for 5 hr (runs 5–7). Moreover, as the bulk of the alkyl group in the ketone increases, the conversions (after 5 hr) of the reaction decrease from 90–100 to 50–60%.

(2) The reactivity of the organozinc compounds used seems to be nearly comparable; the conversions in the reduction of *tert*-butyl phenyl ketone are, however, slightly lower using $\text{Zn}(i\text{-Bu})_2$ than using bis(2-methylbutyl)zinc (runs 9 and 10).

(3) The increase of the concentration of the reagents in toluene solution (runs 14 and 15), as well as the use of an excess of the organozinc compound (run 16), determines higher conversions in the reduction of *tert*-butyl phenyl ketone.

Bis[(*S*)-2-methylbutyl]zincis able to accomplish asymmetric reduction of alkyl phenyl ketones (Table III): all the carbinols recovered have the absolute (*S*) configuration. In agreement with the data obtained in the reduction of the same ketones by (+)-tris[(*S*)-2-methylbutyl]aluminum,[6] the stereoselectivity of the reduction is dependent on the structure of the ketone, increasing in the order Me < Et < *t*-Bu < *i*-Pr. Finally, it is to be noted that the reduction of trifluoromethyl phenyl ketone occurs with very low stereo-