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DIANION DERIVATIVES OF METHYL- AND ISOPROPYL-2.4-PENTADIENEDITHIOATE AS d^5-REAGENTS

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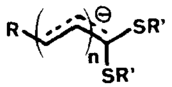
Summary: Li-K-Derivatives of the dianions 4 are generated. Reactions with carbonyl compounds occur at the ω-position to yield 6 - 9.



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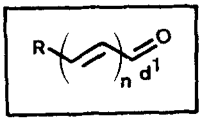
n = 0, 1, 2...



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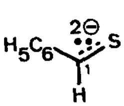

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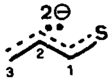

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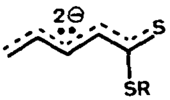
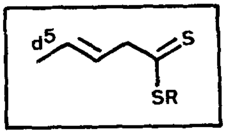


4a: $R = CH_3$
b: $R = i\text{-}C_3H_7$



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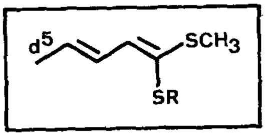

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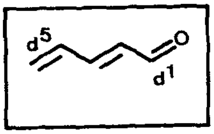
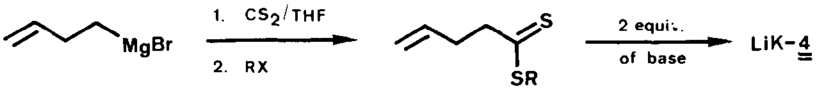


4'''

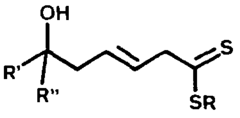
Deprotonated thioacetals 1 show a pronounced preference to react at the thiolated carbon atom with electrophiles[1]. Thus, they are widely used in transformations requiring d^1-synthons[1,2] 1'. In many synthetic situations, reactivity remote from the functional group is desired. We have previously shown[3] that this can be accomplished by employing dianion derivatives which, in addition to exhibiting ω-ambidoselectivity[2], have reactivity umpolung as compared with their neutral counterparts (π-systems vs. doubly "LUMO-filled" π-systems)[2]. Two examples involving sulfur are Li_2-thiobenzaldehyde[3a,3c] 2 and Li_2-thioacrolein[3b,3c] 3. The present communication demonstrates that the Li/K-dithioate **4** corresponds to the d^5-synthons[2] **4'**, **4"**, and **4"'**.

Addition of carbon disulfide to homoallyl Grignard reagent and alkylation of the resulting dithioate with iodomethane or 2-iodopropane (in the presence of HMPT) furnishes the dithioesters **5** in better than 80% yield[4]. As with γ.δ-unsaturated ketones[3d], treatment of **5** first with potassium hydride (0^{o}-20^{o}C) and then with sec-butyllithium/2 TMEDA (-78^{o}C) in THF generates Li/K-derivatives of dianions: **4a** as orange suspension, **4b** as red-brown solution. Both



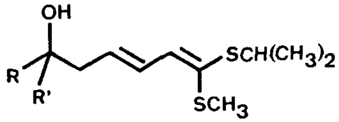
5

(**a** and **b** as in **4**)



6

(**a** and **b** as in **4**)



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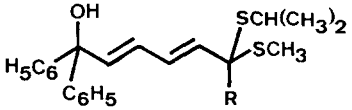

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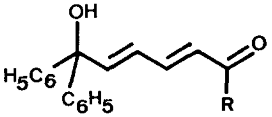

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(**a**: R = CH_3; **b**: R = C_2H_5)

combine with aldehydes and ketones preferentially[5] in the 5-position to give dithioates of type **6** after aqueous workup or ketene thioacetals[6] **7** after quenching with iodomethane; the better yields are obtained with **4b**.

Deprotonation (2 LDA, THF/15% HMPT, -78^{o} - 0^{o}C) and alkylation of the benzophenone adduct **7**, R = R' = C_6H_5, leads to the *6-hydroxy-dienone thioacetals* **8** (cf. ref.[1b]) which were hydrolyzed (CH_3I/aq. THF-acetonitrile, $CaCO_3$)[1a] to the parent carbonyl compounds **9**, cf. **4"'**.

The *yields and structures of chromatographed* (SiO_2) and analytically pure products are listed in the accompanying table, together with some characteristic data.

Table

Yields and some data of the products 5 - 9.

precursors	products	yield [%]	b.p., m.p. or ^{1}H-NMR (δ in ppm)
1-bromo-4-butene	5a	89	43-45^o/1 Torr
1-bromo-4-butene	5b	81	38-40^o/0.6 Torr
5a, benzaldehyde	6a, R' = C_6H_5, R" = H	43	CHO, δ = 4.58 (t,J = 7 Hz)
5a, cyclohexanone	6a, R'-R" = $(CH_2)_5$	38	$-(CH_2)_5-$,δ = 1.4 (m)
5a, benzophenone	6a, R' = R" = C_6H_5	71	64-66^{o}C
5b, propanal	6b, R' = C_2H_5, R" = H	56	CHO, δ = 3.9 (quint,J=7Hz)
5b, 2-methylpropanal	6b, R' = i-C_3H_7, R" = H	49	CHO, δ = 3.28 (m)
5b, 2.2-dimethylpropanal	6b, R' = t-C_4H_9, R" = H	60	$(CH_3)_3C$, δ = 0.9 (s)
5b, benzaldehyde	6b, R' = C_6H_5, R" = H	73	CHO, δ = 4.62 (t,J = 7 Hz)
5b, acetone	6b, R' = R" = CH_3	39	$(CH_3)_2C$, δ = 1.16 (s)
5b, cyclopentanone	6b, R' - R" = $(CH_2)_4$	44	$-(CH_2)_4-$, δ = 1.6 (m)
5b, cyclohexanone	6b, R' - R" = $(CH_2)_5$	55	$-(CH_2)_5-$, δ = 1.43 (m)
5b, benzophenone	6b, R' = R" = C_6H_5	84	53-55^{o}C
5b, benzophenone, CH_3I	7 , R = R' = C_6H_5	80	85-86^{o}C
7 , R = R' = C_6H_5, CH_3I	8a	76	CH_3C, δ = 1.7 (s)
7 , R = R' = C_6H_5, C_2H_5I	8b	85	$\underline{CH_3}CH_2$,δ=1.0 (t,J = 7 Hz)
8a, alkylative hydrolysis	9a	57	128-130.5^{o}C
8b, alkylative hydrolysis	9b	39	110-112^{o}C

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4) J. Meijer, P. Vermeer and L. Brandsma, Rec. Trav. Chim. 92, 601 (1973).

5) A few percents of d^3-product are also formed, but readily removed during chromatographic purification of 6.

6) Only one stereoisomer of 7 is isolated as judged from the ^{1}H-NMR-SCH$_3$ singlett. In analogy with the configurations of the products[3b,3c] from 3, we have drawn E,E-7.

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