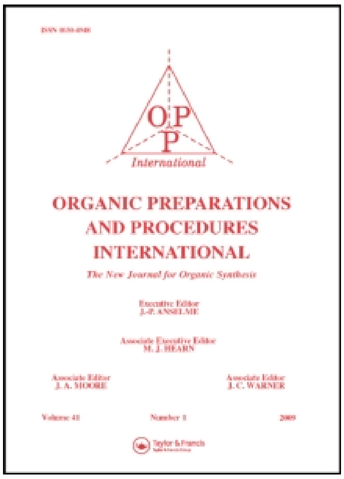

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AN EFFICIENT PREPARATION OF TETRAMETHYLALLENE

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Tetramethylallene (2,4-dimethyl-2,3-pentadiene), formerly commercially available, has disappeared from the marketplace. Moreover, the starting material for the standard preparation of this useful synthetic intermediate, 2,2,4,4-tetramethylcyclobutane-1,3-dione,[1] has become rare and costly. For this reason, we have developed the preparative procedure shown, which starts with commercial diisopropyl ketone.

$$[(CH_3)_2CH]_2C{=}O + H_2NNH_2 \longrightarrow \underset{1}{[(CH_3)_2CH]_2C{=}NNH_2} \xrightarrow{I_2,\ Et_3N}$$

$$\underset{2}{(CH_3)_2CHCI{=}C(CH_3)_2} \xrightarrow[DMSO]{EtONa} (CH_3)_2C{=}C{=}C(CH_3)_2$$

In our procedure, the hydrazone of diisopropyl ketone (1) is converted to 2,4-dimethyl-3-iodo-2-pentene (2) *via* a method first reported by Barton and coworkers.[2] Although the reaction nominally should consume two moles of I_2 for every mole of 1, substantially less iodine is used in practice, owing to a side-reaction that converts 1 to 2,4-dimethyl-3-pentanone azine (and which consumes 1 mole of I_2 per mole of 1). We have been unsuccessful in suppressing this side-reaction, but, since 2 can be readily purified by distillation, it does not affect the purity of the final product.

Dehydrohalogenation of 2 to tetramethylallene is most easily effected by using sodium ethoxide in DMSO. Weaker bases (tributylamine or alcoholic solutions of alkoxides) afford greatly reduced or negligible yields, while more strongly basic media (potassium tert-butoxide in DMSO) cause isomerization of the product. Tetramethylallene prepared by this procedure is >99% pure, showing only one peak in the PMR (1.60 δ) and in GLPC analyses. Sealed-tube pyrolysis of this tetramethylallene affords the dimers previously reported,[3] but dimer yields are low unless an additive is included to suppress rearrangement to the conjugated diene.

EXPERIMENTAL SECTION

Diisopropyl ketone hydrazone (1). - A solution of 33 g of 95% hydrazine (0.97 mol) in 200 ml absolute ethanol was added to 100 g of diisopropyl ketone (0.88 mol) and refluxed for 10-24 hrs. Then approximately 180 ml ethanol was distilled at atmospheric pressure and the pot residue washed three times with saturated aqueous NaCl, dried over KOH pellets, and distilled under reduced pressure, bp 65-66° (6.5 mm), to afford 79 g of 1 (70% yield). PMR ($CDCl_3$): δ 1.03 (d, 6H, J = 7 Hz), 1.08 (d, 6H, J = 7 Hz), 2.51 (septet, 1H, J = 7 Hz), 2.94 (septet, 1H, J = 7 Hz), 5.09 (s, 2H).

2,4-Dimethyl-3-iodo-2-pentene (2). - A solution of 111 g of

1 (0.87 mol) and 373 ml of triethylamine (2.68 mol) in 1100 ml of tetrahydrofuran was cooled in an ice-salt bath. A solution of 355 g of iodine (1.38 mol) dissolved in a minimum of tetrahydrofuran (approximately 800 ml) was added dropwise with mechanical stirring over a period of 4-5 hrs so that the temperature of the reaction did not rise above 0°. After addition was complete, another 20 ml of triethylamine was added dropwise to discharge the color of unreacted iodine. If the reaction has gone to completion, the color will not be discharged completely. The reaction vessel was stoppered and allowed to stand overnight to permit maximum precipitation of triethylammonium iodide. The reaction mixture was then filtered and the residue (approximately 600 g) washed with three 100 ml portions of tetrahydrofuran. The filtrate and washings were combined and reduced to a volume of 700 ml by flash distillation[4] at atmospheric pressure. The solution was then washed once with saturated aqueous sodium bisulfite to remove the color of unreacted iodine, and the distillation continued under reduced pressure to afford 104 g (53%) of a broad middle cut, bp 65-75° (41 mm), of colorless 2. Compound 2 rapidly discolors in light and should be stored in the dark in a freezer if not used immediately after distillation. The PMR spectrum is the same as that previously reported for 2 prepared by a different route.[5] PMR (CDCl$_3$): δ 0.93 (d, 6H, $J = 6.5$ Hz), 1.88 (s, 3H), 1.92 (s, 3H), 2.36 (septet, 1H, $J = 6.5$ Hz).

Tetramethylallene. - In a dry box a tared 1-neck 500 ml round bottom flask equipped with a magnetic spinbar was charged with 17-18 g dry, solid sodium ethoxide and sealed with a serum cap. The flask was removed from the dry box and 110-120 ml DMSO (freshly distilled from CaH_2) added *via* a syringe. The mixture was stirred to dissolve most of the solid, and the serum cap then removed and quickly replaced with a Claisen adapter fitted with an addition funnel (no pressure equalizing arm). The sidearm of the Claisen adapter was fitted with a 75° angle adapter and a long stem distillation adapter whose stem had been cut to about half the length of a 100 ml pear shaped receiving flask. The receiving flask was filled with glass helices to cover at least 1 cm of the stem of the adapter and connected to aspirator vacuum via a drying tube and a stopcock. After the DMSO solution stopped bubbling, the receiving flask was cooled in a Dry Ice-acetone bath and 42 g (0.19 mol) of **2** added to the stirred base. Vacuum was regulated with the stopcock to prevent excessive frothing, and, after addition was complete, the reaction vessel warmed in a 50° water bath with continued stirring for one hour. The product collected in the receiving flask was washed with three portions of ice water to afford 15 g tetramethylallene, which can be freed from traces of DMSO, water, and starting material by distillation over CaH_2 at atmospheric pressure, bp 88-89° (84% yield).

Tetramethylallene: Raman Spectrum (neat, 488 nm exciting line) $\nu_{C=C=C}$ 1970 cm^{-1}; PMR ($CDCl_3$) δ 1.60 (s).

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