Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The conversion of hydroxymercurated olefins into nitromercurated olefins in aqueous solution

MASASHI MATSUO and YASUKAZU SAITO

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo (Japan)

(Received December 31st, 1970)

We have observed that nitromercurated olefins are formed by slow conversion from the hydroxymercurated species, which are formed very rapidly from olefins in aqueous solutions of mercuric salts even in the presence of nitrite ion. Although nitromercuration of olefins has been reported to proceed in aqueous mercuric nitrite[1], neither the reaction sequence nor the mechanism was considered in detail. As a result of our study, we propose a mercurinium ion mechanism for the conversion reaction, since the reaction has been shown to involve stereospecific retention by PMR studies and by gas chromatographic analysis of the olefins obtained after denitromercuration.

When an olefin was introduced into the aqueous solution of mercuric perchlorate in the presence of sodium nitrite, hydroxymercurated olefin was first formed and was then converted gradually into corresponding nitromercurated olefin, as shown by following the reaction by means of time-sequential NMR spectroscopy *in situ*.

This conversion is first order with respect to the hydroxymercurated olefin, and the rate constant at 29.5°C is 8.27×10^{-3} mol^{-1} sec^{-1} for propene in an aqueous solution containing 1.36 mole mercuric perchlorate and 0.466 mole sodium nitrite. The procedure of the reaction analysis was reported previously[2].

The nitromercurated olefin was identified by PMR and IR spectroscopy. The PMR characteristics of the nitromercurated olefins are summarised in Table 1 along with those of the hydroxymercurated olefins. The observed values for nitromercurated propene in chloroform solution agreed with those previously reported. Characteristic IR bands at about 1540 and 1370 cm^{-1} arising from nitro groups were present in the reaction products.

From the PMR changes, the conversions of hydroxy-mercurated 2-butenes into nitromercurated species were found to proceed with retention, since the correspondence between the sets of hydroxy- and nitro-mercurated 2-butenes is clear, especially in the vicinal proton–proton coupling constant of $J_{\alpha\beta}$, which directly reflects the difference between *erythro* and *threo* isomers[3]. If denitromercuration yielding olefins

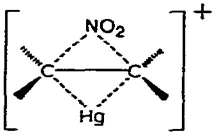
TABLE 1

PMR CHARACTERISTICS OF HYDROXY- AND NITRO-MERCURATED OLEFINS

Olefin	Hydroxy- and nitro-mercurated olefin	Solvent	Chemical shift (τ)				Coupling constant (Hz)		
			α	β	β'	γ	$J_{\alpha\beta}$	$J_{\alpha\beta'}$	$J_{\beta\gamma}$
Propene	$CH_3CH(OH)CH_2Hg^+$	D_2O	7.66	5.79		8.79	5.9		5.9
	$CH_3CH(NO_2)CH_2Hg^+$	D_2O	7.53	5.01		8.42	6.6		6.6
	$CH_3CH(NO_2)CH_2Hg\ NO_2$	$CHCl_3$	7.67	4.96		8.46	6.7		6.8
	$CH_3CH(NO_2)CH_2Hg\ Cl$ (ref.1)	$CDCl_3$	7.69	4.95		8.43			
trans-2-Butene	*erythro*-$CH_3CH(OH)CH(CH_3)Hg^+$	D_2O	6.93	6.13	8.70	8.81	5.4	7.6	6.0
	$CH_3CH(NO_2)CH(CH_3)Hg^+$	D_2O	6.86	5.12	8.43	8.70	6.2	7.6	6.5
cis-2-Butene	*threo*-$CH_3CH(OH)CH(CH_3)Hg^+$	D_2O	6.99	6.14	8.62	8.81	4.0	7.6	6.0
	$CH_3CH(NO_2)CH(CH_3)Hg^+$	D_2O	6.80	4.77	8.43	8.67	3.8	7.8	6.0

proceeds in the anti sense as does deoxymercuration[4], the products formed from nitromercurated *trans*- and *cis*-2-butene on treatment with hydrochloric acid support the above conclusion that retention occurs during the process since the original *trans*- or *cis*-2-butene were regenerated, as shown by gas chromatographic analysis.

The possibility that the reaction might proceed by formation of a deoxymercurated olefin followed by readdition was discussed by Ichikawa[5] and Kreevoy[6] for the conversion reaction from 2-acetoxyethylmercury(II) chloride to 2-ethoxyethylmercury(II) chloride in ethanolic perchloric acid solution. Under the reaction conditions we used, however, such a sequence is unlikely since the olefin would be insoluble in the aqueous medium. It is necessary to assume that the formation of nitromercurated olefin from the hydroxymercurated species proceeds via a mercurinium ion intermediate in order to account for the stereospecific nature of the reaction. In view of the anti-stereochemistry observed for both oxymercuration and deoxymercuration it seems likely that the reaction we have studied proceeds by conversion of one kind of mercurinium ion into another, in which either the oxygen atom of the hydroxy group or the nitrogen atom of the nitro group is attached *trans* to mercury(II) ion with respect to the olefinic carbon—carbon bond, illustrated for the nitro-species as follows:



Breaking of the oxygen—carbon bond of acetoxymercurated olefins has been observed in the reactions with carboxylic acids[7], active methylene compounds[8] and aromatic hydrocarbons[9]. Though the mechanism of these reactions have not been established, it seems likely by analogy with the formation of nitromercurated species from hydroxymercurated olefins, that they involve mercurinium ion intermediates.

ACKNOWLEDGEMENT

The authors are grateful to Professor Y. Yoneda for his encouragement and helpful discussion. They are also indebted to the Kawakami Memorial Fund for financial support.

REFERENCES

1 G.B. Bachman and M.L. Whitehouse, *J. Org. Chem.*, 32 (1967) 2303.
2 Y. Saito and M. Matsuo, *J. Organometal. Chem.*, 10 (1967) 524.
3 L.M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Ed., Pergamon. New York, 1969, p.280.
4 W. Kitching, *Organometal. Chem. Rev.*, 3 (1968) 61.
5 K. Ichikawa, H. Ouchi and S. Araki, *J. Amer. Chem. Soc.*, 82 (1960) 3880.
6 M.M. Kreevoy, G.S. Stokker, R.A. Kretcher and A.K. Ahmed, *J. Org. Chem.*, 28 (1963) 3184.
7 G.B. Slincks and G. Smets, *Tetrahedron*, 22 (1966) 3163.
8 K. Ichikawa, O. Itoh, T. Kawamura, M. Fujiwara and T. Ueno, *J. Org. Chem.*, 31 (1966) 447.
9 K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *J. Amer. Chem. Soc.*, 80 (1958) 6005.