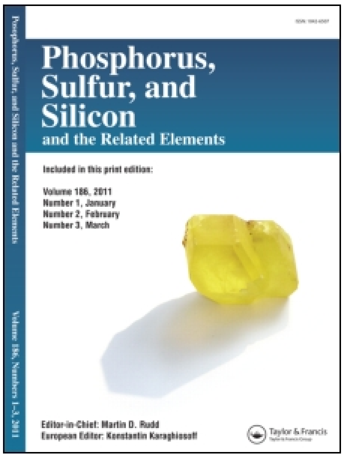

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γ-Diphenylphosphinoxy Carbanions: Slow Reacting Analogues of γ -Halocarbanions

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γ-Diphenylphosphinoxy Carbanions: Slow Reacting Analogues of γ-Halocarbanions

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Carbanion of diphenylphosphinyl ester of 3-hydroxypropyl phenyl sulfone undergoes slow 1,3-intramolecular nucleophilic substitution to give substituted cyclopropane. It can be efficiently trapped by external electrophiles such as aldehydes to produce aldol type anions, which undergo 1,5-intramolecular substitution to give substituted tetrahydrofurans.

Keywords Carbanions; diphenylphosphinates; sulfones tetrahydrofurans

INTRODUCTION

In our preceding articles, we have shown that albeit γ-chlorocarbanions generated by deprotonation of 3-chloropropyl phenyl sulfone, *t*-butyl 4-chlorobutyrate, 4-chloro-butyronitrile, etc., undergo rapid intramolecular 1,3-nucleophilic substitution—so called γ-elimination—to form substituted cyclopropanes; they can be trapped by active electrophiles such as aromatic aldehydes. The resulting aldol-type anions enter intramolecular 1,5-substitution giving substituted tetrahydrofurans.[1,2] Due to the high rate of the γ-elimination, the reaction should be carried out at low temperature by addition of a base, potassium *t*-butoxide, to a solution of the carbanion precursor and the aldehyde in THF, since treatment of the carbanion precursors with a base before the addition of aldehydes resulted in exclusive formation of the cyclopropane. The former procedure, however, could not be applied to the reaction with aliphatic aldehydes, which are stronger CH acids than the carbanion precursors because of the competing aldol reaction. On the other hand, generation of these γ-chlorocarbanions in the presence of imines and the Michael acceptors always gave cyclopropanes;

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Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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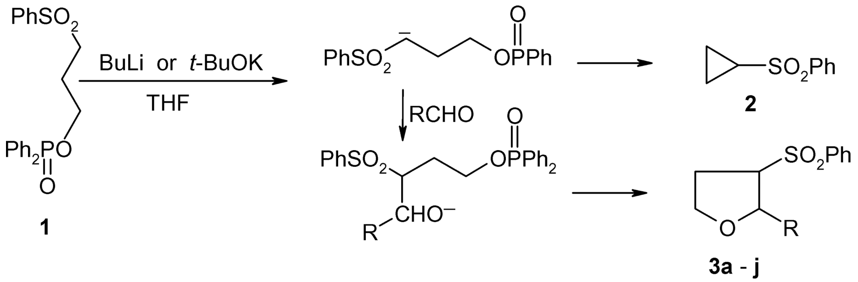
intramolecular substitution was faster than addition to such moderately active electrophiles. We supposed that competition between intramolecular substitution in γ-chlorocarbanions and their addition to external electrophiles to some extent can be controlled by variation of the nucleophilicity of the sulfone carbanion. Indeed, the carbanion of 3-chloropropyl pentachlorophenyl sulfone, albeit cyclized rapidly, reacted with activated imines to produce substituted pyrrolidines[3] and Michael acceptors to give cyclopentanes.[4] One should expect that this competition could be also controlled by variation of the leaving group. Whereas γ-bromocarbanions cyclize faster than γ-chloro carbanions,[2] the carbanion of γ-fluoropropyl phenyl sulfone is completely inert in the sense of substitution of fluorine. The trimethylammonium group was also inefficient in this respect. The carbanion of 3-trimethylammonium propyl phenyl sulfone does not undergo 1,3-substitution, but relatively slow decomposition via Hoffman-type elimination takes place. Its adducts to aldehydes also do not cyclize to tetrahydrofuranes.[5]

In looking for a leaving group that could be replaced by nucleophiles slower than chlorine, we took into consideration the diphenylphosphinoxy group, which, according to Noyce[6] undergoes solvolysis via S_N1 type reaction substantially (ca. 30 times) slower than chlorine. On the other hand, reactions of amines with ethyl diphenylphosphinate do not proceed via S_N2 type substitution, but addition of the amines to the phosphorus atom.[7] Although we were unable to find examples of intermolecular nucleophilic S_N2-type replacement of this group, there are numerous examples of intramolecular nucleophilic substitution of diphenylphospinoxy group by carbanions and *N*-anions located in γ-position, producing substituted cyclopropanes[8] and aziridines.[9] In order to test the possibility of using diphenylphosphinoxy group as a slower reacting analogue of halogens in γ-halocarbanions, we have choosen diphenylphosphinyl ester of 3-hydroxy propyl phenyl sulfone **1**.

RESULTS AND DISCUSSION

In our hands, the carbanion of this sulfone undergoes intramolecular 1,3-substitution of the diphenylphosphinoxy group to form phenylsulfonyl cyclopropane, albeit substantially slower than analogous substitution of chlorine. Thus treatment of **1** with *t*-BuOK in THF and quenching with acid after 5 min leads to the conversion of **1** into **2** not exceeding 10%, whereas under identical conditions, conversion of the lithium salt of the anion of **1** generated by treatment of **1** with BuLi was more than 50%. Nevertheless the potassium salt of the carbanion



SCHEME 1 Reactions of **1** with base and aldehydes.

of **1** reacts with a series of aromatic aldehydes giving the expected tetrahydrofurans (Scheme 1).

The reaction of **1** with aromatic aldehydes proceeded efficiently giving the expected substituted tetrahydrofurans with good yields exclusively as the *trans*-isomers (Table I, entries 2–7). Most of these tetrahydrofurans **3a**, **3b**, **3d**, and **3g** were obtained earlier in an analogous reaction of aldehydes with the carbanion of 3-chloropropyl phenyl sulfone as *trans*-isomers. Physical properties of the tetrahydrofurans obtained in this article are identical to those reported. Similarly, the reaction with pivalic aldehyde gave the expected tetrahydrofuran with excellent yield. Since aliphatic aldehydes are relatively strong CH acids, procedure of the reaction with these aldehydes was changed. First

TABLE I Reactions of 1 with Base and Aldehydes (Scheme 1)

Entry	R	Products, Yield
1	none[a]	**2**, 60%
2	C_6H_5	**3a**, 80%[b]
3	p-MeC_6H_4	**3b**, 76%[b]
4	p-$MeOC_6H_4$	**3c**, 79%
5	PhCH=CH	**3d**, 45%[b]
6	3-Pyridyl	**3e**, 35%
7	2-Furyl	**3f**, 51%
8	Me_3C	**3g**, 89%[b]
9	$CH_3CH(CH_3)$[c]	**2**, 20%, **3h**, 50%
10	$CH_3CH_2CH_2$[c]	**2**, 15%, **3i**, 46%
11	CH_3[c]	**2**, 22%, **3j**, 20%

[a] Experiment without aldehyde, BuLi, −75°C to room temperature, THF.

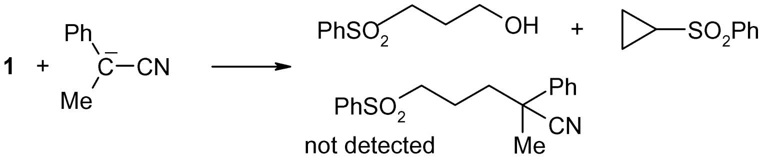
[b] Physical and spectral data: see ref. [1].

[c] Aldehyde was added 15 s after base.

the carbanion was generated by treatment of **1** with base, followed by addition of aldehydes. This procedure, which could not be applied for reactions of γ-chlorocarbanions, worked well for *iso*- and *n*-butyraldehyde. Thus 2-isopropyl-, 2-*n*-propyl 3-phenylsulfonyl tetrahydrofurans could be obtained in reasonable yields (Table I, entries 9–10).

The reaction of the anion of **1** with acetaldehyde was less efficient (Table I, entry 11). It appears that due to high CH acidity of the aldehyde, proton exchange with the anion of **1** resulted in partial recovery of **1** and consumption of the aldehyde.

Although we have not found examples of intermolecular S_N2-type nucleophilic substitution of the diphenylphosphinoxy group, a similar process takes place readily when catalyzed by Lewis acids. For instance, reaction of alkyl diphenyl phosphinates with alkoxytrimethylsilanes catalyzed by trimethylsilyl triflate gave dialkyl esters,[10] whereas their reaction with trimethyl allyl silane resulted in *C*-allylation.[11] To investigate the possibility of an intermolecular S_N2 nucleophilic substitution of the diphenyl phosphinoxy group, we reacted **1** with carbanion of 2-phenylpropionitrile generated in advance. In the reaction mixture, we found the starting compound **1**, 3-hydroxy propyl phenyl sulfone, and cyclopropyl phenyl sulfone; the expected product of an intermolecular S_N2-type substitution was not detected (Scheme 2).



SCHEME 2 Reaction of **1** with carbanion of 2-phenylpropionitrile.

Thus an intermolecular S_N2 reaction with this active carbanion did not take place; it appears that the main process was its addition to the phosphorus atom followed by P—O bond cleavage. Additionally, proton exchange with **1** produced the anion of **1** and subsequently the cyclopropane.

CONCLUSION

We have shown that the diphenyl phosphinoxy group can act as a leaving group in 1,3- and 1,5-intramolecular S_N2-type substitution with the sulfonyl-stabilized carbanion and O^- anions. Thus 3-diphenylphosphinoxy propyl phenyl sulfone can behave as a precursor of the slow-reacting analogue of γ-halocarbanions.

EXPERIMENTAL

All reactions were carried out under argon atmosphere in dried glassware using standard Schlenk techniques. Tetrahydrofuran was distilled from potassium–benzophenone ketyl. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with $CDCl_3$ as standard ($\delta = 7.26$ ppm and 77 ppm, respectively) with a Bruker 500 spectrometer. IR data were recorded on an FT-IR Perkin Elmer Spectrum 2000 using a film (for oils) or KBr pellets (for solids). Mass spectrometric data were obtained with an AMD 604 Intectra GmbH spectrometer in electron ionization mode or with a MarinerTM instrument in electrospray mode. Microanalyses were performed by the analitical laboratory of the Institute of Organic Chemistry, Polish Academy of Sciences.

DIPHENYLPHOSPHINYL ESTER OF 3-HYDROXYPROPYLPHENYL SULFONE (1)

To a solution of 3-hydroxypropylphenyl sulfone (5.00 g, 25.0 mmol) and triethylamine (3.80 g, 37.5 mmol) in benzene (50 mL), diphenylphosphinic chloride (5.60 g, 25.0 mmol) in 10 mL of benzene was added dropwise, and the mixture was refluxed for 2 h. The mixture was washed with water (50 mL), with diluted HCl (50 mL), concentrated $NaHCO_3$, and with brine. The solvent was evaporated, and the residue was purified by passing through silica gel (hexane/ethyl acetate) giving **1** (yield 7.50 g, 79 %). Mp 71–73°C (EtOH). IR (film CH_2Cl_2, ν_{max}/cm^{-1}): 3452, 3059, 2961, 1591, 1483, 1439, 1307, 1225, 1145, 1131, 1113, 1087, 1071, 1019, 997, 953, 822. 789, 754, 730, 694, 597, 559, 534. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.12$–2.19 (m, 2H), 3.24–3.28 (m, 2H), 4.06–4.11 (m, 2H), 7.42–7.47 (m, 4H), 7.51–7.58 (m, 4H), 7.63–7.67 (m, 1H), 7.73–7.78 (m, 4H), 7.88–7.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 24.2$, 52.9, 62.5, 128.0, 128.6, 128.7, 129.3, 130.4, 131.45, 131.53, 132.3, 132.4, 133.8, 138.9. MS (EI 70 eV) m/z (%): 400 (M^{+}, <1), 259 (100), 231 (34), 219 (34), 201 (81), 141 (42), 118 (80), 91 (1), 77 (56), 51 (13), 41 (17). HRMS (EI): Calcd. for: $C_{21}H_{21}O_4PS$ 400.0898, found: 400.0882; Anal. Calcd. for $C_{21}H_{21}O_4PS$: C 62.99, H 5.29, S 8.01, found C 62.74, H 5.22, S 8.22%.

Reaction of Diphenylphosphinyl Ester of 3-Hydroxypropylphenyl Sulfone (1) with Aldehydes: General Procedure

To a solution of **1** (200 mg, 0.5 mmol) and aldehyde (0.75 mmol) in THF (2 mL) at –75°C under argon, *t*-BuOK (112 mg, 1 mmol, in 1 mL of THF) was added dropwise. After 30 min at –75°C, the mixture was warmed to room temperature and kept for 60 min. After that, a solution of NH_4Cl was added, the mixture was extracted with CH_2Cl_2 (3 × 25 mL), and the extracts were washed with brine and dried over $MgSO_4$. Column chromatography with hexane–EtOAc gave the substituted tetrahydrofurans.

trans-*2-(4-Metoxyphenyl)-3-phenylsulfonyl Tetrahydrofuran (3c)*

Mp 75–77 °C (EtOH); IR (film KBr, ν_{max}/cm^{-1}): 3006, 2972, 2880, 2838, 1610, 1584, 1512, 1445, 1304, 1293, 1249, 1147, 1080, 1028, 956, 827, 781, 746, 723, 688, 637, 625, 580, 534, 517. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25–2.34 (m, 1H), 2.50–2.56 (m, 1H), 3.66 (ddd, ^3J(H,H) = 4.2, 5.5, 9.6 Hz, 1H), 3.77 (s, 3H), 3.98 (ddd, ^3J(H,H) = 6.7, 8.5, 8.5 Hz, 1H), 4.15 (ddd, ^3J(H,H) = 3.6, 8.5, 8.5 Hz, 1H), 5.24 (d, ^3J(H,H) = 5.5 Hz, 1H), 6.75–6.79 (m, 2H), 7.04–7.07 (m, 2H), 7.51–7.55 (m, 2H), 7.62–7.66 (m, 1H), 7.86–7.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.6, 55.3, 68.2, 71.0, 80.0, 113.9, 127.1, 128.6, 129.3, 132.2, 133.9, 138.3, 159.4. MS (EI 70 eV) m/z (%): 318 (M^+, <1), 176 (100), 135 (66), 77 (13). HRMS (EI): Calcd. for $C_{17}H_{18}O_4S$: 318.0926, found 318.0938; Anal. Calcd. for $C_{17}H_{18}O_4S$: C 64.13, H 5.70, S 10.07, found C 64.21, H 5.59, S 10.26%.

trans-*2-(Pyridin-3-yl)-3-phenylsulfonyl Tetrahydrofuran (3e)*

Oil, IR (film CH_2Cl_2, ν_{max}/cm^{-1}): 3061, 2954, 2882, 1580, 1480, 1447, 1429, 1306, 1148, 1086, 1072, 1025, 750, 721, 689, 616, 601, 561. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23–2.32 (m, 1H), 2.49–2.56 (m, 1H), 3.65 (ddd, ^3J(H,H) = 4.2, 5.6, 9.7 Hz, 1H), 4.01 (ddd, ^3J(H,H) = 6.7, 8.5, 8.5 Hz, 1H), 4.16 (ddd, ^3J(H,H) = 3.7, 8.5, 8.5 Hz, 1H), 5.32 (d, ^3J(H,H) = 5.6 Hz, 1H), 7.19 (dd, ^3J(H,H) = 4.8, 7.9 Hz, 1H), 7.51–7.57 (m, 3H), 7.63–7.67 (m, 1H), 7.85–7.89 (m, 2H), 8.37 (s, 1H), 8.48 (d, ^3J(H,H) = 4.85 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.7, 68.5, 70.8, 78.2, 123.3, 128.5, 129.5, 133.7, 134.2, 135.8, 138.0, 147.6, 149.3. MS (EI 70 eV) m/z (%): 147 (100), 117 (14), 106 (81), 91 (12), 77 (40), 65 (14), 51 (31), 39 (19). HRMS (ESI): Calcd. for $C_{15}H_{15}NO_3SNa$: 312.0665, found: 312.0669.

trans-*2-(Fur-2-yl)-3-phenylsulfonyl Tetrahydrofuran (3f)*

Mp 79–80 °C (EtOH). IR (film CH_2Cl_2, ν_{max}/cm^{-1}): 3145, 3120, 3064, 2975, 2897, 2876, 1585, 1506, 1444, 1298, 1147, 1086, 1060, 1011, 958, 920, 882, 815, 748, 716, 685, 618, 599, 569, 538. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38–2.46 (m, 1H), 2.56–2.63 (m, 1H), 3.95–4.10 (m, 3H), 5.22 (d, ^3J(H,H) = 6.0 Hz, 1H), 6.06 (d, ^3J(H,H) = 3.2 Hz, 1H), 6.18 (dd, ^3J(H,H) = 1.8, 3.2 Hz, 1H), 7.23–7.25 (m, 1H), 7.48–7.53 (m, 2H), 7.58–7.63 (m, 1H), 7.83–7.87 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 67.0, 68.0, 74.1, 108.6, 110.3, 128.4, 129.2, 133.9, 138.0, 142.8, 151.1. MS (EI 70 eV) m/z (%): 136 (100), 95 (61), 77 (18). HRMS (ESI): Calcd. for $C_{14}H_{14}O_4SNa$: 301.0505, found: 301.0492; Anal. Calcd. for $C_{14}H_{14}O_4S$: C 60.42, H 5.07, S 11.52, found: C 60.47, H 5.00, S 11.69 %.

Reaction of 1 with Aliphatic Aldehydes, Synthesis of 3h, 3i, and 3j: General Procedure

To a solution of **1** (200 mg, 0.5 mmol) in THF (2 mL) at –75 °C under argon, *t*–BuOK (112 mg, 1 mmol, in 1 mL of THF) was added dropwise and then, after 15 sec, the aldehyde (0.75 mmol) was added. After 30 min at –75 °C the mixture was warmed to room temperature and kept for 60 min. After that, the solution of NH_4Cl was added, the mixture was extracted with CH_2Cl_2 (3 × 25 mL), and the extract was washed with brine and dried over $MgSO_4$. Column chromatography with hexane–EtOAc gave the substituted tetrahydrofurans.

trans-*2-Propyl-3-phenylsulfonyl Tetrahydrofuran (3h)*

Oil; IR (film CH_2Cl_2, ν_{max}/cm^{-1}): 3065, 2960, 2874, 1585, 1447, 1304, 1145, 1086, 1046, 949, 929, 837, 752, 720, 691, 602, 547. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, ^3J(H,H) = 7.1 Hz, 3H), 1.23–1.48 (m, 4H), 2.06–2.16 (m, 1H), 2.33–2.40 (m, 1H), 3.29–3.35 (m, 1H), 3.74 (ddd, ^3J(H,H) = 7.0, 8.5, 8.5 Hz, 1H), 3.88 (ddd, ^3J(H,H) = 4.1, 7.7, 8.5 Hz, 1H), 4.23 (ddd, ^3J(H,H) = 3.3, 6.0, 8.5 Hz, 1H), 7.55–7.60 (m, 2H), 7.64–7.68 (m, 1H), 7.88–7.92 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 18.9, 28.5, 37.2, 67.1, 68.3, 78.5, 128.5, 129.3, 133.9, 138.4. MS (EI 70 eV) m/z (%): 211 (39), 147 (17), 141 (51), 125 (11), 112 (81), 84 (100), 77 (85), 69 (23), 55 (22), 51 (29), 41 (51). HRMS (ESI): Calcd. for $C_{13}H_{18}O_3SNa$: 277.0869, found: 277.0871. Anal. Calcd. for $C_{13}H_{18}O_3S$: C 61.39, H 7.13, S 12.61, found: C 61.44, H 7.30, S 12.73 %.

trans-*2-Isopropyl-3-phenylsulfonyl Tetrahydrofuran (3i)*

Oil; IR (film CH_2Cl_2, ν_{max}/cm^{-1}): 2962, 2877, 1468, 1447, 1306, 1148, 1086, 934, 749, 720, 691, 581, 548. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, ^3J(H,H) = 6.6 Hz, 6H), 1.60–1.68 (m, 1H), 2.04–2.13 (m, 1H), 2.36–2.43 (m, 1H), 3.45 (ddd, ^3J(H,H) = 3.5, 5.0, 9.5 Hz, 1H), 3.79 (ddd, ^3J(H,H) = 6.5, 8.4, 8.4 Hz, 1H), 3.90 (ddd, ^3J(H,H) = 3.6, 8.4, 8.4 Hz, 1H), 4.15 (t, ^3J(H,H) = 5.0 Hz, 1H), 7.57–7.61 (m, 2H), 7.66–7.70 (m, 1H), 7.91–7.95 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8, 18.9, 28.8, 32.0, 66.4, 67.5, 83.3, 128.8, 129.4, 133.9, 138.4. HRMS (ESI): Calcd. for $C_{13}H_{18}O_3SNa$: 277.0869, found 277.0880.

trans-*2-Methyl-3-phenylsulfonyl Tetrahydrofuran (3j)*

Oil; IR (film CH_2Cl_2, ν_{max}/cm^{-1}): 3069, 2977, 2892, 2871, 1585, 1477, 1384, 1304, 1292, 1258, 1146, 1103, 1088, 1026, 997, 940, 897, 870, 749, 719, 692, 642, 603, 583, 545, 442. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.20$ (d, ^3J(H,H) = 6.2 Hz, 3H), 2.13–2.22 (m, 1H), 2.37–2.40 (m, 1H), 3.28 (ddd, ^3J(H,H) = 5.2, 6.7, 10.1 Hz, 1H), 3.71–3.77 (m, 1H), 3.93 (ddd, ^3J(H,H) = 3.9, 7.8, 8.6 Hz, 1H), 4.31 (quintet, ^3J(H,H) = 6.3 Hz, 1H), 7.57–7.62 (m, 2H), 7.66–7.70 (m, 1H), 7.90–7.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 20.6$, 28.7, 67.1, 69.6, 75.3, 128.6, 129.4, 134.0, 138.5; MS (EI 70 eV) m/z (%): 141 (12), 84 (100), 77 (41), 55 (17), 51 (24), 43 (83). HRMS (ESI): Calcd. for $C_{11}H_{14}O_3SNa$: 249.0556, found: 249.0550.

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