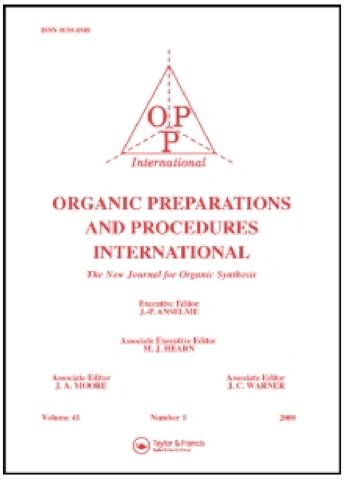


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF 2,3-DIHYDRO-3-METHYL-1-(2-NAPHTHYL)-1*H*-BENZ[*E*]INDENE AND 1,1,3-TRIMETHYL-3-PHENYLINDAN

W. P. Duncan[a]; E. J. Eisenbraun[a]; A. R. Taylor[b]; G. W. Keen[b]
[a] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, USA [b] Research and Development Department, Continental Oil Company, Ponca City, Oklahoma, USA

To cite this Article Duncan, W. P. , Eisenbraun, E. J. , Taylor, A. R. and Keen, G. W.(1975) 'SYNTHESIS OF 2,3-DIHYDRO-3-METHYL-1-(2-NAPHTHYL)-1*H*-BENZ[*E*]INDENE AND 1,1,3-TRIMETHYL-3-PHENYLINDAN', Organic Preparations and Procedures International, 7: 5, 225 — 229

To link to this Article: DOI: 10.1080/00304947509355152

URL: http://dx.doi.org/10.1080/00304947509355152

ORGANIC PREPARATIONS AND PROCEDURES INT. 7(5), 225-229 (1975)

SYNTHESIS OF 2,3-DIHYDRO-3-METHYL-1-(2-NAPHTHYL)-1*H*-BENZ[*e*]INDENE AND 1,1,3-TRIMETHYL-3-PHENYLINDAN

W. P. Duncan and E. J. Eisenbraun*

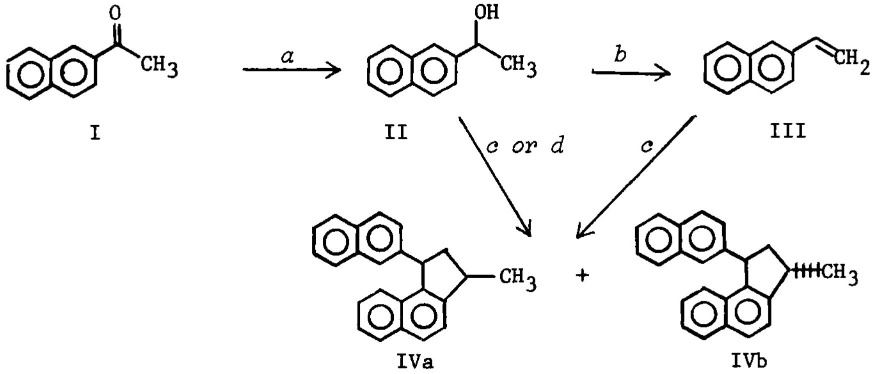
Department of Chemistry, Oklahoma State University
Stillwater, Oklahoma 74074 U.S.A.

and A. R. Taylor and G. W. Keen

Research and Development Department, Continental Oil Company
Ponca City, Oklahoma 74601 U.S.A.

cis- and *trans*-2,3-Dihydro-3-methyl-1-(2-naphthyl)-1*H*-benz[*e*]indene (IVa and IVb) have been prepared from II or III as shown in Scheme I.[1] Pure IVa was obtained in 34-40% overall yield by recrystallization. NMR analysis indicates that the 2-naphthyl and methyl groups of IVa are *cis* to each other as shown by the downfield shift of the methyl proton resonance to 1.39 δ.[2] Of the reagents used, Amberlyst-15 (A-15) gave better yields of IVa and IVb than PPA and was the most convenient to use.[3,4] Once formed, IVa and IVb are stable to the reaction conditions used in their preparation.[5]

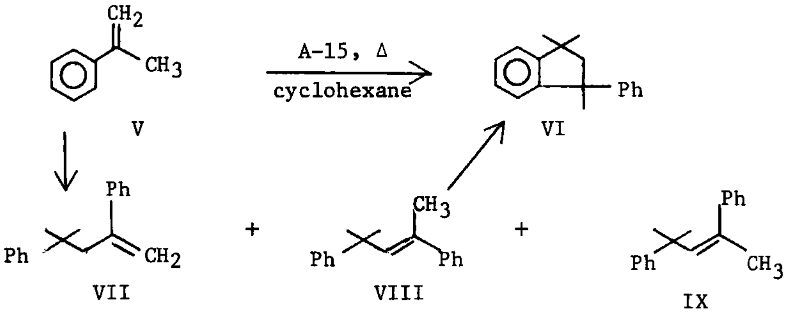
SCHEME I



^{a}$(C_4H_9)_2AlH$ in benzene. ^{b}$KHSO_4$, Δ, mineral oil. ^{c}PPA, Δ. ^{d}A-15 in cyclohexane at reflux.

In contrast to II or III, which react *via* a secondary benzylic carbonium ion, α-methylstyrene (V) would be expected to dimerize and cyclize in good yield.[6] Thus V, upon refluxing with A-15 in cyclohexane, gave 1,1,3-trimethyl-3-phenylindan (VI) in 80-84% yield. Larger-scale reactions are conveniently carried out using A-15 and conditions may be adjusted so that the dimerization is complete in 3 to 4 hr. The reaction is easily followed with gas chromatography using a UC W-98 column. We determined optimum reaction conditions for dimerization of one mole of α-methylstyrene by varying proportions of resin as reported in Table I.

SCHEME II



Amberlyst-15 may be reused for the dimerization of V and its efficiency appears to improve with use. Continued magnetic stirring reduces the particle size of the catalyst and it is likely that this influences the catalyst activity by increasing diffusion at the surface. A decrease in reaction time did not change the yield (ca. 80%) when 1 mole of V, 0.6 ℓ of cyclohexane, and 92 g of A-15 were magnetically stirred at reflux for 7 hr and the A-15 then collected and reused in additional runs for 4, 2.5, 0.8, and 0.8 hr respectively. Changes in volume of solvent also showed no effect.

An attempt[7] was made to isolate pure samples of the dimerized olefins VII, VIII, and IX which occur as intermediates to VI in the dimerization of V with A-15 as shown in Scheme II.

TABLE I

DIMERIZATION OF ONE MOLE OF α-METHYLSTYRENE (V)

Run	Cyclohexane used, ℓ	A-15 used, g	Time, hr	Temp., °C	Yield of VI, %
1	2.5	25	74	25	80
2	1.0	50	11	80	81
3	1.0	25	11	80	80
4	0.5	25	11	80	81
5	0.6	92	7	80	84
6	2.0	94	2.5	80	80

EXPERIMENTAL

cis- and *trans*-2,3-Dihydro-3-methyl-1-(2-naphthyl)-1*H*-benz[*e*]indene (IVa and IVb) and 1-(2-Naphthyl)-ethanol (II), and 2-Vinylnaphthalene (III).— II and III were prepared as outlined previously.[8]

Acid-Catalyzed Dimerization of II to IV with PPA.— A mixture of II (65.0 g, 0.38 mole) and PPA (650 g) was allowed to stand at room temperature for 24 hr. A deep purple color developed immediately. The reaction was completed by heating on a steam bath for 0.5 hr with occasional stirring. The resulting reaction mixture was poured into 2 ℓ of cold water with stirring. After complete decomposition was evident, the aqueous mixture was extracted several times with 500-ml portions of ether, washed with distilled water, dried (Na_2SO_4) and concentrated (rotary evaporator) to give 60.5 g of crude products. Glc analysis indicated a mixture of three nonsteam-volatile products, of which the major peak made up 80% of the mixture.[9] The resulting reaction mixture was distilled under reduced pressure (bp 200-203°/0.1 mm), eluted through a basic alumina column with petroleum ether (bp 60-68°), and recrystallized from 2-propanol to give pure IVa, 17.5 g (30%): mp 124-126°; ir (CCl_4) 3.27, 3.37 3.48, 6.05, 6.18, 6.58, 6.87, 7.25, 7.48, 9.07, 11.22, and 11.64 μ; pmr (CCl_4, TMS) δ 6.83-6.90 (m, 13, ArH), 4.81 (t, 1, dibenzylic), 3.54-3.20 (m, 1, benzylic) 3.15-2.80 (m, 1, one proton of -$C\underline{H}_2$), 1.94-1.59 (m, 1, one proton of $C\underline{H}_2$), 1.39 (d, 3, $C\underline{H}_3$).

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.00, H, 6.55.

Dimer IVb was not isolated. Its presence in the mother liquor from IVa is supported by pmr absorption: δ 4.88 (t, dibenzylic), 3.7-3.3 (m, benzylic), 2.5-2.2 (m, -CH_2-), and 1.33 (d, CH_3).

Acid-Catalyzed Dimerization of 2-Vinylnaphthalene (III) with PPA.— A mixture of III (4.62 g, 0.03 mol) and PPA (25 g) was caused to react as described above. Using the work-up procedure described for II gave pure IVa, 1.5 g (30%), mp 124.5-126.5°.

Acid-Catalyzed Dimerization of II with Amberlyst-15.— To a 3-ℓ reaction flask provided with a reflux condenser and magnetic stirrer was added II (86 g, 0.50 mol), cyclohexane (2 ℓ), and A-15 (94 g). After being heated at reflux for 5 hr, the reaction mixture was cooled, decanted, and concentrated (rotary evaporation). Distillative and chromatographic work-up as before followed by recrystallization from 2-propanol gave 31 g (40%) of IVa, mp 124-126°.

1,1,3-Trimethyl-3-phenylindan (VI).— In a procedure like that described for the preparation of IV with A-15 (except that the product was not eluted through a column of alumina), α-methylstyrene (118 g, 1.0 mol) gave 99.5 g of VI, bp 115-118°/1.0 mm (lit.[10] 154-155°/8 mm). A small sample of the clear viscous oil triturated with 95% ethanol gave colorless crystals of VI, mp 50-52° (lit.[11] 51-52°). These crystals were then used to seed the entire reaction product to give 99 g of VI, mp 50-52°. Recrystallization from 95% ethanol gave 97 g (83%) of pure VI, mp 51-52°. The pmr spectrum, other spectral data, and physical properties agreed with reported values.[10,11] The results of these experiments using A-15 and V are reported above and in Table I.

Acknowledgments.— This work was supported in part by National Science Foundation Science Faculty Fellowship, Grant 60052 to W. P. Duncan, 1970-72, and an American Petroleum Institute Assistantship to A. R. Taylor, 1972-74. We thank Dr. O. C. Dermer for having read the manuscript and Dr. J. W. Burnham for helpful discussions.

REFERENCES

1. L. A. Paquette and T. R. Phillips, J. Org. Chem., 30, 3883 (1965).
2. R. H. Bible, Jr., "Interpretation of NMR Spectra," Plenum Press, New York, N.Y., 1965, p. 25. Examination of molecular models indicate that the methyl substituent is in the plane of the *cis*-naphthyl ring; thus deshielding of the methyl group is expected.
3. Literature and a gift sample of Amberlyst-15 sulfonic acid resin were obtained from Rohm and Haas Co., Independence Mall West, Philadelphia, Pa. 19105. We thank Dr. C. T. Dickert for his assistance.
4. The solid A-15 catalyst is readily filtered from the reaction mixture.
5. After exposing to PPA for three days and then warming on a steam bath for 3 hr, IVa was recovered unchanged.
6. F. S. Dainton and R. H. Tomlinson, J. Chem. Soc., 151 (1953).
7. Two glc peaks were obtained on both Carbowax 20M and UC W-98 columns. Though these peaks were separated at the baseline, our attempts to collect fractions uncontaminated by material represented by the other peak were not successful. The fractions collected still contained about 15% contaminant according to glc determinations. However, this was adequate purification to permit assignment of structure VII to the first peak (2.3 min and 2.6 min retention time at 200° and 240° 5% Carbowax 20M and 6% UC W-98 respectively) and of VIII and IX to the other peak (retention time 3.0 and 3.3 min on the same columns). The ratio of peaks at 1.54 and 1.48 δ observed in the pmr spectrum of the latter fraction indicates that the ratio of VIII:IX is approximately 1:1.
8. W. P. Duncan, J. E. Russell, E. J. Eisenbraun, G. W. Keen, P. W. Flanagan and M. C. Hamming, J. Org. Chem., 37, 142 (1972).
9. The gas chromatography studies using a Hewlett-Packard model 5750 instrument were made at 240° on a 0.25-in. x 12-ft. column of 80-100 mesh Chromosorb G (acid-washed) treated with DMCS and coated with 5% silicone rubber UC W-98.
10. M. J. Rosen, Org. Synth. Coll. Vol. 4, 665 (1963).
11. C. S. Schoepfle and J. D. Ryan, J. Am. Chem. Soc., 52, 4021 (1930).

(Received July 22, 1975; in revised form October 21, 1975)