Conversion of ω,ω'-Polyenedials to Monoaldehydes

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During our total syntheses of cross-conjugated carotenals [1–3] attempts were made to convert 8,8'-diapo-20-acetoxycarotene-8,8'-dial (*1*) *via* the bisallylic diol *2* to the corresponding diphosphonium salt *3*, [4,5] Scheme 1. Whereas treatment of the diol *2* with triphenylphosphonium bromide did not provide the target compound, the monoaldehydes *4a* and *4b*, isolated as a major product (15 % yield), were identified from spectral criteria. Their formation is ascribed to the presence of HBr, causing protonation and dehydration as formulated in Scheme 1 *via* an unstable intermediate enol.

Crocetindiol (*6*), prepared from crocetindial (*5*), gave on similar treatment no diphosphonium salt *7*, but provided a *cis* and *trans* isomer of the monoaldehyde *8* (13 % yield) corresponding to *4a,b* above.

In support of the acid catalyzed dehydration, crocetindiol (*6*) was treated with 5×10^{-4} M HBr in chloroform (containing 1 % ethanol). The monoaldehyde *8* (*cis* and *trans*; yield 9 %) represented 52 % of the product. In addition, crocetindial (*5*, 18 % of the product mixture) and a product with properties compatible with the ethoxyaldehyde *9* (30 % of the product mixture) were obtained. The latter products are ascribed to facile allylic oxidation and to well-known allylic etherification under acidic conditions of allylic alcohols in the presence of ethanol.[6]

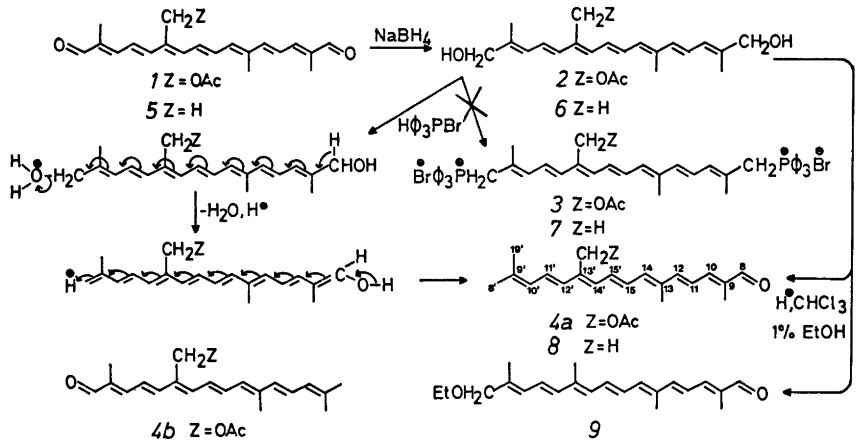
These data demonstrate the possible conversion of ω,ω'-polyenedials to monoaldehydes by acid-catalyzed dehydration of the corresponding bisallylic diols, and indicate that the transformation could be an alternative route to polyenic monoaldehydes. For synthetic purpose yields might be improved using shorter reaction periods, in inert atmosphere and in dry, non-nucleophilic solvent.

8,8'-Diapo-20-acetoxycarotene-8,8'-diol (*2*), prepared in a quantitative yield by $NaBH_4$-reduction in CH_3OH at 0 °C had λ_{max} (ether) 377, *397* and 421 nm.

8,8'-Diapo-20(20')-acetoxycarotene-8-al (4a *and* 4b). *2* (200 mg) was treated with triphenylphosphonium bromide (386 mg) in CH_2Cl_2 (30 ml) at room temperature for 22 h. From the least polar fraction obtained by chromatography on a polyamide column, rechromatographed (TLC) on silica, a presumed mixture of *4a* and *4b* was obtained; yield 29.6 mg (15 %), m.p. 148 – 151 °C; λ_{max} (acetone) *426* ($E_{1\%,\,1cm}$ = 2 600) and 444 nm; ν_{max} (KBr) 1730, 1663, 1610 (s), 1579 (m), 1536 (s), 1225, 1178 and 969 (s) cm^{-1}; δ ($CDCl_3$) 1.83 s (6 H, CH_3-8',19'), 1.90 s and 2.01 s (6H, CH_3-9,13(20')), 2.06 s (3 H, $-OCOCH_3$), 4.99 s (2 H, $-OCH_2O-$; 13'-*trans* [7]), 5.85 – 7.0 (olefinic H) and 9.44 s (1 H, –CHO); *m/e* (160 °C), 340 (M, 100 %), 297 (M – 43, 0.7 %), 281 (M – 59, 4 %) and 265 (M – 75, 2.2 %).

Crocetindiol (*6*). *5* (2 g), reduced with $NaBH_4$, provided *6* (1,48 g, 73 %) with λ_{max} (methanol) (357), 375, *396* and 420 nm.

8,8'-Diapocaroten-8-al (*8*). (a) *6* (27 mg) was treated with triphenylphosphonium bromide (50 mg) in $CHCl_3$ (40 ml) for 15 h. TLC (silica) provided *cis-8* (0.87 mg), *trans-8* (2.73 mg) and crocetindial (*5*, 0.05 mg). *Cis-8* had λ_{max} (acetone)



Scheme 1.

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427 nm; *m/e* 282 (M, 100 %). *trans-8* had λ_{max} (acetone) 431 nm; δ ($CDCl_3$) 1.83 s (6 H) *gem.* dimethyl, 1.98 s (6 H) CH_3-20,20′, 1.90 s (3 H) CH_3-19, 5.99–6.88 (10 H) olefinic and 9.45 (1H) aldehyde; *m/e* 282 (M, 100 %).

(b) To *6* (27 mg) in $CHCl_3$ (40 ml) was added 0.022 N HBr in $CHCl_3$ (1 ml). After 15 h separation by TLC afforded *cis-8* (0.54 mg), *trans-8* (1.84 mg), *9* (1.38 mg) and *5* (0.86 mg). The ethoxyaldehyde *9* had λ_{max} (acetone) 427 nm; δ ($CDCl_3$) *ca.* 1.25 CH_3CH_2-, 1.84 s (3 H) CH_3-19′, 1.99 s (6 H) CH_3-20,20′, 1.91 (3 H) CH_3-19, 3.95 s (2 H) CH_2-8, 3.46 q, (2 H) $-OCH_2CH_3$, 6.18–6.9 (10 H) olefinic and 9.45 (1 H) aldehyde; *m/e* 326 (M, 100 %), 281 (M – 45, 4.4 %).

Further experimental details are given elsewhere.[3]

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1. Johansen, J. E. and Liaaen-Jensen, S. *Acta Chem. Scand. B 29* (1975) 315.
2. Johansen, J. E. and Liaaen-Jensen, S. *Tetrahedron 33* (1976) 381.
3. Johansen, J. E. *Chemical studies on selected algal and bacterial carotenoids*, Dr.techn. thesis, Univ. Trondheim, Trondheim 1977.
4. Schöllkopf, U. *Angew. Chem. 71* (1959) 260.
5. Surmatis, J. D. and Ofner, A. *J. Org. Chem. 26* (1961) 1171.
6. Isler, O., Ed., *Carotenoids*, Birkhäuser, Basel 1971, Chapter 3.
7. Chae, Q., Song, P.-S., Johansen, J. E. and Liaaen-Jensen, S. *J. Am. Chem. Soc. 99* (1977) 5609.

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Formation of 2-Oxazolidinones from *N*-Benzyloxycarbonyl-2,2′-dichlorodiethylamine; Demonstration of Chloride Catalysis

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As part of our studies of nitrogen analogs of crown ethers, we have tried to prepare the derivative *1* of 1,4,7,10-tetraazacyclododecane which after hydrogenolytic removal of the benzyloxycarbonyl group would permit selective alkylation reactions of one amine function. For this synthesis urethane-protected 2,2′-dichlorodiethylamine *2a* was allowed to react with the disodium salt of *N*,*N*′,*N*″-tris-*p*-toluenesulfonyl diethylenetriamine *3* in DMF.[1] However, besides unreacted starting material *3* (7 %), the only isolated products were the 2-oxazolidinone derivative *4* (9 %), which is actually an isomer of the desired product *1*, and the monobenzylated trisulfonamide *5* (12 %).

Similarily, in an attempt to prepare the urethane derivative *6* of 1,4,7-trioxa-10-aza-cyclododecane from protected 2,2′-dichlorodiethylamine *2a* and diethylene glycol with potassium *tert*-butoxide as a base, the benzyloxycarbonyl group proved to be unstable. The isolated products were 3-ethenyl-2-oxazolidinone *7* (25 %), benzyl chloride (29 %) and the monobenzyl ether of diethylene glycol (17 %).

The formation of 2-oxazolidinones and the various benzylated products can be rationalized by either of the two reaction paths shown in Scheme *1*. According to Path I, an S_N2 substitution in the benzylic position of *2a* gives a new benzylic compound $PhCH_2X$ and a carbamate anion.[2] This anion does not decarboxylate under the reaction conditions, but cyclizes to yield 3-(2-chloroethyl)-2-oxazolidinone *8*,[3] which is further transformed to *4* and *7*. A pyrolytic mechanism, as proposed by Katchalsky *et al.*[4] for the related formation of 2-oxazolidinone from *N*-carbalkoxy-2-haloalkylamines, seems unlikely here because of the low reaction temperatures (80–100 °C).

In an experiment designed to exclude the less plausible alternative Path II,[5] both urethanes *2* were allowed to react in DMSO at 170 °C with one equivalent of NaCl and thereafter with Na_2CO_3. The benzyl derivative *2a* furnished 40 % of the cyclized product *7* besides benzyl chloride and other unidentified products, whereas the ethyl derivative *2b* failed to yield any 2-oxazolidinones under the same conditions. These results render Path II very improbable, since both compounds *2* should show the same tendency to undergo the initial substitution of chloride by the carbonyl oxygen.

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