ACTA CHEMICA SCANDINAVICA 3 (1948) 256—258

Monosubstitution Derivatives of Cadalene. II *

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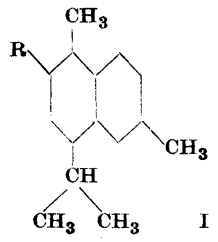
In a previous paper [1], one of us has shown that the nitration, Friedel-Crafts-acetylation, and bromination of cadalene lead to products with the substituent in the same position. By degradation reactions it was also shown that the entering substituent most probably occupies the 2-position (I; R = NO_2, CH_3CO, Br resp.), although the 3-position could not be definitely excluded.



I

After that work had been published, a paper by Campbell and Soffer [2] came to our knowledge, where the synthesis of 2-methylcadalene (I; R = CH_3) is described. By converting one of the substituting groups NO_2, CH_3CO or Br into CH_3 it would be possible to procure unequivocal evidence of the 2-position for these substituents.

This has now been done by treating the Grignard-reagent from bromocadalene with ethyl orthoformate and hydrolysing the acetal (I; R = $CH(OC_2H_5)_2$), which was not isolated, to the aldehyde [3] (I; R = CHO). This was reduced by Clemmensen-reduction to methylcadalene (I; R = CH_3). This compound was an oil, but was characterised as the picrate, the trinitrobenzolate, and the styphnate. These had m. p:s in good agreement with the values given by Campbell and Soffer [2] for the corresponding derivatives of

* Part I, Gripenberg, J. *Ann. Acad. Sci. Fennicae Ser. A.* **59** (1943) no. 14.

their 2-methylcadalene. Professor M. D. Soffer was kind enough to carry out mixed melting point determinations on these derivatives, for which we are grateful. He reported the following m. p:s.

	Present authors	Campbell and Soffer	Mixed melting point
Picrate	140—140.5°	138.5—139°	139.5—140.5°
Styphnate	170°	170°	170°
Trinitrobenzolate	167—168°	169—169.5°	167—169.5°

(The m. p:s of the picrate and the trinitrobenzolate are somewhat lower than the m. p:s reported in the experimental part. This is probably due to partial decomposition of the products on standing.)

As no depression of the m. p:s was observed, it seems safe to assume that the parent hydrocarbons were identical.

Briggs, Gill, Lions and Taylor [4] have, in a somewhat different way, also been able to connect the derivatives obtained by direct substitution of cadalene with the synthetic 2-methylcadalene.

The constitution originally assigned to nitro-, acetyl- and bromocadalene and the products obtained from them [1] can hence be regarded as correct.

EXPERIMENTAL

2-Cadalenealdehyde. The Grignard-reagent was prepared with 1.1 g Mg from bromocadalene (13 g) and then ethyl orthoformate (6 g) was added. The ether was distilled off, and the mixture was heated for half an hour on a water-bath. The thick oil obtained was poured into water, a small amount of acetic acid was added, and the acetal extracted with ether. The ether solution was warmed with 2 *N* hydrochloric acid on a water-bath. The ether was then evaporated and the remaining oil fractionated in a vacuum. The following fractions were obtained:

I	—170°/8 mm	1.1 g
II	170—180°/8 mm	1.4 g
III	190—200°/8 mm	3.5 g
Residue		3.0 g

Fraction III solidified and was recrystallised from light petroleum, m. p. 85.5—86.5°.

$C_{16}H_{18}O$ (226.2)	Calc. C 84.88	H 8.04
	Found » 85.00	» 7.55

The semicarbazone was prepared in the usual way and had after recrystallisation from alcohol m. p. 222—223°.

$C_{17}H_{21}ON_3$ (283.2)	Calc. C 72.06	H 7.47
	Found » 71.87	» 7.31

2-Methylcadalene. 2-Cadalenealdehyde (3 g) was reduced with amalgamated zinc (10 g) and hydrochloric acid (100 ml; 1 : 1) in the usual way. The reduction product was extracted with ether and steam distilled. 1 g of a colourless oil was obtained. This was without further purification converted into the picrate, styphnate and trinitrobenzolate.

The picrate, red needles from alcohol, had m. p. 143—144°.

The styphnate, orange red needles from alcohol, had m. p. 169—170°.

The trinitrobenzolate, yellow needles from alcohol, had m. p. 170—170.5°.

SUMMARY

The conversion of bromocadalene into 2-methylcadalene is described. The previously proposed structure for bromocadalene, and other derivatives of cadalene is thereby verified.

The analyses were carried out by Mr. K. Salo, University of Helsinki.

REFERENCES

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4. Briggs, L. H., Gill, N. S., Lions, F., and Taylor, W. I. *J. Chem. Soc.* In press.

Received February 16, 1949.