# Novel Single Step Preparation of 2- and 2,3-Substituted 1,3-Dienes

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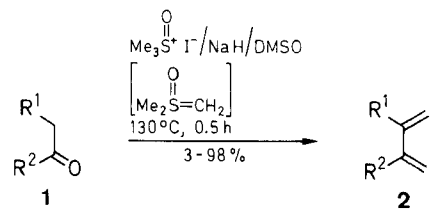
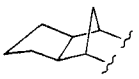
An efficient method for preparing 2- and 2,3-substituted 1,3-dienes **2**, from ketones **1** by treatment with dimethyloxosulfonium methylide in the presence of sodium methylsulfinylmethide is described.

Recently we have reported the unusual transformation of 3-methylenebicyclo[3.3.1]nonan-7-one oxide by treatment with dimethyloxosulfonium methylide.[4] Surprisingly the colorless oil thus obtained turned out to be 4,5-dimethylenetricyclo[4.3.1.$0^{3,8}$]decan-1-ol **(2j)** instead of the diepoxide which we hoped to be the major product in accordance with Corey's synthetic procedure.[2,3] As far as conjugated dienes represent a useful starting material for a variety of interesting structures, and the hitherto known routes to substituted 1,3-dienes usually are multistep and proceed in low overall yields,[4-8] we have now checked the validity of the reaction towards other alicyclic and aliphatic carbonyl compounds. The reaction does in fact work, and accordingly, we report here a new procedure for the synthesis of 1,3-dimethylenes from ketones. This transformation has been achieved involving only a single step by the reaction of ketones **1a–m** with dimethyloxosulfonium methylide in dimethyl sulfoxide at 130 °C in the presence of sodium methylsulfinylmethide as a catalyst.

As indicated in the Table high yields of dienes were obtained in most cases. Cyclopentanone **(1h)** gave only 3% yield of the desired product. Only traces of olefinic product were formed in the case of acetophenone **(1a)** as detected by NMR spectroscopy. Reaction with 1-adamantylacetic aldehyde **(1d)** demonstrates that aldehydes can be used also for the preparation of 1,3-dimethylenes. This work is in progress now.




| 1,2 | $R^1$ | $R^2$ | 1,2 | $R^1$ | $R^2$ |
|---|---|---|---|---|---|
| **a** | H | Ph | **i** | |  |
| **b** | H | 1-adamantyl | **j** | |  |
| **c** | *t*-Bu | H | **k** | |  |
| **d** | 1-adamantyl | H | **l** | |  |
| **e** | Pr | Pr | **m** | |  |
| **f** | $-(CH_2)_2-$ | | | | |
| **g** | $-(CH_2)_4-$ | | | | |
| **h** | $-(CH_2)_5-$ | | | | |

All starting materials, except 1-hydroxyprotoadamantane-4-one **(1)** which was prepared from 3-methylenebicyclo[3.3.1]nonane-7-one oxide by treatment with sodium methylsulfinylmethide,[1] were purchased from Synthon Reagent Co. DMSO was dried over molecular sieves 5Å. NaH (Fluka) and trimethyloxosulfonium iodide (Synthon) are commercially available. Analytical TLC plates and

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**Table.** 1,3-Dienes **2a–l** Prepared

| Product | Yield[a] (%) | bp (°C)/mbar or mp (°C)[b] | Molecular Formula[c] or Lit. bp (°C)/mbar | IR (film) $\nu$ ($cm^{-1}$) | $^1$H-NMR ($CCl_4$/TMS) $\delta$, $J$ (Hz) | $^{13}$C-NMR ($CDCl_3$/TMS) $\delta$ | MS (70 eV) $m/z$, $M^+$ (%) |
|---|---|---|---|---|---|---|---|
| **2b** (≡ **2d**) | 37[d,e] | 92/1.3 | $C_{14}H_{20}$[1] (188.3) | 1625 | 1.60 (m, 12H), 1.94 (m, 3H), 4.64 (m, 1H) 4.92 (dd, 1H, $J_1$ = 11, 2), 4.99 (m, 1H), 5.29 (dd, 1H, $J$ = 11, 17), 6.35 (dd, 1H, $J$ = 11, 17) | 26.8 (d), 35.2 (t), 38.8 (t), 39.3 (t), 105.1 (t), 112.7 (t), 134.5 (t), 155.2 (s) | 188 (71) |
| **2c** | 15 | 102–104/1020 | 103.5–104/1013[9] | 1628 | | | 110 (42) |
| **2e** | 89 | 145/1020 | $C_9H_{16}$ (124.2) | 1620 | 0.60–1.80 (m, 8H), 2.20 (m, 4H), 4.45 (m, 2H), 5.02 (m, 2H) | 12.2 (g), 20.8 (q), 26.2 (t), 27.2 (t), 30.6 (t), 108.5 (t), 112.2 (t), 145.2 (s), 149.1 (s) | 124 (55) |
| **2f** | 3 | 47/147 | 80–82/173[7], 45/133[8] | 1640, 1628 | 1.70 (m, 2H), 2.42 (m, 4H), 4.85 (s, 2H), 5.36 (s, 2H) | – | 94 (62) |
| **2g** | 94 | 126/1008 | 73–74/181[6] | 1645 | 1.40–1.80 (m, 4H), 2.35 (m, 4H), 4.62 (m, 2H), 4.87 (m, 2H) | – | 108 (75) |
| **2h** | 98 | 140/1012 | $C_9H_{14}$[f] (122.2) | 1625, 1605 | 1.40–1.80 (m, 6H), 2.30 (m, 4H), 4.69 (m, 2H), 5.10 (m, 2H) | – | 122 (88) |
| **2i** | 71 | 75/7 | $C_{12}H_{16}$ (160.3) | 1668 | 1.40–3.00 (m, 10H), 4.65 (m, 2H), 4.95 (d, 1H, $J$ = 2), 5.11 (d, 1H, $J$ = 2) | 32.1 (t), 34.4 (d), 34.6 (d), 37.1 (d), 38.3 (t), 38.4 (t), 39.8 (t), 41.2 (t), 103.9 (t), 105.4 (t), 149.3 (s), 152.3 (s) | 176 (100) |
| **2j** | 65 | 57 | $C_{12}H_{16}O$ (176.3) | 1638 | 1.30–3.00 (m, 11H), 3.57 (m, 1H), 4.50 (d, 1H, $J$ = 2), 4.65 (s, 1H), 4.85 (d, 1H, $J$ = 2), 5.07 (s, 1H) | 32.8 (t), 35.6 (t), 38.2 (t), 41.4 (t), 45.3 (d), 47.1 (d), 47.4 (d), 77.1 (s), 106.4 (t), 108.3 (t), 149.9 (s), 152.4 (s) | 176 (100) |
| **2k** | 15 | 71/5 | $C_{13}H_{18}$ (174.3) | 1620 | 1.50–2.00 (m, 12H), 2.60 (m, 2H), 4.55 (d, 2H, $J$ = 1), 5.00 (d, 2H, $J$ = 1) | 25.7 (d), 34.3 (t), 35.9 (t), 38.6 (d), 107.2 (t), 154.6 (s) | 174 (100) |
| **2l** | 17[h] | 64/5 | $C_{12}H_{18}$ (162.3) | 1625 | 0.67 (s, 3H), 0.82 (s, 3H), 0.90 (s, 3H), 1.10–1.80 (m, 4H), 2.10 (s, 1H), 4.55 (m, 1H), 4.65 (m, 1H), 5.05 (m, 2H) | 10.5 (g), 16.1 (g), 18.3 (g), 25.5 (t), 32.8 (t), 44.8 (d), 50.4 (s), 52.6 (s), 96.9 (t), 98.5 (t), 151.1 (s), 154.5 (s) | 162 (54) |
| **2m** | 92 | 71/4 | $C_{12}H_{16}$ (160.3) | 1634 | 1.0–2.0 (m, 10H), 2.45 (m, 2H), 4.65 (s, 2H), 4.90 (s, 2H) | 25.9 (t), 30.2 (t), 30.8 (t), 45.5 (d), 48.0 (d), 98.1 (t), 150.7 (s) | 160 (100) |

[a] Yield of isolated product. Compound **2a** was obtained only in traces.
[b] Not corrected.
[c] Satisfactory microanalyses obtained: C ± 0.25, H ± 0.08.
[d] Conversion of starting ketone 56%.
[e] Compound **2b** (≡ **2d**) was also obtained from **1d** in 12% yield.
[f] No physical data have been published for **2h**. Spectroscopic data were previously reported.[5]
[g] Conversion of starting ketone 23%.
[h] Conversion of starting ketone 56%.

silica gel (200–400 mesh) were purchased from Chemapol. Mass spectra were obtained using a Varian MAT 7A with EI ionisation. IR spectra were recorded on a Specord 75-IR spectrophotometer, NMR spectra on a Bruker WP 200 spectrometer ($^1$H, 200 MHz; $^{13}$C, 50.3 MHz).

**1,3-Dienes 2a–m; General Procedure:**
To a well-stirred suspension of NaH (5 mmol) in dry DMSO (5 mL) trimethyloxosulfonium iodide (3 mmol) is added at r.t. under $N_2$. The mixture is stirred for 15 min, gently heated to 130 °C and the appropriate carbonyl compound **1** (1 mmol) in dry DMSO (1 mL) is added immediately. After stirring for additional 30 min at 130 °C, the mixture is cooled and extracted with dry pentane. The pentane extract is washed with water, dried ($MgSO_4$), and concentrated. The final purification of the diene is carried out by chromatography on silica gel (eluent: pentane) or by distillation *in vacuo*.

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