Synthesis of Cyclobutanocrown Ethers by Intramolecular Photocycloaddition

Kazuhiko Mizuno,* Tetsuya Hashizume, and Yoshio Otsuji*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591, Japan

Irradiation of divinyloxy compounds {CH_2=$CHOCH_2[CH_2OCH_2]_nCH_2OCH$=$CH_2$; n = 1—4} in the presence of 1,4-dicyanonaphthalene in benzene gave *cis*- and *trans*-cyclobutanocrown ethers in good yields.

Intramolecular photocycloaddition has received a great deal of attention from both synthetic and mechanistic viewpoints.[1–4] We now report a novel synthesis of cyclobutanocrown ethers by the intramolecular photocycloaddition of the divinyloxy compounds (**1a**—**d**) {CH_2=$CHOCH_2[CH_2OCH_2]_nCH_2OCH$=$CH_2$; n = 1—4, respectively} using 1,4-dicyanonaphthalene (**4**) as sensitizer.

Irradiation of benzene solutions (100 ml) of (**1a**—**d**) (1—5 mmol) containing (**4**) (0.1—0.5 mmol) for 40—100 h with a high-pressure mercury arc through a Pyrex filter gave the *cis*- and *trans*-cyclobutanocrown ethers (**2a**—**d**) and (**3a**—**d**) respectively in good yields (Table 1). †‡ Cyclization did not occur in the absence of (**4**). The photoreaction in acetonitrile in the presence of (**4**) gave polymeric materials as the major isolable products.

The photocycloadducts were photochemically and thermally stable under the reaction or purification conditions and were isolated by distillation using a Kügelrohr apparatus and by column chromatography on silica gel. The structures of the products were assigned from their spectral (^{1}H n.m.r., i.r., and mass) properties and elemental analyses.§ The ^{1}H n.m.r. spectra of the photoproducts in the region of the cyclobutane protons were very similar to those of the *cis*- and *trans*-photocyclodimers of ethyl vinyl ether, (**5**) and (**6**), respectively.[5]

Table 1. Photocycloaddition of divinyloxy compounds (**1**) in the presence of 1,4-dicyanonaphthalene (**4**).

Substrate (1)	Irradn. time/h	% Yield[a] [(2) + (3)]	Product ratio[b] [(2):(3)]	Ring size	$k_q\tau$[c] /mol^{-1}dm^3
a	100	61	3[d] : 97	9	46
b	40	80	60 : 40	12	56
c	40	73	65 : 35	15	46
d	80	70	78 : 22	18	[e]

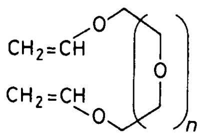
[a] Total isolated yields based on the substrates used. [b] The product ratios were determined by g.l.c. analyses of the reaction mixtures. [c] The $k_q\tau$ values were obtained from the fluorescence quenching of (**4**) in aerated benzene solutions. [d] Not isolated. [e] Not determined.

---

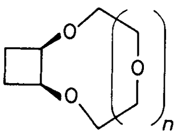
† The u.v. spectra showed that the charge-transfer complexes of (**1a**—**d**) with (**4**) are not formed in the ground states.

‡ The divinyloxy compounds (**1a**—**d**) were prepared by mercury(II) catalysed transvinylation of the corresponding diols with ethyl vinyl ether. Details will be published in the full paper.

§ *E.g.* for compound (**2b**): oil, i.r. ν_{max} (neat) 2840, 1130 cm^{-1}, ^{1}H n.m.r. δ (CCl_4) 1.1—1.3 (2H, m, CH_2), 1.7—1.9 (2H, m, CH_2), 3.3—3.7 (12H, m, CH_2), 3.7—3.9 (2H, m, CH), m/z 202 (M^+, vw), 174 ($M^+ - C_2H_4$). For compound (**3b**): oil, ^{1}H n.m.r. δ (CCl_4) 1.8—2.0 (4H, m, CH_2), 3.4—3.8 (12H, m, CH_2), 3.9—4.0 (2H, m, CH), m/z 202 (M^+, vw), 174 ($M^+ - C_2H_4$).

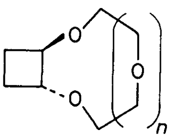


(1a-d)

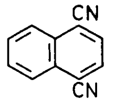


(2a-d)

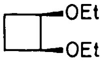
a; n = 1
b; n = 2
c; n = 3
d; n = 4



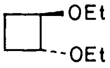
(3a-d)



(4)



(5)



(6)

The mass spectra of all the cycloadducts contained characteristic fragments due to a reverse [2+2] cleavage ($M^+-C_2H_4$).[5,6]

For (**1a**), the *trans*-fused cyclobutane (**3a**) was the predominant product. Molecular models show that the 9-membered cyclobutanocrown ethers (**2a**) and (**3a**) are highly strained and that the conformation of the intermediate leading to the *cis*-isomer (**2a**) is less favourable compared with that leading to the *trans*-isomer (**3a**). Conversely, the formation of the *cis*-isomers (**2b**—**d**) predominated for (**1b**—**d**).

The fluorescence of (**4**) was efficiently quenched by (**1a**—**d**) in benzene. The photocycloaddition is presumed to proceed *via* the exciplex or the intramolecular triplex involving excited (**4**) and the two vinyloxy groups [(**1**) · · · · (**4**)]*, in accord with the intermolecular photocyclodimerizations of alkyl vinyl ethers.[5]

The synthetic advantages of this method are: (1) a new type of crown ether can be synthesized in good yields;[7] (2) photocyclization of (**1a**—**d**) is accomplished under neutral and mild conditions; (3) the high-dilution method is not necessary in this photocyclization {[(**1**)] = 0.01—0.05 mol dm^{-3}}.

Received, 6th June 1983; Com. 726

References

1 M. A. Winnik, *Chem. Rev.*, 1981, **81**, 491; Y. Kanaoka, *Acc. Chem. Res.*, 1978, **11**, 407.
2 R. S. Davidson, in 'Molecular Association,' ed. R. Foster, Academic Press, London, 1975, p. 215.
3 J.-P. Desvergne, N. Bitit, A. Castellan, and H. Bouas-Laurent, *J. Chem. Soc., Perkin Trans.* 2, 1983, 109; J. J. McCullough, W. K. MacInnis, C. J. Lock, and R. Faggiani, *J. Am. Chem. Soc.*, 1982, **104**, 4644, and references cited therein.
4 J. A. Ors and R. Srinivasan, *J. Chem. Soc., Chem. Commun.*, 1978, 400; I. Yamashita, M. Fujii, T. Kaneda, and S. Misumi, *Tetrahedron Lett.*, 1980, **21**, 541; J.-P. Desvergne and H. Bouas-Laurent, *J. Chem. Soc., Chem. Commun.*, 1978, 403.
5 K. Mizuno, T. Hashizume, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, 1983 772.
6 S. Kuwata, Y. Shigemitsu, and Y. Odaira, *J. Org. Chem.*, 1973, **38**, 3803.
7 'Macrocyclic Polyether Syntheses,' eds. G. W. Gokel and S. H. Korzeniowski, Springer-Verlag, New York, 1982; 'Host Guest Complex Chemistry I and II,' ed. F. Vögtle, Springer-Verlag, New York, 1981.