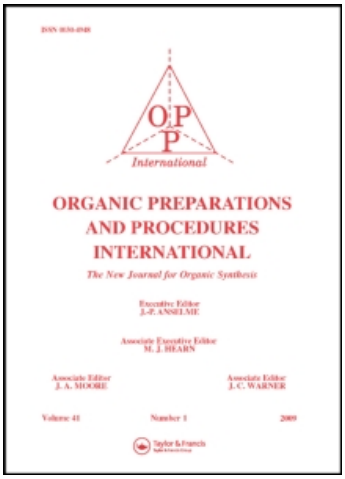


Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

4-METHYLPENT-4-EN-2-ONE (*iso*-MESITYL OXIDE)

R. D. Gillard[a]; B. T. Heaton[a]; M. P. Pilbrow[ab]
[a] The Chemical Laboratory, The University of, Kent Canterbury, England [b] Universität Erlangen-Nurnberg, Erlangen, West Germany

To cite this Article Gillard, R. D. , Heaton, B. T. and Pilbrow, M. P.(1974) '4-METHYLPENT-4-EN-2-ONE (*iso*-MESITYL OXIDE)', Organic Preparations and Procedures International, 6: 3, 131 — 134
To link to this Article: DOI: 10.1080/00304947409355085
URL: http://dx.doi.org/10.1080/00304947409355085

ORGANIC PREPARATIONS AND PROCEDURES INT. 6(3), 131-134 (1974)

4-METHYLPENT-4-EN-2-ONE (iso-MESITYL OXIDE)

R. D. Gillard, B. T. Heaton* and M. F. Pilbrow**

The Chemical Laboratory
The University of Kent
Canterbury, England

Although the interconversion of 4-methylpent-4-en-2-one (unconjugated isomer) and 4-methylpent-3-en-2-one (mesityl oxide) is catalysed by acid, it has previously been very difficult to obtain the less stable, unconjugated isomer pure because its boiling point is very close to that of mesityl oxide.[1,2] It has long been known that mesityl oxide reacts with platinum (II)[3-5] and it has been recently shown[6] that this reaction is accompanied by a 1,3-hydrogen shift on the organic ligand, resulting in the coordination of the unconjugated isomer to platinum (eq. 1). Reaction of this platinum complex with tributylphosphine results in the liberation of 4-methylpent-4-en-2-one in better than 99.9% purity. Other potentially bidentate alkenyl ligands do not undergo isomer-

$$Me_2C{=}CHCOCH_3 + Na_2PtCl_4 \longrightarrow \underline{cis}\text{-}[PtCl_2(CH_2{=}CMeCH_2COCH_3)] \quad (1)$$

$$\underline{cis}\text{-}[PtCl_2(CH_2{=}CMeCH_2COCH_3)] + 2PBu_3 \longrightarrow CH_2{=}CMeCH_2COCH_3 + [PtCl_2(PBu_3)_2] \quad (2)$$

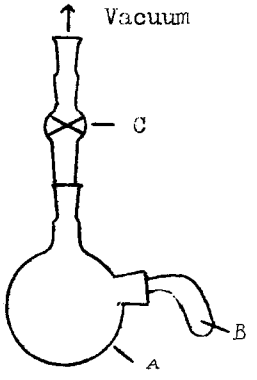
isation on reaction with platinum,[7,8] although we have recently shown that group VIA metal carbonyls isomerise 2-(alkenyl)-pyridines specifically to 2-(substituted allyl)-

pyridines, which are not otherwise readily prepared.[9]

EXPERIMENTAL

cis-(4-Methylpent-4-en-2-one)dichloroplatinum (II). - A suspension of 1.0 g. (2.6 mmoles) of sodium chloroplatinite and 8 ml. of mesityl oxide was heated to boiling for 2 min. in a 50-ml. flask fitted with a reflux condenser. The resulting hot black solution was quickly filtered and the filtrate on cooling in an ice-salt bath, gave yellow-orange crystals which were collected on a Buchner funnel and washed twice with 1 ml. of acetone to yield 0.5 g. (52%) of product, mp. 180-190° (dec.). The IR spectrum of the product has been described by Parshall and Wilkinson[5] and the nmr spectrum by Gillard et al.[6]

4-Methylpent-4-en-2-one. - A 50 ml. 2-necked flask, as shown in the diagram, was attached to a conventional vacuum line. Flask A contains 0.5 g. (1.3 mmole) of cis-(4-methylpent-4-en-2-one)dichloroplatinum and a magnetic stirrer; the side-arm B contains 4 ml. of tributylphosphine. Flask A and side-arm B were both cooled in liquid nitrogen and then evacuated to



0.001 mm. of Hg. Tap C was then closed and both A and B warmed to room temperature. The side-arm was rotated so that the tributylphosphine fell into A and stirring continued for 1 hr. when all the yellow crystals disappeared. Tap C was opened and the folatile product condensed into an evacuated receiver cooled in liquid nitrogen to give 0.11-0.13 g. (85-92%) of 4-methylpent-4-en-2-one, bp. 121°. The nmr and IR spectra of the product have been described by Gillard et al.[6] and Gray et al.[1] respectively. Glc on a column packed with 10% silicone oil on 80-100 mesh silanised chromosorb support, showed the compound to be better than 99.9% pure.

REFERENCES

*To whom inquiries should be addressed.

**Present address: Universität Erlangen-Nurnberg
8520 Erlangen, West Germany

1. H. F. Gray, R. S. Rasmussen and D. D. Tunnicliff, J. Am. Chem. Soc., 69, 1630 (1947).
2. F. H. Stross, J. M. Monger and H. De V. Finch, ibid., 69, 1627 (1947).
3. H. Zeise, J. prakt. Chem., 20, 193 (1840).
4. W. Prandtl and K. A. Hofmann, Ber., 33, 3981 (1900).
5. G. W. Parshall and G. Wilkinson, Inorg. Chem., 4, 986 (1962).
6. R. D. Gillard, B. T. Heaton and M. F. Pilbrow, J. Chem. Soc. (A), 353 (1970).
7. B. T. Heaton and D. J. A. McCaffrey, J. Organometal. Chem., 43, 437 (1972).

8. B. T. Heaton and D. J. A. McCaffrey, ibid., In press (paper 5685).

9. B. T. Heaton and D. J. A. McCaffrey, ibid., 66, C46 (1974).

(Received October 5, 1974; in revised form March 27, 1974)