CIDNP Detection of the Transient 4-Benzylcyclohexa-2,5-dienone in the Photorearrangement of Benzyl Phenyl Ether

By Rainer Bausch, Heinz-Peter Schuchmann, and Clemens von Sonntag
(*Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstr,* 34, D-4330 *Mülheim a. d. Ruhr*)

Reinhard Benn*
(*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz* 1, D-4330 *Mülheim a. d. Ruhr*)

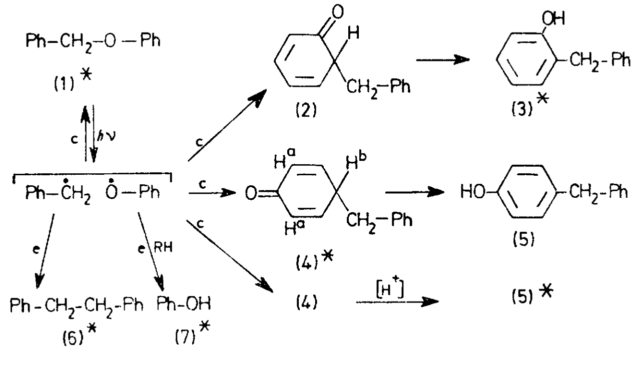
and Herbert Dreeskamp
(*Lehrstuhl B für Physikalische Chemie der TU Braunschweig, Hans-Sommer-Str.* 10, D-3300 *Braunschweig, West Germany*)

Summary The photolysis of benzyl phenyl ether gives rise to CIDNP in the intermediate 4-benzylcyclohexa-2,5-dienone; this rearranges to 4-benzylphenol to which polarisation is transferred in the presence of acid.

In the photolysis of aliphatic,[1] aromatic,[2] and enol[3] ethers the homolytic cleavage of the C–O bond is the predominant primary process. With aromatic ethers, fragment recombination can lead to rearranged products, *e.g.* substituted phenols. A special case, the photo-Claisen rearrangement, has been studied by Adam *et al.*[4] When photolysing *p*-tolyl methylallyl ether they observed CIDNP signals due to the final products 2-methylallyl-4-methylphenol and 4-methyl-4-methylallylcyclohexa-2,5-dienone. The formation of the phenol was explained *via* the intermediate 2-methylallyl-4-methyl cyclohexa-3,5-dienone. However, the rearrangement to the phenol was too fast to detect this intermediate in polarisation.

We studied the photorearrangement of benzyl phenyl ether (**1**) which lacks a substituent in the 4-position. This leads to the formation of the labile 2- and 4-substituted cyclohexadienones (**2**) and (**4**) respectively. It is shown here that the 4-substituted cyclohexadienone (**4**) is sufficiently long-lived for its polarisation to be seen. This finding substantiates the proposed[2,4] mechanism for the rearrangement of aromatic ethers into the corresponding phenols.

Compound (**1**) was irradiated in C_6D_{12} solution *in situ* and the polarised ^{1}H n.m.r. spectra (Figure) of (**1**), (**3**), (**6**), and (**7**) were identified by comparison with those of authentic samples. The polarised resonances at δ 6·22 (dd in enhanced absorption) were assigned to the 2,6-vinyl protons of (**4**); the 3,5-vinyl resonances are hidden under the aromatic proton signals. The 2,6-vinyl multiplet was analysed, to obtain $^3J_{2,3}$ *ca.* 11 and $^4J_{2,4}$ *ca.* -2 Hz assuming plausible values of other coupling constants. The methylene resonance of (**4**) would be expected around δ 2·81.[5] The observed resonances in emission at δ 2·88 and 2·78 must be assigned either to the doublet of the methylene protons (A_2M system) or to part of an A_2B system. The triplet expected in enhanced absorption, if the former case holds, was not observed.



* Polarised; c, cage reaction; e, escape reaction.

Using Kaptein's rule[6] the net polarisation of the starting material is consistent with the cleavage of an O–CH_2 bond from the singlet state ($\mu = -1$), recombination ($\epsilon = +1$), and $g(\mathrm{PhO}\cdot) - g(\mathrm{Ph\dot{C}H_2}) > 0$. With these parameters Kaptein's rule predicts enhanced absorption for the 2,6-vinyl protons of (**4**), as observed. Similarly, the polarisations of the phenols (**3**) (cage product, $\epsilon = +1$) and (**7**) (escape product, $\epsilon = -1$) are in accord with this rule.

Observation of the polarised spectrum at short intervals immediately after turning off the light revealed that all resonances assigned to (**4**) disappeared significantly faster ($\tau_{\frac{1}{2}}$ *ca.* 4 s) than the other polarisations ($T_1 > 20$ s). Traces of acid suppressed the signals of (**4**) entirely and the polarised spectrum of *p*-benzylphenol (**5**) was detected instead. Compounds (**3**), (**5**), (**6**), and (**7**) are the main final products [quantum yields at λ 254 nm: ϕ (**3**) *ca.* 0·3, ϕ (**5**) *ca.* 0·3, ϕ (**6**) *ca.* 0·2, and ϕ (**7**) *ca.* 0·25].

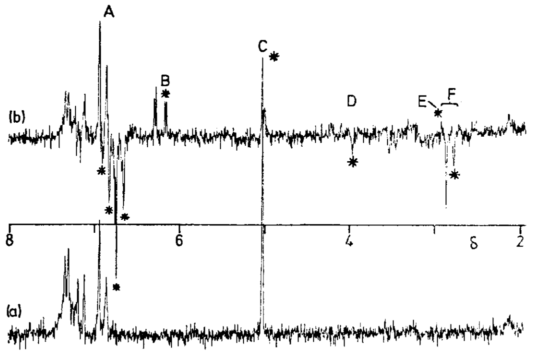


FIGURE. 90 MHz ^{1}H n.m.r. spectra of benzyl phenyl ether in C_6D_{12}; spectrum (a) with, and (b) without, u.v. irradiation. Signals A: compound (**7**), 5H, aryl; B: (**4**), 2H, H^a; C: (**1**), 2H, CH_2; D: (**3**), 2H, CH_2; E: (**6**), 4H, $CH_2 \times 2$; F: (**4**), 3H, CH_2 and H^b. Polarised spectrum is represented by *.

To confirm the influence of a substituent in the 4-position, the photo-CIDNP of benzyl 4-t-butylphenyl ether was investigated. It showed the polarised spectrum of 4-benzyl-4-t-butylcyclohexa-2,5-dienone which was stable even in the presence of acid. In agreement with earlier results,[4] the 2-substituted cyclohexadienone derivatives [*e.g.*, (**2**)] are too short-lived at room temperature to be detected in the CIDNP experiment, and polarisation is transferred to their rearrangement products.

(*Received*, 1*st March* 1976; *Com.* 207.)

---

[1] See *e.g.*: R. Ford, H.-P. Schuchmann, and C. von Sonntag, *J.C.S. Perkin II*, 1975, 1338.

[2] See *e.g.*: J. A. Elix and D. P. Murphey, *Austral. J. Chem.*, 1975, **28**, 1559.

[3] J. P. Pinhey and K. Schaffner, *Austral. J. Chem.*, 1968, **21**, 2265.

[4] W. Adam, H. Fischer, H.-J. Hansen, H. Heimgartner, H. Schmid, and H. R. Waespe, *Angew. Chem.*, 1973, **85**, 669.

[5] R. Barner, A. Boller, J. Borgulya, E. G. Herzog, W. von Philipsborn, C. von Planta, A. Fürst, and H. Schmid, *Helv. Chim. Acta*, 1965, **48**, 94.

[6] R. Kaptein, *Chem. Comm.*, 1971, 732.