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Mendeleev Commun., 2019, **29**, 19–21

Mendeleev Communications

Unusual iodination of arylsulfonylallenes

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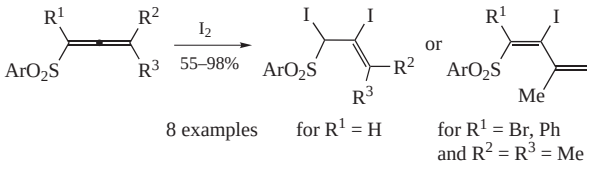
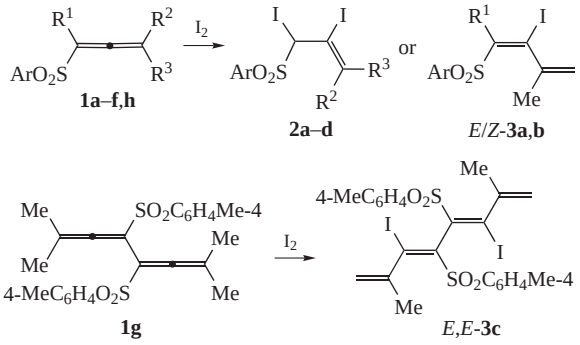
DOI: 10.1016/j.mencom.2019.01.005

Arysulfonylallenes ($ArSO_2$–CR^1=C=CR^2R^3), depending on their structure, react with iodine to give two types of products, diiodo alkenes $ArSO_2$–CHI–CI=CR^2R^3, when R^1 = H, or iodo dienes $ArSO_2$–CR^1=CI–C(Me)=CH_2, when R^1 = Br, Ph and R^2 = R^3 = Me, in yields of 55–98%. The plausible reaction mechanisms have been proposed.



Allenes are extensively used for synthesis of complex molecules.[1–3] Reactions of various allenes with electrophiles have been widely studied.[1,4] Surprisingly, the range of the described electrophilic reactions of arylsulfonyl allenes ($ArSO_2$–CR^1=C=CR^2R^3) is scarce. Such allenes participate in halohydroxylation (Hal = I, Br) and addition–elimination of bromine.[5,6] Note that attempts to iodinate these allenes failed.[5]

We have found that iodination of allenes **1** in CH_2Cl_2 or $CHCl_3$ solutions required heating in high pressure glass tube (Scheme 1, Table 1). Diiodination occurred at 1- and 2-positions of allenes **1a**–**d** unsubstituted at the 1-position of the allene triad, which afforded diiodo alkenes **2a**–**d**† (see Table 1, entries 1–4). On the other hand, 1-substituted allenes **1e**–**h** reacted with I_2 under milder conditions (entries 4–8) thus forming monoiodo dienes **3a**–**c**.‡ The structures of new compounds **2a**–**d** and **3a**–**c** were determined by NMR and IR spectroscopy and high-resolution mass spectrometry. The X-ray study was performed for compounds **2a**, *E*-**3b** and **5**§ (Figure 1, for details, see Online



1	Ar	R^1	R^2	R^3
a	Ph	H	Me	Me
b	4-ClC_6H_4	H	Me	Me
c	4-MeC_6H_4	H	Me	Me
d	4-MeC_6H_4	H	$(CH_2)_5$	
e	4-MeC_6H_4	Br	Me	Me
f	4-MeC_6H_4	Ph	Me	Me
h	4-MeC_6H_4	Ph	Bu^t	Me

2	Ar	R^2	R^3
a	Ph	Me	Me
b	4-ClC_6H_4	Me	Me
c	4-MeC_6H_4	Me	Me
d	4-MeC_6H_4	$(CH_2)_5$	

3	Ar	R^1
a	Ph	Br
b	4-MeC_6H_4	Ph

Scheme 1

† *General procedure for the synthesis of diiodo alkenes* **2a**–**d** *from allenes* **1a**–**d**. A mixture of allene **1** (0.144 mmol) and iodine (36.4 mg, 0.144 mmol) in $CHCl_3$ (10 ml) was stirred in a glass autoclave for 30 min at 80 or 130 °C as indicated in Table 1. After cooling, the solvent was distilled off under reduced pressure (without heating) to leave pure product.

1,2-Diiodo-3-methyl-1-(phenylsulfonyl)but-2-ene **2a**. Yield 66.5 mg (98%). Black solid, mp 60 °C (decomp.). ^{1}H NMR (400 MHz, $CHCl_3$) δ: 7.96–7.91 (m, 2H), 7.71–7.65 (m, 1H), 7.57–7.52 (m, 2H), 6.24 (s, 1H), 1.84 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.0, 134.5, 129.7, 129.0, 127.4, 95.0, 49.1, 33.4, 20.8. IR (KBr, ν/cm^{-1}): 1307 (S=O), 1581 (C=C); HRMS (ESI), *m*/*z*: 484.8544 $[M+Na]^+$ (calc. for $C_{11}H_{12}I_2NaO_2S$, *m*/*z*: 484.8539).

For characteristics of compounds **2b**–**d**, see Online Supplementary Materials.

‡ *General procedure for synthesis of iodo alkenes* **3a**–**c** *from allenes* **1e**–**h**. A mixture of allene **1** (0.144 mmol) and iodine (72.8 mg, 0.288 mmol) in $CHCl_3$ (10 ml) was stirred in a glass autoclave at 40 °C for 30 min. After cooling, the solvent was distilled off under reduced pressure (without heating) to leave pure product.

(1Z)-1-Bromo-2-iodo-3-methyl-1-(phenylsulfonyl)buta-1,3-diene **3a**. Yield 57.1 mg (93%), mp 70 °C (decomp.). ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.82–7.72 (m, 2H), 7.77–7.55 (m, 3H), 5.66 (s, 1H), 5.60–5.49 (m, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, acetone-d_6) δ: 140.9, 138.5, 134.2, 130.8, 129.4, 128.8, 126.8, 120.3, 20.7. HRMS (ESI), *m*/*z*: 432.8528 $[M+Na]^+$ (calc. for $C_{11}H_{10}BrINaO_2S$, *m*/*z*: 434.8527).

For characteristics of compounds **3b**,**c**, see Online Supplementary Materials.

§ *Crystal data for* **2a**: $C_{11}H_{12}I_2O_2S$ (*M* = 462.07), triclinic, space group $P\bar{1}$, at 100(2) K: *a* = 8.0871(7), *b* = 8.4818(6) and *c* = 11.6632(9) Å, α = 98.836(6)°, β = 97.451(7)°, γ = 117.945(8)°, *V* = 679.45(11) Å^3, *Z* = 2, d_{calc} = 2.259 g cm^{-3}, μ(MoKα) = 4.766 mm^{-1}, *F*(000) = 432.0. Total of 6246 reflections were measured and 6246 independent reflections (R_{int} = 0.0448) were used in a further refinement, which converged to wR_2 = 0.0712 and GOF = 1.086 for all independent reflections [R_1 = = 0.0363 was calculated against *F* for 6246 observed reflections with $I > 2\sigma(I)$].

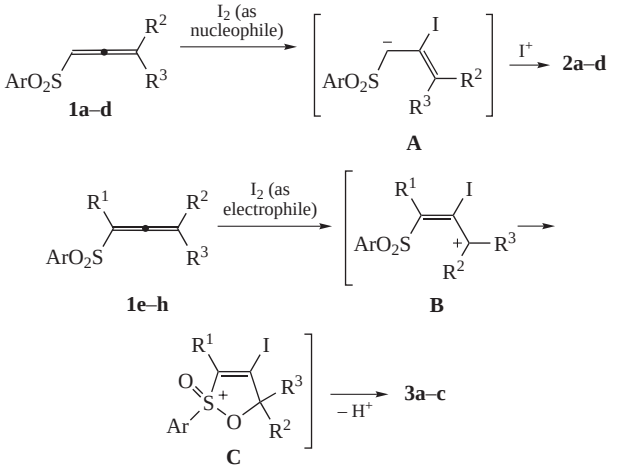
Crystal data for **3b**: $C_{18.25}H_{16.5}IO_2S$ (*M* = 426.77), monoclinic, space group $P2_1/n$, at 100(2) K: *a* = 16.4248(4), *b* = 5.65370(10) and *c* = = 19.5043(5) Å, β = 111.012(3)°, *V* = 1690.75(7) Å^3, *Z* = 4, d_{calc} = = 1.677 g cm^{-3}, μ(CuKα) = 16.071 mm^{-1}, *F*(000) = 844.0. Total of 14807 reflections were measured and 3199 independent reflections (R_{int} = 0.0471) were used in a further refinement, which converged to wR_2 = 0.1232 and GOF = 1.063 for all independent reflections [R_1 = 0.0438 was calculated against *F* for 14807 observed reflections with $I > 2\sigma(I)$].

Table 1 Iodination of allenes **1a–h** with iodine.

Entry	Starting allene	Solvent	*T*/°C	Product	Yield (%)
1	**1a**	$CHCl_3$	130	**2a**	98
2	**1b**	$CHCl_3$	80	**2b**	98
3	**1c**	$CHCl_3$	130	**2c**	98
4	**1d**	$CHCl_3$	130	**2d**	61
5	**1e**	CH_2Cl_2	40	*Z*-**3a**	93
6	**1f**	CH_2Cl_2	40	*E*-**3b**	55
7	**1g**	CH_2Cl_2	40	*E*,*E*-**3c**	98
8	**1h**	CH_2Cl_2	40	**3b** (*E*/*Z* = 1:1)	70

Supplementary Materials). *trans*-Arrangement of arylsulfonyl group and iodine atom around C(1)=C(2) bond in compounds *Z*-**3a** and *E*,*E*-**3c** was assigned analogously to that of *E*-**3b** derived from X-ray analysis.

Plausible mechanisms of iodination of allenes **1** is presented in Scheme 2. Allenes **1e–h** with substituents at the 1-position (R^1 = Br, Ph, or bis-allene **1g**), would react with iodine as an electrophile giving allyl-type cations **B** and cyclic species **C**. Similar cyclic cations generated from phosphoryl allenes under the action of Brønsted acids were thoroughly studied by us previously.[7,8] The species **B** or **C** undergo deprotonation to produce iodo dienes **3a–c**. On the other hand, allenes **1a–d** being unsubstituted at the 1-position react with iodine as a nucleophile to afford intermediate anions **A** stabilized by electron-withdrawing $ArSO_2$ group. The final quenching of anions **A** with iodine cation leads to diiodo alkenes **2a–d**.



Scheme 2

Allene **1h** bearing bulky *tert*-butyl group is transformed into a *E*,*Z* mixture of compound **3b** (see Table 1, entry 8); the same product *E*-**3b** was obtained from allene **1f** (entry 6). Thus, the formation of **3b** from **1h** is caused by decay of *tert*-butyl group under the reaction conditions (Scheme 3). Electrophilic addition of iodine to allene **1h** leads to cation **D**, in which a shift of methyl group from CMe_3 fragment occurs that gives rise to cation **E**. The latter undergoes C–C bond cleavage with a loss of propene molecule C_3H_6 and proton (isopropyl cation may be eliminated) affording *E*/*Z*-**3b**.

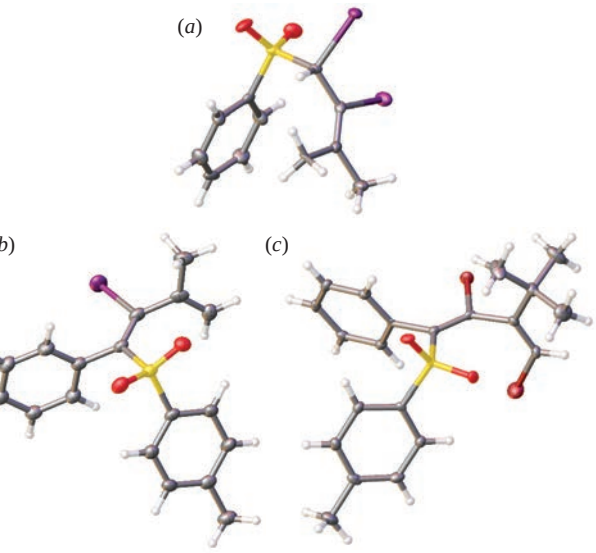
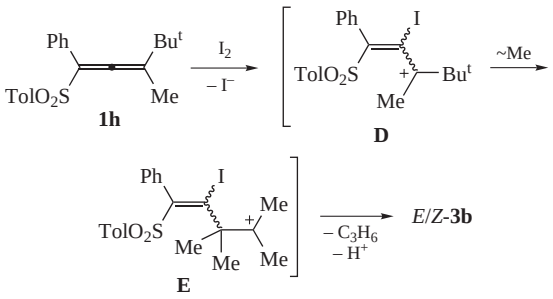
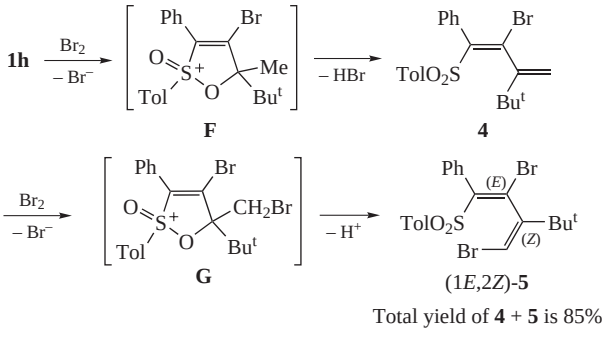


Figure 1 Molecular structure for compounds (*a*) **2a**, (*b*) *E*-**3b** and (*c*) **5**.



Scheme 3

Taking into account unusual reactivity of allene **1h**, we examined its reaction with bromine (Scheme 4). Allene **1h** reacted with 2 equiv. of bromine forming mixture of bromobutadienes **4** and **5**.¶ Being treated with one more equivalent of Br_2, the mixture is transformed into dibromobutadiene (1*E*,2*Z*)-**5**. Most probably, allene **1h** on contact with Br_2 forms at first cation **F**, which is deprotonated into butadiene **4**. The latter reacts, in turn, with Br_2 giving rise to intermediate cation **G**, which is deprotonated with formation of product **5**. The formation of cyclic species **F**, **G** (see Scheme 4) and **C** (see Scheme 2) may take place analogously to the cyclization of phosphoryl allenes.[7,8]



Scheme 4

Crystal data for **5**: $C_{21}H_{22}Br_2O_2S$ (M = 498.26), monoclinic, space group $P2_1/c$, at 100(2) K: a = 7.83654(12), b = 17.8958(3) and c = = 14.6788(2) Å, β = 93.0497(16)°, V = 2055.66(6) Å^3, Z = 4, d_{calc} = = 1.610 g cm^{-3}, μ(CuKα) = 6.048 mm^{-1}, F(000) = 1000.0. Total of 8963 reflections were measured and 3895 independent reflections (R_{int} = 0.0264) were used in a further refinement, which converged to wR_2 = 0.1583 and GOF = 1.107 for all independent reflections [R_1 = 0.0528 was calculated against F for 8963 observed reflections with $I > 2\sigma(I)$].

CCDC 1580907, 1843278 and 1843308 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

¶ For procedure and characteristics of compounds **4** and **5**, see Online Supplementary Materials.

In conclusion, we conducted for the first time direct iodination of arylsulfonylallenes that provides an access to various diiodo alkenes and iodo dienes.

This study was supported by the Russian Science Foundation (grant no. 18-13-00008).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.005.

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Received: 8th August 2018; Com. 18/5664