**Tetrahedron Letters No.38, pp. 4621-4624, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

REACTIONS OF ORGANIC ANIONS. XI. CATALYTIC ALKYLATION OF INDENE

M. Mąkosza

Department of Organic Technology II,
Institute of Technology (Politechnika), Warsaw, Poland

(Received 18 July 1966)

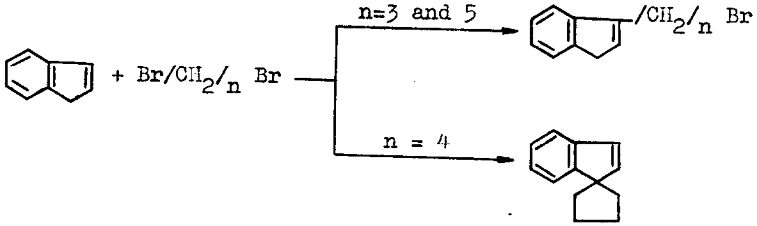
Indene derivatives substituted with alkyl groups in the five-membered ring are usually prepared either by alkylation of the indenyl anion with alkyl halides or by dehydration of the corresponding indanols, obtained in turn by reduction of the indanones, or by treating the latter with metalorganic compounds (1). The alkylation of indene in the anionic form is effected generally in the presence of $NaNH_2$, NaH, C_6H_5Na, Na, and other strong bases in a strictly anhydrous medium (1,2). Application of alkali hydroxides was reported to give less satisfactory results (3).

We have found recently that indene, having acidity of the order of the phenylacetonitrile derivatives, similarly as the latter (4) undergoes alkylation with alkyl halides in the presence of an aqueous NaOH solution and with triethylbenzylammonium chloride as a catalyst. The yields of that reaction are satisfactory, being not inferior to those obtained in the alkylation effected by classical methods, i.e., with strong condensation agents in a strictly anhydrous medium.

Alkylation of indene leads initially to the formation of a 1-alkyl derivatives, which because of base being present undergoes rapid isomerization to give the corresponding 3-alkyl indene (1). This was confirmed by comparing some physical data (b.p., and n_D^{20}) of the product obtained with those mentioned in the literature.

In the case of particularly active halides, such as benzyl and allyl chlorides, dialkylation took place to a considerable extent. This way may be used for preparing certain dialkylated indenes as it has been demonstrated with diallyl indene (68% yield).

The alkylation of indene with dibromoalkanes had a special interest to us, since we expected the formation of several products[x], the cyclic and bromoalkyl derivatives being the most interesting ones:

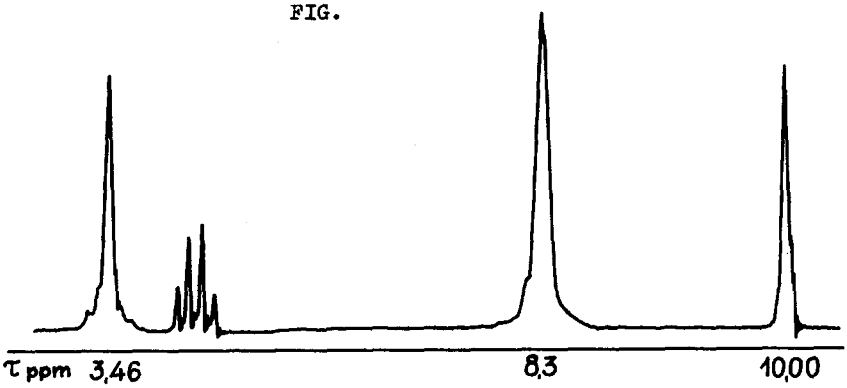


When n=3 and 5, the product consisted mainly of bromoalkyl derivatives; when n=4, it was spiro [cyclopentano-1,1-indene] whose structure was confirmed by NMR spectrum and by preparation of the dibromo derivative.

---

[x] The only paper published on that subject reported the alkylation of 1,3-diphenylindene with methylene dibromide (5).

FIG.



The NMR spectrum (see fig.) showed signal of the aromatic protons (τ = 3.46 ppm), cyclopentane ring protons (τ = 8.3 ppm) and the AB - system of vinyl protons of the cyclopentadiene rings with the coupling constant amounting to 4.5 cps (τ = 4.16 and 4.0 ppm). The NMR spectrum was obtained in CCl_4 with the Varian H.R. 60 Spectrometer and tetramethylsilane as a internal standard.

Some of our results are presented in the table.

TABLE

Yields and Physical Properties of Some 3-Substituted Indenes
(R - Substituent)

No.	R	Yield (%)[x]	b.p.	n_D^{20}
1.	CH_3-	62	65°/8	1.5581
2.	n-C_3H_7-	68	105/7	1.5482
3.	n-C_4H_9-	63	117/9	1.5409
4.	CH_2=CH-CH_2-	73	107/8	1.5654
5.	$(C_2H_5)_2NCH_2CH_2CH_2$-	46	125/0.4	1.5336
6.	$CH_2CH_2CH_2Br$	45	136/3	1.5858
7.	$CH_2CH_2CH_2CH_2CH_2Br$	52	143/1	1.5707

[x] The yields are based on the amount of the starting indene; satisfactory analyses have been obtained for all compounds.

References

1. A. M. Weidler, Acta Chem. Scand. 17, 2724 (1963).
2. T. Cuvigny, H. Normant, Bull. Soc. Chim. France 2000 (1964), 1872 (1965).
3. W. Marckwald, Ber. 33, 1504 (1900).
4. M. Makosza, B. Serafinowa, Roczniki Chem., 39, 1401, 1595, 1799 (1965).
5. P. M. G. Bavin, J. Chem. Soc., 5484 (1964).