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INDICE

ANDRI E., DE ASMUNDIS C., FANUCCI F. - Il problema della ricristallizzazione delle facies micritiche . . . . . Pag. 1

MENESINI E. - Studio della variabilità di *Balanus perforatus perforatus* BRUGUIÈRE (cl. Cirripedia, Ord. Thoracica) in popolazioni fossili e viventi . . . . . » 15

LEONI L., PETRACCO C. - Ricerche sulla microdurezza dei silicati. III - Alcuni nesosilicati e sorosilicati . . . . . » 53

LEVI-MINZI R., RIFFALDI R. - Ulteriori indagini sulle reazioni Cd-acido umico » 74

RADI G. - La Tecchia della Gabellaccia (Carrara). Note paletnologiche . . » 81

DE POMPEIS C., AGRIPPA C. - Un insediamento dell'età del bronzo lungo il tratturo prospiciente San Clemente a Casauria . . . . . » 103

LEONI L., PALASCIANO A., TROYSI M. - Ricerche sulla microdurezza dei silicati. III - I granati . . . . . » 110

BOSSIO A., EL-BIED RAKICH K., GIANNELLI L., MAZZEI R., RUSSO A., SALVATORINI G. - Corrélation de quelques sections stratigraphiques du miopliocène de la zone atlantique du Maroc avec les stratotypes du bassin Méditerranéen sur la base des Foraminifères planctoniques, Nannoplancton calcaire et ostracodes . . . . . » 121

MENICAGLI R., PICCOLO O., LARDICCI L. - New optically active naphthalene derivatives: absolute configurations of 2-methyl-3- and 2,2-dimethyl-3-(α- and β-naphthyl)-butanes . . . . . » 138

MONTEFORTI B. - La « zona di Berceto » nell'evoluzione tettonica dell'Appennino settentrionale dal Paleocene al Pliocene . . . . . » 142

ORLANDI P. - La datolite del Monte Dragnone e i minerali che la accompagnano . . . . . » 165

ORLANDI P. - Il granato di M.te Ferrato e i minerali che lo accompagnano » 170

PITTI C., SORRENTINO C., TOZZI C. - L'industria di tipo Paleolitico superiore arcaico della grotta La Fabbrica (Grosseto). Nota preliminare . . . » 174

LEONI L., MELLINI M., SANTACROCE R. - Na-rich alkali-feldspar phenocrysts from metaluminous and peralkaline silicic volcanic rocks . . . . » 202

ORLANDI P., BIANCHI G. - Nota di mineralogia toscana - I minerali delle geodi dei marmi di Carrara . . . . . » 220

LANDINI W. - Osservazioni sulle placche faringee di alcuni labridi del Pliocene della Toscana . . . . . » 230

MENESINI E. - Studio di una Malacofauna del Pliocene medio del Bacino della Fine (Toscana Marittima): osservazioni paleoambientali . . . » 251

Conto rendite e spese anno 1975 . . . . . » 273

Elenco dei Soci per l'anno 1976 . . . . . » 275

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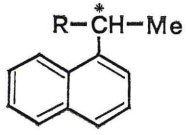
R. MENICAGLI, O. PICCOLO, L. LARDICCI (*)

NEW OPTICALLY ACTIVE NAPHTHALENE DERIVATIVES: ABSOLUTE CONFIGURATIONS OF 2-METHYL-3- AND 2,2-DIMETHYL-3-(α- AND β-NAPHTHYL)-BUTANES

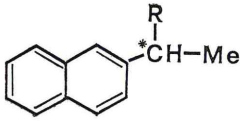
Riassunto — Sono stati preparati nuovi idrocarburi α- e β-naftil sostituiti otticamente attivi caratterizzati da differente ingombro sterico all'atomo di carbonio asimmetrico. Le loro configurazioni sono state assegnate per correlazione con derivati naftalenici noti in letteratura.

Summary — New chiral α- and β-naphthyl hydrocarbons with a different steric requirement at the asymmetric carbon atom were prepared and their configurations were established by correlation to known naphthalene derivatives.

The results we obtained in the study of the chiroptical properties of asimmetrically perturbed naphthalene chromophore (CIARDELLI et Al. [1975]) in optically active 2-naphthyl-butanes (MENICAGLI et Al. [1974]) and in hydrocarbon polymers with α-naphthyl groups in the side chains (CIARDELLI et Al. [1975]) encouraged us to extend the investigation to new α- and β-naphthalene derivatives of formula (**Ia, b**) and (**IIa, b**), having a different steric requirement at the asymmetric carbon atom.



R= Pr^i (Ia)
Bu^t (IIa)

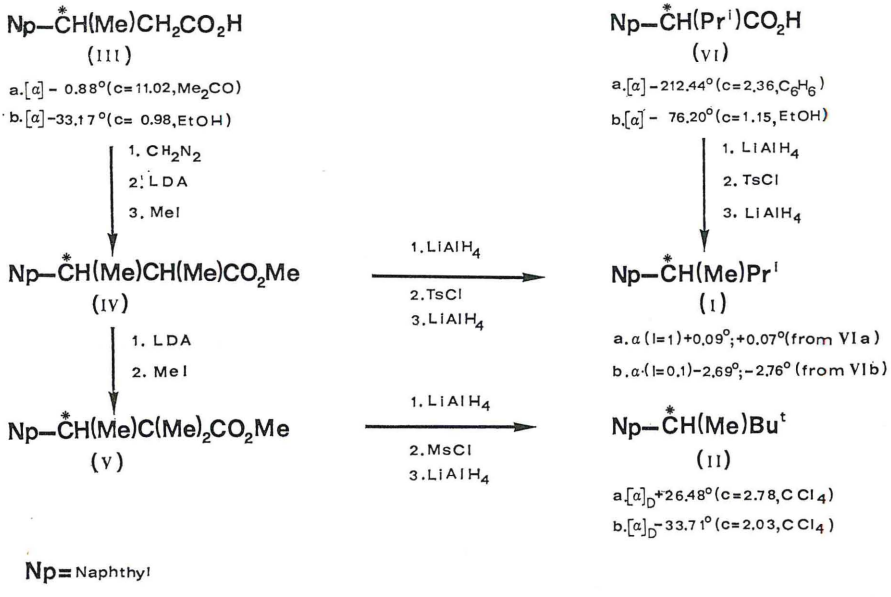


(Ib)
(IIb)

(*) Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica della Facoltà di Scienze M.F.N. della Università di Pisa.

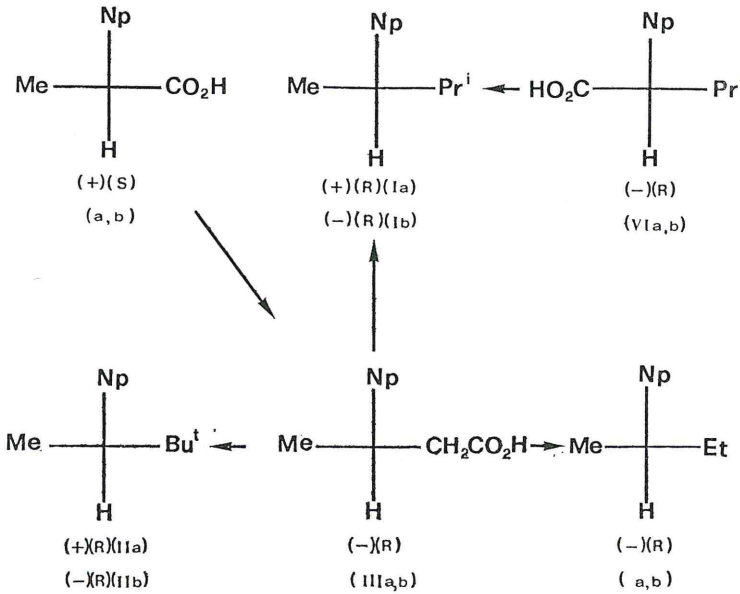
Compounds (**Ia**, **b**) and (**IIa**, **b**) were prepared starting from (R)-3-naphthyl-butanoic acids (**IIIa**, **b**) (Scheme), whose absolute configurations had been previously established (MENICAGLI et Al. [1974]) (Chart).

Scheme



The methyl esters of (**IIIa**, **b**) were converted into the corresponding α-methyl derivatives (**IVa**, **b**) (92 and 98 per cent yield) that, through an usual procedure (MENICAGLI et Al. [1974]) (Scheme), afforded, after preparative g.l.c. purification (2.7 m x 9.5 mm 3 per cent SE 301 on Chromosorb G 60/80 columns at 140°C, and 2,7 m x 9.5 mm 20 per cent APZ L on Chromosorb A 45/60 columns at 160°C respectively), (**Ia**) {35 per cent yield; bp. 92-93°C/0.4 mm Hg; ms: m/e 198 (M^+,20 per cent), 155 (100 per cent)} and (**Ib**) {35 per cent yield; bp. 97°C/0.5 mm Hg; ms: m/e 198 (M^+,21 per cent), 155 (100 per cent)}.

Chart



Compounds (**Va, b**) obtained *via* a further α-methylation reaction from (**IVa, b**) (90 and 98 per cent yield) gave (**IIa**) (35 per cent yield) and (**IIb**) (Scheme), that, after preparative g.l.c. purification in the above reported conditions, showed respectively bp. 114°C/0.25 mm Hg {ms: m/e 212 (M^+, 15 per cent), 155 (100 per cent)} and mp. 53-62°C, bp. 101-102°C/0.25 mm Hg {ms: m/e 212 (M^+,14 per cent), 155 (100 per cent)}.

It should be noted that $LiAlH_4$ reduction of the tosylate of 2,2-dimethyl-3-naphthyl-1-butanols gave a very poor yield of the corresponding hydrocarbons, in particular in the case of the β--naphthalene derivative: the carbinols were almost quantitatively recovered. The reduction of the methanesulphonates of 2,2-dimethyl-3-naphthyl-1-butanols (Scheme), while affording a satisfactory yield (79 per cent) of (**IIa**), did not appear quite suitable for the preparation of (**IIb**), because the hydride fission of O-S bond is once more the more important reaction.

The structure of the new hydrocarbons (**Ia, b**) and (**IIa, b**)

were confirmed by NMR spectroscopy. In the course of this investigation (Scheme) (**IIIa, b**) were configurationally related through (**Ia, b**) with the *i*-propylnaphthylacetic acids (**VIa**) (CASADIO et Al. [1962]) and (**VIb**) (1) (Chart), recovered by resolution of their racemates with (+)α-phenyl-ethylamine in ethanol.

On the basis of the chemical correlations adopted (Scheme) the absolute configurations of (**Ia, b**), (**IIa, b**) and (**VIa, b**) are so established (Chart), as none of the steps of the involved sequences should substantially affected the chiral centre of known configuration of the compounds (**IIIa, b**).

REFERENCES

CIARDELLI F., SALVADORI P., CARLINI C., MENICAGLI R., LARDICCI L. (1975) - Chirally perturbed α-naphthyl chromophore in helical polymers. *Tetrahedron Lett.*, 1779-1782.

MENICAGLI R., LARDICCI L., BOTTEGHI C. (1974) - Optically active α- and β-naphthalene derivatives: some chemical correlations. *Chem. & Ind.*, 920-921.

CASADIO S., PALA G., BRUZZESE T., MARAZZI UBERTI E. (1962) - Acidi naftilacetici - Nota I - Sintesi ed attività coleretica di acidi 1-naftilacetici α-sostituiti. *Il Farmaco, Ed. Sc.*, **17**, 797-809.

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(1) (R)(S)(**VIb**) was prepared by reacting methyl-2-naphthylacetate with sodium amide and *i*-propylbromide in liquid ammonia.