

LOW TEMPERATURE REACTION OF AROMATIC HYDROCARBONS WITH
ETHYLENE AND SOLVATED ELECTRONS

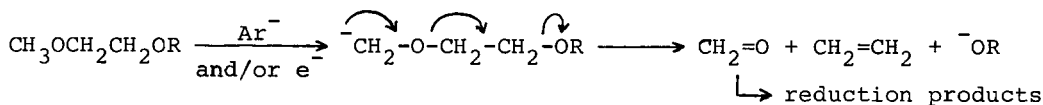
William E. Russey¹⁾ and Matthias W. Haenel⁺

Max-Planck-Institut für Kohlenforschung

Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a.d. Ruhr, W.-Germany

A wide variety of aromatic hydrocarbons can be ethylated at benzylic and aromatic positions by treatment with ethylene and potassium in glyme/octaglyme at -25°C.

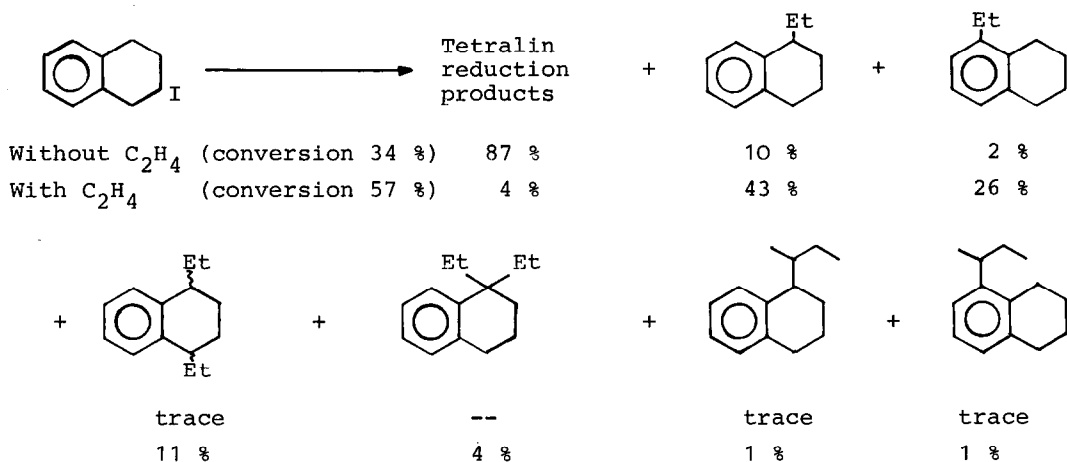
In the course of continuing studies on the reductive cleavage of coal with the "blue solution" formed by alkali metals in polyethers²⁾ we were led to investigate the behaviour under these conditions of a variety of potential model systems³⁾. In the cases of several aromatic hydrocarbons it was found that a complex mixture resulted, occasionally including significant amounts of substances showing molecular weight increases of 28, corresponding to the addition of ethylene. We have since established that these products are the result of ethylene incorporation, whereby the ethylene results from decomposition of the solvent glymes^{4,5)}. Such decomposition can be formally represented as an anionic ether cleavage process of the form:



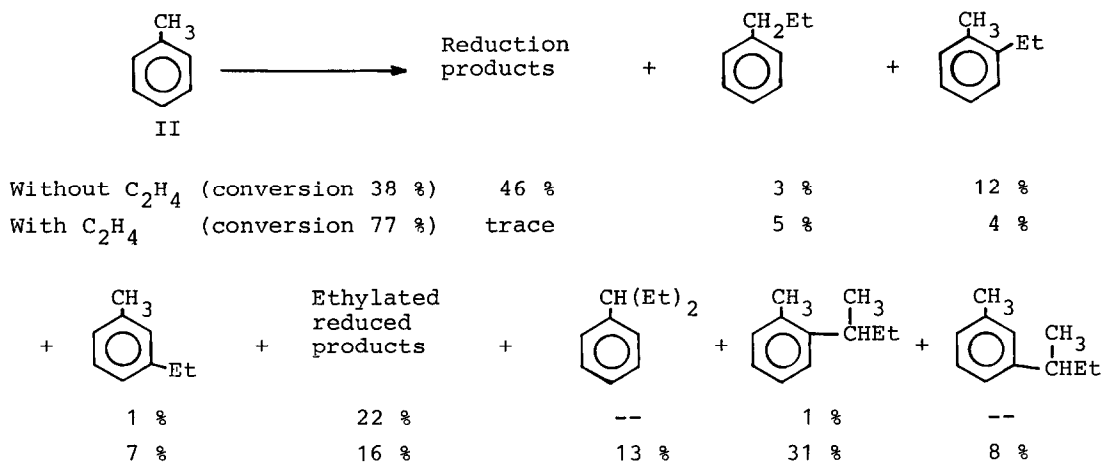
The assertion that free ethylene is involved is based on the observation in a wide variety of cases that the yield of "M + 28" products can be vastly increased by introducing gaseous ethylene directly into the "blue solution" reaction mixture.

In general, it has been found that ethyl groups are introduced both at aromatic and benzylic positions. For example, with tetralin (I) as substrate, the typical product distributions are as shown in scheme 1⁶⁾. The reaction mixtures were analyzed by gas chromatography⁷⁾ and structures of the products assigned primarily on the basis of mass spectral (GC-MS) fragmentation patterns^{8,9)}. A comparable set of products results from the analogous treatment of toluene (II, scheme 2). In this case, structures were verified by direct GC comparison (n-propylbenzene, o- and m-ethyltoluene) and by a combination of mass spectrometry⁸⁾ and ¹³C-NMR analysis¹⁰⁾ of fractions purified by preparative GC¹¹⁾ (sec-butyltoluenes, 3-phenylpentane). It is of interest to note that only ortho and meta ring substituted products could be found in the product mixture, the corresponding para compounds being totally absent (GC).

Scheme 1:



Scheme 2:



The absence of para product follows logically from the known behaviour of substituted benzenes in Birch-type reduction, wherein the first-formed intermediates only permit addition at ortho and meta positions¹²⁾. Several mechanisms for the reactions, including the observed rearomatization, can of course be written (e.g., involving various anions or radicals from both components), and it is assumed that several competing processes are involved. The relative yields of the various products obtained are strongly dependent of the reaction conditions employed (alkali metal, solvent composition, reaction temperature, protonation conditions, etc.)¹³⁾. The product distribution bears some resemblance to that reported by Pines et al.¹⁴⁾ in the high temperature, high pressure reaction of aromatic compounds with alkenes in the presence of alkali metals and "promoters".

Other substrates investigated to date include bibenzyl (III), anthracene (IV), phenanthrene (V), 9,10-dihydrophenanthrene (VI), and fluorene (VII). In the case of III, the vast majority of the observed product mixture results as expected^{3,15)} from initial cleavage of the benzylic $-\text{CH}_2-\text{CH}_2-$ linkage, leading to toluene (17 %), propylbenzene (5 %), and 3-phenylpentane (49 %). Smaller amounts (ca. 10 %) of mono- and diethylated C_{14} material could also be detected¹⁶⁾.

V was found to be considerably more reactive in the present sense than VI, and IV was nearly inert. Both VI and VII produced, along with the expected reduced and/or ethylated products, significant amounts of hydro- and hydroethylated dimers whose structures are currently under investigation. Work in progress is designed to further elucidate the scope and mechanistic aspects of this virtually unexplored low-temperature reaction⁵⁾.

References and Notes:

- 1) Permanent address: Department of Chemistry, Juniata College, Huntingdon, Pennsylvania 16652, USA. Support of this work by the Deutscher Akademischer Austauschdienst (DAAD) is gratefully acknowledged.
- 2) K. Niemann, Thesis, Max-Planck-Institut für Kohlenforschung, Mülheim-Ruhr and Universität Bochum, 1977; H.-P. Hombach and K. Niemann, *Compendium* 77/78, Erg. Band Erdöl und Kohle, Petrochemie, p. 295; K. Niemann and H.-P. Hombach, *Fuel* 58, 853 (1979); and K. Niemann and U.-B. Richter, *Fuel* 58, 838 (1979) and *Fuel* 60 (1981), in press.
- 3) L. Schanne and M.W. Haenel, *Tetrahedron Letters* 1979, 4245.
- 4) Experiments with ^{14}C - and ^3H -labelled glymes have conclusively shown that this ethylene incorporation reaction plays an insignificant role in the reductive solubilization of coal reported previously²⁾ (C. Bennett, E. Boden, M. Angst and W.E. Russey, in preparation).
- 5) J.C. Carnahan, jr., and W.D. Closson [*J. Org. Chem.* 37, 4469 (1972)] observed the formation of 1-ethylidihydronaphthalenes from alkali metal-naphthalene solutions at 25°C in tetrahydrofuran or glyme, and subsequently showed that ethylene was involved. P.D. Bartlett, S. Friedman and M. Styles [*J. Am. Chem. Soc.* 75, 1771 (1953)] and P.D. Bartlett, S.J. Tauber and W.P. Weber [*J. Am. Chem. Soc.* 91, 6362 (1969)] showed that only secondary and tertiary alkyl lithium reagents can add to ethylene at -60°C. However, according to K. Ziegler and H.-G. Gellert [*Liebigs Ann. Chem.* 567, 185 (1950)] and A. Maercker and W. Theysohn [*ibid.* 747, 70 (1971)] also primary alkyl lithium and according to A. Maercker and J. Troesch [*J. Organomet. Chem.* 102, C1 (1975)] even phenyl and benzyl lithium add ethylene formed by decomposition of diethyl ether or tetrahydrofuran. V. Rautenstrauch [*Angew. Chem.* 87, 254 (1975), *Angew. Chem. Int. Ed. Engl.* 14, 259 (1975)] discusses the reaction of ethylene with lithium in the presence of naphthalene, biphenyl and

dimethoxymethane at -10°C , but provides no information regarding the nature of products derived from the aromatic components. The first mention of such a process appears to be that of K. Ziegler and K. Bähr [Ber. Deutsch. Chem. Ges. 61, 253 (1928)] involving phenylisopropyl potassium addition to stilbene.

- 6) Reactions were conducted at -22°C in a solvent mixture comprised of anhydrous glyme (50 ml, 0.48 moles) and "octaglyme"³⁾ (10 ml, 0.025 moles calculated on the basis of pure octamer). The blue solution was produced by addition under an argon atmosphere of small pieces of potassium (3.9 g, 0.10 moles) followed by saturation where appropriate, with gaseous ethylene. An ethylene atmosphere was maintained during and following introduction of the aromatic substrate (0.025 moles). After stirring at -22°C for ca. 16 hours residual potassium was removed and a dilute solution of butanol in glyme was added, followed by a normal work-up. Product yields are based on GC analysis, excluding unreacted substrate.
- 7) G. Schomburg and B. Heinecke, MPI für Kohlenforschung, Mülheim-Ruhr.
- 8) D. Henneberg, M. Scheppat and W. Joppek, MPI für Kohlenforschung, Mülheim-Ruhr.
- 9) Mass spectra of pertinent compounds are reported and interpreted in R. Gretler, E. Askitoglu, H. Kühne and M. Hesse, *Helv. Chim. Acta* 61, 1730 (1978).
- 10) R. Mynott, MPI für Kohlenforschung, Mülheim-Ruhr.
- 11) G. Schomburg and H. Kötter, MPI für Kohlenforschung, Mülheim-Ruhr.
- 12) H.O. House, "Modern Synthetic Reactions", W.A. Benjamin, Inc., Menlo Park, CA, 1972, Chapt. 3; N.L. Holy, *Chem. Rev.* 74, 243 (1974).
- 13) G. Decher and W.E. Russey, in preparation.
- 14) For an extensive review of this and related work see H. Pines, *Synthesis* 1974, 309.
- 15) C.J. Collins, H.-P. Hombach, B. Maxwell, M.C. Woody and B.M. Benjamin, *J. Am. Chem. Soc.* 102, 851 (1980). These investigations were initiated by H.-P. Hombach at the Oak Ridge National Laboratory during his tenure there in 1978 as a visiting scientist while on leave from the MPI für Kohlenforschung, Mülheim-Ruhr.
- 16) C.J. Collins, H.-P. Hombach, B.E. Maxwell, B.M. Benjamin and D. McKamey [*J. Am. Chem. Soc.* 103, 1213 (1981)] recently in a footnote reported identifying 1,2-diphenylbutane (11 %) along with toluene (85 %) in the product mixture from a "blue solution" reaction of bibenzyl (in the absence of added ethylene). Under our reaction conditions, also without added ethylene, we find, apart from toluene approximately equal amounts of propylbenzene, 1,2-diphenylbutane, and a substance tentatively identified (MS) as ring-ethylated bibenzyl (total ca. 7 %).

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