Tetrahedron Letters No. 19, pp. 1669-1672, 1970. Pergamon Press. Printed in Great Britain.

OXIDATIVE DIMERIZATION OF ELECTRON-RICH ALKENES (1)

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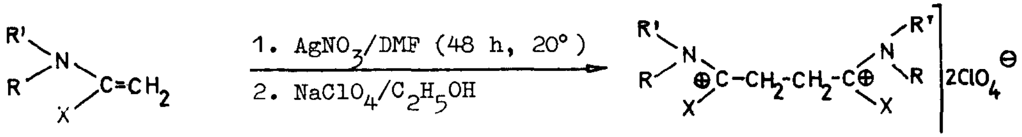
(Received in UK 16 March 1970; accepted for publication 26 March 1970)

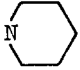
As recent investigations have shown, electron-rich alkenes may be coupled by electrochemical (3,4) and chemical (5,6) oxidation. Radical cations are assumed to be intermediates in both reaction pathways.

If the new linkage is not formed within one molecule, oxidation of 2-substituted 1.1-diamino-ethylenes with silver nitrate results in rather poor yields (6).

As our investigations have shown, reactivity of ß-unsubstituted ethylenes **1** with silver nitrate is still less. Even after long times of reaction, the yield of dimerization products **2** is moderate. For better characterization, the nitrates primarily formed are converted into perchlorates.

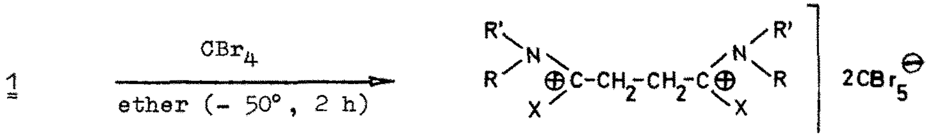


1 **2**

	R	R'	X
1a	CH$_3$	CH$_3$	N(CH$_3$)$_2$
b	(CH$_2$)$_5$		
c	CH$_3$	CH$_3$	OC$_2$H$_5$

	yield (%)	m.p.
2a	21	253°
b	13	269-71° (decomp.)

On the other hand, ethylenes 1a-c may be oxidized fast and in good yield with carbon tetrabromide (7,8).



	R	R'	X		yield (%)	m.p.
1a	CH_3	CH_3	$N(CH_3)_2$	3a	96	110-15° (decomp.)
b	$(CH_2)_5$			b	69	108-12° (decomp.)
c	CH_3	CH_3	OC_2H_5	c	65	94° (decomp.)

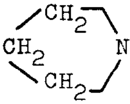
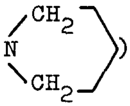
At - 50°, 0.02 moles CBr_4 in 40 ml abs. ether are added dropwise within one hour to a solution of 0.01 mole 1 in 30 ml abs. ether. Stirring is continued for another hour. The compounds 3a-c crystallize in analytically pure form.

Besides by ^1H-NMR spectra (Table 1), the structure of the oxidation products 3 *) has been proven chemically. Mild alkaline hydrolysis of 3b yields succinic acid dipiperidide the identity of which with authentic material is ascertained by IR spectra and mixed m.p.

Under the reaction conditions employed in this investigation, ketene diethyl acetal is not oxidized.

*) The structure of the pentabromo-carbonate anion which we have also obtained from the oxidation of triaminobenzenes with CBr_4 (8) is at the time being investigated by X-ray diffraction.

Table 1 - ^{1}H-NMR spectra of compounds 3 (in τ, TMS as internal standard)

2a	(CD_3CN)	7.80 (s, $>\overset{\oplus}{C}-CH_2-$), 6.78 (s, $N\langle^{CH_3}_{CH_3}$)
3b	($CDCl_3$)	~ 8.18 (m, ), 7.35 (s, $>\overset{\oplus}{C}-CH_2-$), 6.28 (m, )
3c	($CDCl_3$, 50°)	8.32 (t, $CH_3-\overset{\vert}{\underset{\vert}{C}}-O-$), 7.92 (s, $>\overset{\oplus}{C}-CH_2-$), 7.00 (s, $N-CH_3$), 6.55 (q, $-O-CH_2-$)

The gradation of reactivity towards electrophiles of ketene O.O-, O.N- and N.N-acetals must be attributed to varying stabilization of the positive charge at the α carbon atom. The experimental results available indicate comparable influence of substituents on the oxidation of olefinic double bonds. One might infer that stabilization of the positive charge in the radical cation which primarily is formed may be just as crucial in oxidation as stabilization of the σ-complex intermediate is in electrophilic reaction. Though pointing in the same direction, substituent influence differs in magnitude for stabilization of cations and radicals (10). Therefore, the sparse experimental information does not yet allow definite conclusions as to whether cation or radical stabilization is dominant in oxidative dimerization of electron-rich alkenes.

We thank cand.chem. W.Schneider for his experimental assistance, the Deutsche Forschungsgemeinschaft for a grant.

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