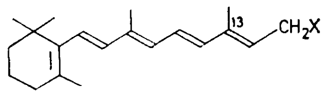
Electrochemical Reductive Cleavage from Polyenes and Carotenoids

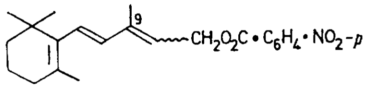
By Jean G. Gourcy, Martin Hodler, Bulent Terem, and James H. P. Utley*
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary Cathodic cleavage of acetate from vitamin A acetate (**1**) and crustaxanthin tetra-acetate (**8**) gives novel and convenient routes to, respectively, axerophtene (**3**) and 3,4,3′,4′-tetradehydro-β-carotene (**10**); these hydrocarbons are sensitive and have hitherto been obtained with difficulty.

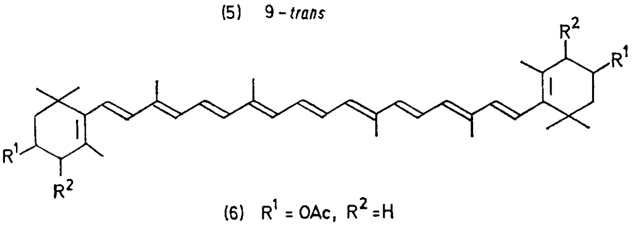
Cathodic cleavage reactions form the basis of several useful preparative methods.[1,2] By analogy with benzylic systems[2] allylic acetates, derived from polyenes and carotenoids, should undergo hydrogenolysis, thus providing a new route to sensitive compounds hitherto obtained with difficulty. Polarographic studies on vitamin A derivatives support this view.[3]



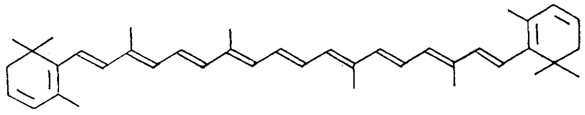
(1) X = OAc
(2) X = $O_2C·C_6H_4·NO_2$-*p* (13-*cis*)
(3) X = H



(4) 9-*cis*
(5) 9-*trans*



(6) R^1 = OAc, R^2 = H
(7) R^1 = H, R^2 = OAc
(8) R^1 = R^2 = OAc
(9) R^1 = R^2 = H



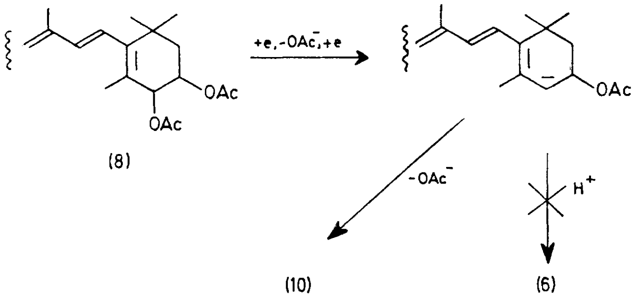
(10)

Cyclic voltammetry shows that a number of polyene and carotenoid acetates are reduced irreversibly at accessible cathodic potentials (Table). The expectation of hydrogenolysis is reinforced by the observation that for isozeaxanthin diacetate (**7**) the second and third reduction peaks correspond to those found for the expected cleavage product, β-carotene (**9**). Controlled potential preparative electrolyses were carried out under nitrogen at mercury using conventional H-cells and *ca.* 0·1 g of substrate. Vitamin A acetate (**1**) [$1·2 \times 10^{-2}$M in dimethylformamide (DMF)–Bu_4NI (0·1M), −1·35 V (*vs.* Ag–AgI)] consumed 1·5 F mol^{-1} and gave axerophtene (**3**) as the major isolated product (25% yield). Using conditions with greater proton availability [MeCN–Bu_4NOAc–HOAc(0·1M)] otherwise similar electrolysis gave, after the consumption of 2 F mol^{-1}, (**3**) a pure sample of which was isolated in 71% yield. The reaction was clean; t.l.c. analysis suggested that (**3**) was the only product, the less than quantitative yield resulting from loss during isolation. Previous methods for the preparation of axerophtene (**3**) result in the formation of its isomer, anhydrovitamin A, which can only be removed with great difficulty.[7] Attempts cathodically to cleave at −0·55 V (*vs.* Ag–AgI) the *p*-nitrobenzoate of vitamin A (**2**) failed. The major products of such electrolysis involved electroreduction of the aromatic nitro-group. It appears therefore that electron transfer to the polyene 'electrophore' is necessary. The peak potentials associated with electron transfer to the polyene chain vary predictably with the degree of conjugation and the polar effect of the ester group [Table, compounds (**1**), (**2**), (**4**), and (**5**)].

Table. Cyclic voltammetric data for polyene and carotenoid esters[a]

Compound	$-E_p$[b]
(**1**)	1·32; 1·68; 2·10
(**2**)[c,d]	0·55; 0·83; 1·87
(**4**)[c]	0·52; 2·00
(**5**)[c]	0·52; 2·10
(**6**)	1·00
(**7**)	0·87; 1·07; 1·54
(**8**)	0·67
(**9**)[d]	1·08; 1·50

[a] Hg drop, DMF–Bu_4NI(0·1M), 0·1 V s^{-1}; [b] V *vs.* Ag–AgI; [c] MeCN–Bu_4NOAc–HOAc(0·1M); [d] Vitreous carbon cathode.



Scheme

The controlled potential electrolysis of crustaxanthin tetra-acetate (**8**) was carried out with a view to selective cleavage of the allylic 4,4′-acetate group (R^2). The product of hydrogenolysis, zeaxanthin diacetate (**6**), was not formed under any of the conditions tried. Electrolysis in acetonitrile solution 0·1M in Bu_4NClO_4, Bu_4NOAc–HOAc, or $LiClO_4$ gave 3,4,3′,4′-tetradehydro-β-carotene (**10**) as the only significant product. Optimum conditions for formation of (**10**) involved reduction of (**8**) at −1·0 V (*vs.* Ag–AgI) in MeCN–Bu_4NClO_4 (0·1M). After the passage of 3 F mol^{-1} a pure sample of (**10**) was isolated in 45% yield. This hydrocarbon is relatively unstable and the method of preparation reported herein is considerably more convenient than existing routes.[8] The mechanism is probably that given in the Scheme; the elimination step must be very fast because even electrolysis in the highly protic solvent[9] MeCN–guanidinium perchlorate (0·4M) failed to capture the carbanion and intercept elimination. Satisfactory u.v., n.m.r., and mass spectra were obtained in confirmation of structures given.

We thank F. Hoffmann la Roche and Co. A.G. (Basel) for samples, the Royal Society for support (to J.G.G.), the S.R.C. for a fellowship (to B.T.), and Dr. G. P. Moss and Professor B. C. L. Weedon, F.R.S., for much helpful advice.

(*Received*, 12*th July* **1976**; *Com.* 796.)

---

[1] M. E. Rifi, *Tetrahedron Letters*, 1969, 1043; R. Gerdil, *Helv. Chim. Acta*, 1970, **53**, 2097; K. B. Wiberg, G. A. Epling, and M. Jason, *J. Amer. Chem. Soc.*, 1974, **96**, 912; J. Casanova and H. R. Rogers, *J. Org. Chem.*, 1974, **39**, 3803; R. Renaud, *Canad. J. Chem.*, 1974, **52**, 376.

[2] J. P. Coleman, Naser-ud-din, H. G. Gilde, J. H. P. Utley, B. C. L. Weedon, and L. Eberson, *J.C.S. Perkin II*, 1973, 1903.

[3] V. G. Mairanovski, L. A. Vakulova, and G. I. Samokhvalov, *Elektrokhimiya*, 1967, **3**, 23.

[4] R. L. Christensen and B. E. Kohler, *Photochem. and Photobiol.*, 1973, **18**, 293.

[5] O. Isler, M. Montavon, R. Rüegg, and P. Zeller, *Annalen*, 1957, **603**, 129.

[6] R. Breslow and R. F. Drury, *J. Amer. Chem. Soc.*, 1974, **96**, 4702.