Tetrahedron Letters,Vol.24,No.17,pp 1783-1786,1983 0040-4039/83/171783-04$03.00/0
Printed in Great Britain

ORGANIC SYNTHESES WITH SULFONES (PART XXVIII[8]) ; SYNTHESIS OF TERPENOID COMPOUNDS BY WAY OF MICHAEL ADDITION REACTIONS TO CONJUGATED DIENYL SULFONES.

M. Julia*, D. Lavé, M. Mulhauser, M. Ramirez-Muñoz and D. Uguen.

Laboratoire de Chimie de l'Ecole Normale Supérieure
24 rue Lhomond, 75231 Paris Cedex 05, France.

Abstract : Michael additions of ethanol and ketones to allyl-dienyl sulfones yielded di-allylic sulfones which were transformed into isoprenoïd compounds by either Ramberg-Bäcklund reaction or thermolysis.

Allyl dienyl sulfones are obtained by alkylation of the readily available Z-2 methyl-1,3 butadienyl sulfinate 1. Addition reactions lead to diallyl sulfones [1]. A recent paper[2] describing the Ramberg-Bäcklund reaction (R.B.) on such a diallyl sulfone prompted us to submit the present letter.

The addition of various nucleophiles such as ethanol, t-butyl acetoacetate and phenylthioacetone to the sulfone 2 proved possible leading to 3a (E+Z), 3b (E) [3], 3d (E), eventually transformed into 3c, 3e, 4 and 5.

The R.B. reaction was then carried out under Meyers conditions [4a] or by a two step procedure [4b]; the results are shown in the table. It proved indeed possible to attach an isoprene unit to the original synthon through a double bond.

RAMBERG-BACKLUND REACTION

Substrate	Product	Yield (%)
3a , R=H	6a, R=H	82
3a, R=Prenyl	6a, R=Prenyl	55
3e, R=Prenyl	6e, R=Prenyl	91
4 , R=Prenyl	7[5a] R=Prenyl	50
5, R=Prenyl	8[5b] R=Prenyl	70
10	11 (X= OEt)	81

The possibility of working out a recurrent method for the building-up of unsaturated polyisoprenoid compounds was then investigated : starting with benzyl chloride the steps 9 → 10 → 11 (X=OEt) were carried out as above. Conversion of the ether 11 (X=OEt) into the corresponding primary chloride 11 (X=Cl) followed by another alkylation gave 12 thus paving the way to a recurrent isoprenylation.

A different way of joining the isoprene units to the growing chain was the pyrolysis pioneered by Lacombe and Stewart [6].

The isomeric tertiary allylic sulfones 13 are now readily available by treatment of the corresponding allylic esters with the dienesulfinate 1 under palladium(0) catalysis [7].

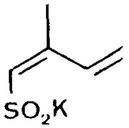
PYROLYSIS

Substrates	Mixture composition (%)	Total Yield (%)
14c, R = Prenyl	15c [5a] (60), 16c (19), (21)*	86
14a, R = H	15a (58), 16a (26), (14) *	73
14a, R = Prenyl	15a (65), 16a (35)	60

*unidentified isomeric products.

Addition of either ethanol or t-butylacetoacetate led to the di-allylic sulfones 14ac (R = H, Prenyl) which were pyrolysed at 180-200,C (Table) to give predominantly the head to tail products accompanied by minor amounts of isomeric compounds formed by 1-2' coupling (lavandulyl skeleton).

ACKNOWLEDGMENTS : We thank the C.N.R.S. (L.A. 32) for financial and material assistance.



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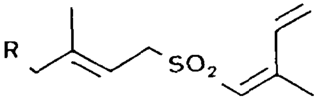

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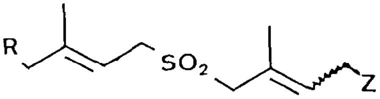


6 a c e

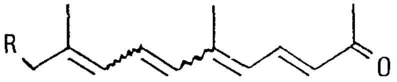
3a ; Z = $-\mathrm{OEt}$

3b ; Z = $-\mathrm{CH(CO_2t.But)-CO-CH_3}$

3c ; Z = $-\ \mathrm{CH_2-CO-CH_3}$

3d ; Z = $-\ \mathrm{CHSPh\cdot CO\cdot CH_3}$

3e ; Z = $-\ \mathrm{CH_2-CMeOH-CH=CH_2}$



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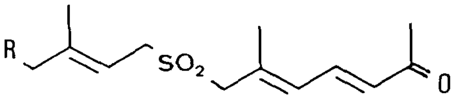

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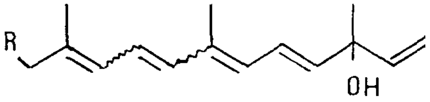

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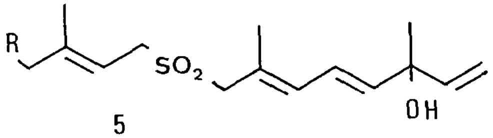

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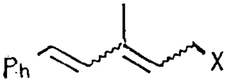
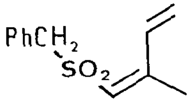


11 X=OEt, Cl



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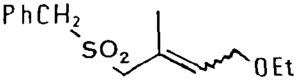

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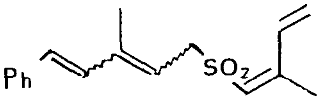

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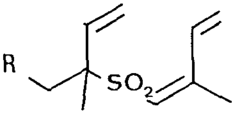

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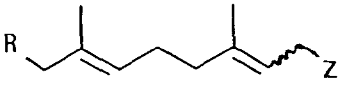
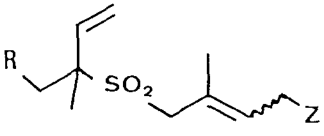
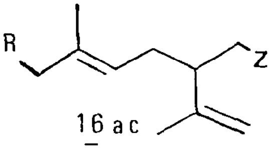


15 a c



14 a b c



16 a c

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3 a The stereochemistry will be discussed in the full paper. b All new compounds have given a satisfactory analytical and spectrochemical (^{1}H, ^{13}C NMR, I.R., Mass) data which will be described with the experimental details in the full paper.

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(Received in France 4 January 1983)