A New General Route to 1,2-Diarylethylenes, 1,4-Diarylbutadienes and 1,6-Diarylhexatrienes Through Cycloaromatization of β-Oxodithioacetals

Ch. Srinivasa Rao, Okram M. Singh, Hiriyakkanavar Ila,* Hiriyakkanavar Junjappa*
Department of Chemistry, North-Eastern Hill University, Shillong – 793003, Meghalaya, India
*Received 31 January 1992*

A new general route for the title olefins 5a–e, 12, 13, 8a–e and 11a–e has been developed through nucleophilic addition of respective Grignard reagents i.e. allyl-, benzyl-, 1-(naphthylmethyl) magnesium halides to 5-aryl-1,1-bis(methylthio)pent-4-en-3-ones, 7-aryl-1,1-bis(methylthio)hepta-4,6-dien-3-ones and 9-phenyl-1,1-bis(methylthio)nona-4,6,8-trien-3-one followed by cycloaromatization of the resulting 3-substituted 1,1-bis(methylthio)alken-3-ols in the presence of boron trifluoride–diethyl ether complex.

In our earlier work, we have shown that allyl,[1] propargyl[2] and azaallyl[3,4] anions undergo regioselective 1,2-addition to α-oxoketene dithioacetals to give the corresponding tertiary alcohol thioacetals in high yields. These alcohols on treatment with boron trifluoride–diethyl ether complex underwent cationic cyclization to afford the corresponding cycloaromatized products. Thus it was possible to construct aromatic rings from open-chain precursors carrying built-in functional groups, leading to regiospecifically substituted aromatics. However, benzylmagnesium chloride underwent sequential 1,4- followed by 1,2-addition to afford the corresponding alcohols, which on subsequent cycloaromatization yielded naphtho-annulated products carrying an undesirable benzyl group.[5] This limitation of 1,4-addition was subsequently circumvented by reacting β-oxodithioacetals[6] with benzylmag-

nesium chloride to give the tertiary alcohols, which on boron trifluoride–diethyl ether complex catalyzed cyclization afforded sulfur free aromatics.[7] This methodology was further extended for the synthesis of substituted and condensed phenanthrene derivatives by cyclizing 1- or (2-naphthyl)methylmagnesium chloride with either α-oxoketene or β-oxodithioacetals.[7] During the course of these studies, we had also reported the reaction of α-cinnamoylketene dithioacetals with allylmagnesium halide to afford the substituted stilbenes[8] under the described conditions. However, this reaction was not

1,2	R	n	1,2	R	n
a	Ph	1	d	4-MeOC$_6$H$_4$	2
b	4-MeOC$_6$H$_4$	1	e	Ph	3
c	Ph	2	f	2-naphthyl	1
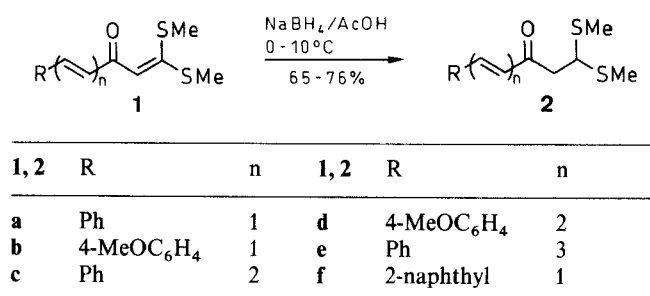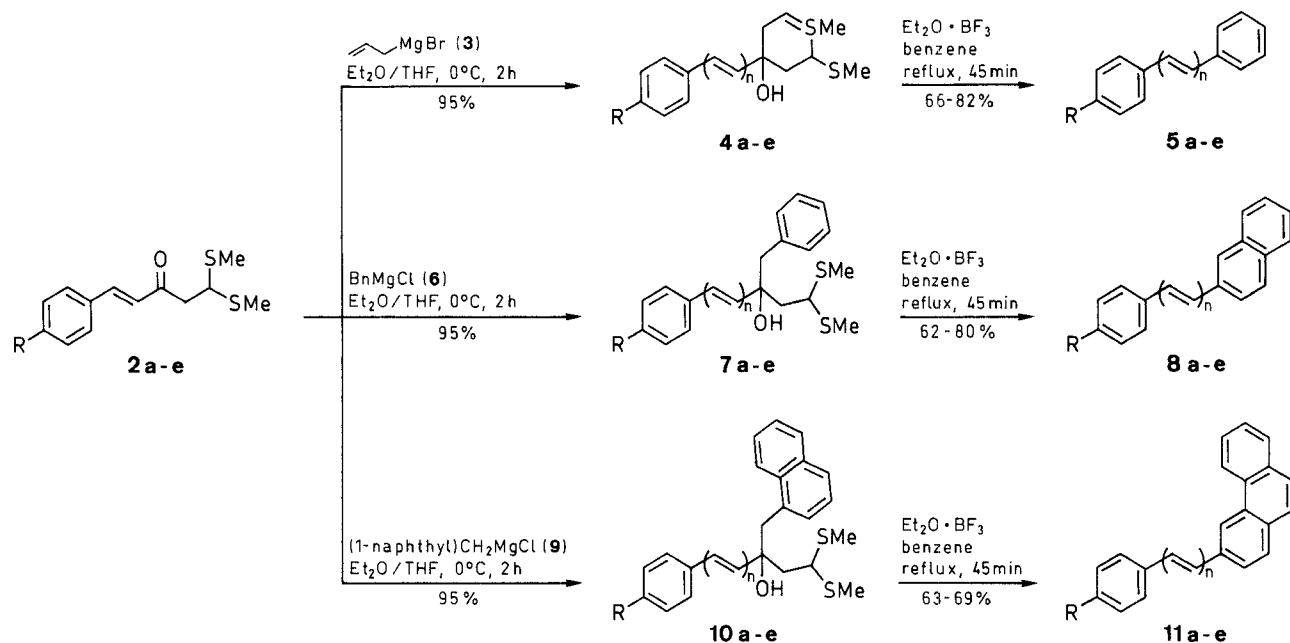
Scheme 1

Scheme 2

| 2, 4, 5, 7, 8, 10, 11	R	n	2, 4, 5, 7, 8, 10, 11	R	n
a	H	1	d	MeO	2
b	MeO	1	e	H	3
c	H	2			

successful when extended for the synthesis of 4-methoxy derivatives and higher enyl analogs of stilbenes. We therefore considered it of interest to overcome these limitations by subjecting β-oxodithioacetals 2a–e to cycloaromatization studies with allyl-, benzyl- and (1-naphthyl)methylmagnesium halides. Thus, the synthesis of 1,2-diarylethylenes, the corresponding 1,4-butadienes and 1,3,5-hexatrienes has been described in this communication.

The desired cinnamoyl 2a,b, 3-(2-naphthyl)propenoyl 2f dithioacetals and their higher enyl analogs, 2c–e, were prepared in good yields by regio- and chemoselective conjugate 1,4-reduction of the respective α-oxoketene dithioacetals with sodium borohyride in acetic acid according to our earlier reported procedure.[6]

In a typical experiment, when 2a was reacted with allylmagnesium bromide, the corresponding tertiary alcohol thioacetal 4a was formed in nearly quantitative yield. The tertiary alcohol 4a on treatment with boron trifluoride–diethyl ether complex in refluxing benzene yielded stilbene (5a) in 78% yield. Similarly 4-methoxy-stilbene (5b) which could not be synthesized earlier from 1b[8] was obtained in 66% yield from 2b under identical conditions. The corresponding dienyl, 4c,d, and trienyl, 4e, tertiary alcohol thioacetals also underwent boron trifluoride etherate catalyzed cyclization to afford 1,4-di-arylbutadienes 5c,d and 1,6-diphenyl-1,3,5-hexatriene (5e) in 78–82% overall yields. All these reactions were found to be clean and free from side products and tar. The methodology could be similarly extrapolated for the synthesis of 1-aryl-2-(2-naphthyl)ethylenes 8a,b, the respective dienes 8c,d and triene 8e by reacting 2a–e with

benzylmagnesium chloride and subsequently cyclizing the resulting tertiary alcohols 7a–e under the described conditions. Similarly the 1-aryl-2-(3-phenanthryl)ethyl-enes 11a,b and their higher enyl analogs 11c–e were prepared in 63–69% overall yields by reacting 1-(naph-thyl)methylmagnesium chloride 9 with 2a–e under similar conditions.

The 2-naphthyl derivative 2f also underwent facile cy-cloaromatization with benzylmagnesium chloride to yield 1,2-bis(2-naphthyl)ethylene (12) in 68% yield. The di-arylethylene 13, a precursor[9] for hexahelicene was simi-larly obtained in 64% yield by treatment of 2f with 9 under standard conditions.
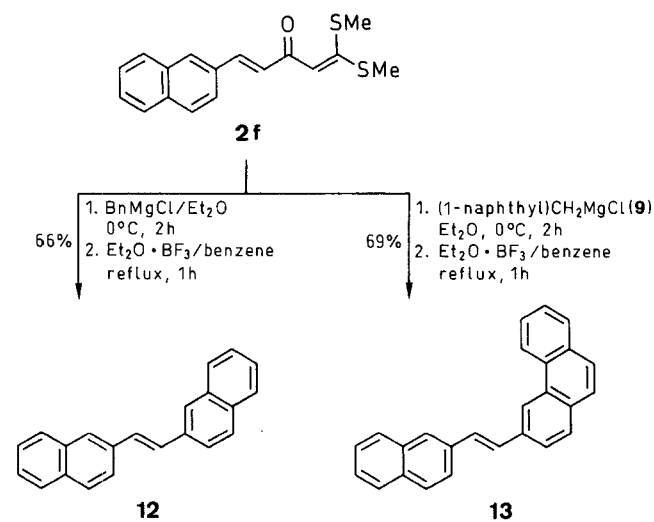
Scheme 3

Table. Compounds 5a–e, 8a–e, 11a–e, 12 and 13 Prepared

Product	Yield[a] (%)	mp[b] (°C)	Lit. mp (°C)
5a	78	123–124	124–125[13]
5b	66	134–135	136[13]
5c	82	151–152	153[14]
5d	78	160–161	161–162[15]
5e	81	200–201	200–202[16]
8a	80	147–148	148–149[17]
8b	68	177–178	178–179[17]
8c	72	170–171	171–172[18]
8d	71	164–165	165–167[19]
8e	62	152–153	153–154[22]
11a	69	151–152	153[20]
11b	65	158–159	159[21]
11c	69	146–147	147–148[22]
11d	68	195–196	196–197[22]
11e	63	250–252	253–254[22]
12	66	257–258	258–259[23]
13	69	273–274	274–275[9]

[a] Yield of pure isolated product.

[b] Melting points were uncorrected and determined on Thomas Hoover apparatus.

In summary, a new efficient synthesis of 1,2-diarylethylenes, 1,4-diarylbutadienes and 1,6-diaryl-1,3,5-hexatrienes has been formulated.[10] The overall strategy of creating an aromatic ring through its acyclic precursors yielding otherwise inaccessible ethylenes has been successfully realized. The method is successfully extended for the synthesis of diphenyl-, 5a,b, phenyl, naphthyl-, 8a–e, phenyl phenanthryl-, 11a–e, dinaphthyl-, 12, and naphthyl, phenanthryl-substituted, 13, olefins. Many of these olefins are useful substrates for photocyclization to condensed aromatics[11] and in Diels–Alder reactions. The 1,6-diphenylhexatrienes are useful molecular probes in the study of membrane fluidity.[12]

1,2-Diarylethylenes 5a–e, 12, 13, 1,4-Diaryl-1,3-butadienes 8a–e and 1,6-Diaryl-1,3,5-hexatrienes 11a–e; General Procedure:

To a well stirred and cooled (0°C) suspension of allyl/benzyl/1-(naphthylmethyl)magnesium halide, prepared from allyl bromide (1.90 g, 16 mmol), BnCl (1.98 g, 16 mmol) or 1-(naphthylmethyl) chloride (2.3 g, 16 mmol) and Mg turnings (1.2 g, 0.52 atom) in dry Et₂O (40 mL), a solution of β-oxodithioacetal 2a–f [6] (8 mmol) in dry THF (30 mL) was added and the mixture was further stirred at 0°C for 1 h. It was then poured into sat. aq NH₄Cl (300 mL), extracted with Et₂O (3 × 30 mL), dried (Na₂SO₄) and evaporated in vacuo to give crude alcohol acetals in nearly quantitative yields which were used as such for cyclization without further purification.

To a solution of crude alcohol, obtained as above, in dry benzene (60 mL), Et₂O · BF₃ (10 mL), was added and the reaction mixture was refluxed for 45 min (*Attention!* Evolution of MeSH!). After cooling, it was poured into H₂O (300 mL), dried (Na₂SO₄) and evaporated to give crude olefins 5a–e, 8a–e, 11a–e, 12 and 13 which were further purified by passing through silica gel column using hexane as eluent (Table).

All the olefins thus prepared were characterized by comparison of their physical and spectral data with those reported in the literature (Table). All the above olefins were shown to have all *trans* stereochemistry.

(1) Singh, G.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1984**, *25*, 5095.

(2) Gupta, A.K.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1987**, *28*, 1459.

(3) Balu, M.P.; Ila, H. Junjappa, H. *Tetrahedron Lett.* **1987** *28*, 3023.

(4) Thomas, A.; Ila, H.; Junjappa, H. *Tetrahedron* **1990**, *46*, 4295 and references therein.

(5) Balu, M.P.; Singh, G.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1986**, *27*, 117.

(6) Srinivasa Rao, Ch.; Chakrasali, R.T.; Ila, H.; Junjappa, H. *Tetrahedron* **1990**, *46*, 2195.

(7) Srinivasa Rao, Ch.; Balu, M.P.; Ila, H.; Junjappa, H. *Tetrahedron* **1991**, *47*, 3499.

(8) Asokan, C.V.; Ila, H.; Junjappa, H. *Synthesis* **1987**, 284.

(9) Laarhoven, W.H.; Cuppen, TH. J.H.M., Nivard, R.J.F. *Tetrahedron* **1970**, *26*, 4865.

(10) For recent literature on synthesis of stilbenes and 1,4-diarylbutadienes:
Paventi, M.; Hay, A.S. *Synthesis* **1990**, 878 and references therein.

(11) Martin, R.H.; Flammang-Barbieux, M.; Cosyn, J.P.; Gelbcke, M. *Tetrahedron Lett.* **1968**, 3507.
Bogaert-Verhoogen, D.; Martin, R.H. *Tetrahedron Lett.* **1967**, 3045.
Carruthers, W. *J. Chem. Soc. C* **1967**, 1525 and references therein.

(12) Beck, A.; Heissler, D.; Duportail, G. *Tetrahedron* **1991**, *47*, 1459.

(13) Wheeler, O.H.; Battle de Pabon, H.N. *J. Org. Chem.* **1965**, *30*, 1473.

(14) McDonald, R.N.; Campbell, T.W. *J. Org. Chem.* **1959**, *24*, 1969.

(15) Guesten, H.; Salzwedel, M. *Tetrahedron* **1967**, *23*, 173 (Ger).

(16) *C.R.C. Hand book of Data on Organic Compounds*; Weast, R.C.; Astle, M.J., Ed.; C.R.C. Press Inc.: **1985**, Vol. 1, p. 726.

(17) Siegrist, A.E.; Liechti, P.; Meyer, H.R.; Weber, K. *Helv. Chim. Acta.* **1969**, *52*, 2521.

(18) Hayward, R.J.; Leznoff, C.C. *Tetrahedron* **1971**, *27*, 2085.

(19) S. Iraelasvili, *Proc. Int. Congr. Pure Appl. Chem. (London)*, **1947**, *2*, 138; *Chem. Abstr.* **1975**, *82*, 45631.

(20) Laarhoven, W.H. Cuppen TH. J.H.M., Nivard, R.J.F. *Tetrahedron* **1970**, *26*, 1069.

(21) De Jong, M.H.; Laarhoven, W.H. *Recl. Trav. Chim. Pays Bas* **1973**, *92(5)*, 673 (Eng); *Chem. Abstr.* **1973**, *79*, 17903.

(22) Mikhailov, B.M.; Tersarkisyan, G.S. *Izv. Akad. Nauk, SSSR Octd. Khim. Nauk.* **1960**, 1267; *Chem. Abstr.* **1961**, *55*, 543a.

(23) Spatz, S.M. *J. Org. Chem.* **1961**, *26*, 4160.