Pergamon

Tetrahedron, Vol. 53, No. 15, pp. 5397-5402, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00258-5

Concerning the Mechanism of the Reductive Cleavage of α-Nitrocumene and Cumyl Chloride

Donald B. Denney*, Dorothy Z. Denney and Steven P. Fenelli

Department of Chemistry, Rutgers, The State University of New Jersey
P. O. Box 939 Piscataway, NJ 08854-0939

Abstract: The reductive cleavages of α-nitrocumene and cumyl chloride by sodium naphthalenide in tetrahydrofuran have been studied. It is concluded that the cumyl carbanion is the first intermediate formed in these reactions.

The reductive cleavages of benzylic chlorides and benzylic nitro compounds have received considerable study.[1,2] In the absence of nucleophiles the major products are the reduced arene, 2, and the dimer, 3. In the presence of nucleophiles, Nu⁻, the substitution product, 4, is often obtained.[3] Under these circumstances only catalytic amounts of electrons are required to effect the substitution reactions.[3]

$$\underset{\underline{1}}{\mathrm{ArC(R)_2X}} + e^- \longrightarrow \underset{\underline{2}}{\mathrm{ArC(R)_2H}} + \underset{\underline{3}}{\mathrm{ArC(R)_2C(R)_2Ar}} + \mathrm{X}^- \qquad (1)$$

$$\mathrm{X = Cl, NO_2}$$

$$\underline{1} + \mathrm{Nu}^- \longrightarrow \underset{\underline{4}}{\mathrm{ArC(R)_2Nu}} + \mathrm{X}^- \qquad (2)$$

There have been two mechanisms that have been proposed for these reductive cleavages. One suggests that the first step involves electron transfer to the substrate to give the radical anion, 5, which then dissociates to the radical, 6, and X⁻. Dimerization of 6 leads to bicumyl, 3. The arene can be formed by attack on the solvent or a second electron can be added to 6 to give carbanion, 7, which then attacks on the solvent.

$$\underset{\underline{1}\ \ \mathrm{X = Cl, NO_2}}{\mathrm{ArC(R)_2X}} + e \longrightarrow \underset{\underline{5}}{\mathrm{ArC(\dot{\bar{R}})_2X}} \longrightarrow \underset{\underline{6}}{\mathrm{Ar\dot{C}(R)_2}} + \mathrm{X}^- \qquad (3)$$

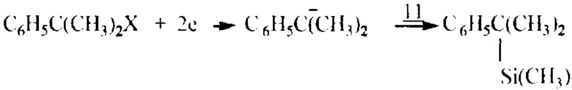
$$\underset{\underline{5}}{} + e \longrightarrow \underset{\underline{7}}{ArC(R)_2^-} + X^- \qquad (4)$$

The other mechanism suggests that 5 is formed and it then reacts with a second electron to give the carbanion, 7. The key difference between these two mechanisms is that the first involves benzylic radicals as intermediates, whereas the second involves direct formation of benzylic carbanions.

The reductive cleavages of α- nitrocumene, 8, and α-chlorocumene, 9, have now been investigated. Earlier Hoffmann et al.[4] studied the reductive cleavage of α-nitrocumene both by sodium and electrochemically. More recently Guthrie and co-workers[5] have studied the reductive cleavage of α-nitrocumene by several techniques.

There does not seem to have been a systematic study of the reductive cleavage of α-chlorocumene. Bazier and Churma[6] have studied the electrochemical reduction of benzyl chloride and Bank and Bank[7] have studied its reduction by sodium naphthalenide.

The two compounds have been reduced by sodium napthalenide, 10, in tetrahydrofuran and the nature of the products has been determined. Chlorotrimethylsilane, 11, has been used as a carbanion trapping agent. The formation of cumyltrimethylsilane is taken to indicate the production of cumyl carbanion, 13. Total conversion to 12 is a two electron process. On the other hand conversion of 8 or 9 to bicumyl, 14, is a one electron process.



$$C_6H_5C(CH_3)_2X + 2e \rightarrow C_6H_5\bar{C}(CH_3)_2 \xrightarrow{11} C_6H_5\underset{\displaystyle Si(CH_3)_3}{\underset{|}{C}}(CH_3)_2 \qquad (5)$$

8 X = NO_2 13 12
9 X = Cl

$$2C_6H_5C(CH_3)_2X + 2e \longrightarrow [C_6H_5C(CH_3)_2]_2 + 2X^- \qquad (6)$$

8 X = NO_2 14
9 X = Cl

In fact, addition of sodium naphthalenide to 8 (2:1) yielded cumene, 8.8%, and bicumyl, 91.2%. In a similar fashion 9 yielded 23.9% of cumene and 76.1% of bicumyl. These results show that the two substrates give somewhat different product ratios. The results do not seem to distinguish between the two mechanisms.

When 8 and 9 were allowed to react with sodium naphthalenide (1:1) both cumene and bicumyl were formed and in both cases there were substantial amounts of recovered starting material, 8, 56% and 9, 51%. When the order of addition was reversed, i.e. α-nitrocumene was added to sodium naphthalenide the yield of bicumyl rose to 70% and there was 25% of recovered α-nitrocumene. This result suggests that some side reactions are suppressed. The presence of excess sodium napthalenide can favor the formation of α-nitrocumyl radical anion and the cumyl carbanion which are thought to be the precusors to bicumyl, see below.

When 8 and 9 were treated with sodium naphthalenide in the presence of trimethylchlorosilane (1:2:1) major differences in the product ratios were obtained. Both yielded some starting material, 8, 15%, 9, 26%. Cumene was a minor product in both cases, 8, 10%, and 9, 14%. The astonishing differences came in the yields of the other products. Only 1% of cumyltrimethylsilane was formed from 8 whereas 9 yielded 38%. Bicumyl was formed in 73% from 8 and in 22% yield from 9. Very clearly the two substrates are giving very different product ratios. The results are certainly not easily explained on the basis that a common intermediate, the cumyl radical, is formed in both systems.

What if a common intermediate, cumyl carbanion, was formed? The cumyl carbanion, 13, should react equally well with trimethylchlorosilane irrespective of its source. The major difference in the reactivity of the two substrates is that 8 gives much more bicumyl than 9 and 9 gives much more of the silane. How can these results be explained? A particularly appealing rational involves reaction of the common cumyl carbanion with the radical anions derived from 8 and 9. These are, of course, bimolecular reactions and thus their overall rates will depend on the concentrations of 15 and 16 at any given point in time. The radical anion 15 will be formed much more rapidly and in greater amounts than 16 and thus reaction to give bicumyl will be more highly favored than that of 16 with 13. Under these circumstances the alternative attack on trimethylchlorosilane becomes more viable.

$$C_6H_5C(CH_3)_2X \;+\; 2e \;\longrightarrow\; C_6H_5\bar{C}(CH_3)_2 \;+\; Cl^- \qquad (7)$$

8 X = NO_2
9 X = Cl
13

$$13 \;+\; (CH_3)_3SiCl \;\longrightarrow\; C_6H_5C(CH_3)_2Si(CH_3)_3 \qquad (8)$$

12

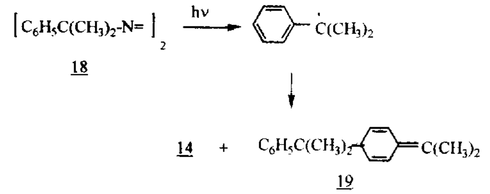
$$C_6H_5\overset{-\bullet}{C}(CH_3)_2X \;+\; C_6H_5\bar{C}(CH_3)_2 \;\longrightarrow\; C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5 \;+\; X^- \qquad (9)$$

15 X = NO_2
16 X = Cl
13
17

The postulate that nucleophiles can react with radical anions is not a new one. Russell et al.[8] have suggested that some radical anions react with nucleophiles in an $S_{RN}2$ process. Denney and Denney[9] and Denney, Denney and Perez[10] have postulated that aromatic radical anions react with nucleophiles by an $S_{RN}2$ mechanism.

The major conclusion that can be drawn from this investigation is that the α-nitrocumyl and the α-chlorocumyl radical anions do not dissociate on the time scale of these reactions but rather they react with an electron in a dissociative process to give the cumyl carbanion.[11] In fact, Russell and Metcalfe[12] have prepared the α-nitrocumyl radical anion by allowing the benzene diazonium ion to react with 2-nitropropanide ion in the presence of dithionate ion, the radical anion was detected by ESR spectroscopy. There was no evidence for its further cleavage to cumyl radical and nitrite ion.

Skinner et al.[13] have studied the photochemical decomposition of the azo compound 18. They obtained from this reaction bicumyl, 14, and the α-p-dimer, 19. The presence of the α-p-dimer was determined by its characteristic ^1H NMR spectrum as recorded at 100 MHz in the CW mode. Small amounts of cumene and α-methylstyrene were also detected.



(10)

If the reductive cleavage of α–nitrocumene and cumyl chloride proceeds through the cumyl radical it seems reasonable to conclude that the α-p-dimer should be produced as it was from 18. Both α-nitrocumene and cumyl chloride have been reduced by sodium naphthalenide, 1:1 and 2:1. The solvent, THF, was removed at reduced pressure. Each sample was investigated by ^1H (200 MHz) and ^{13}C (75MHz) NMR. In no case was there any evidence obtained for the production of the α-p-dimer. These results are of course negative, but given the sensitivity of modern FT NMR spectrometers it seems reasonable to conclude that essentially no α-p-dimer was formed. Since the dimer was observable in a CW experiment at 100 MHz we feel it would have been observable under these conditions. This conclusion supports the proposal that bicumyl is produced by attack of the cumyl carbanion on the radical anions produced from α-nitrocumene and cumyl chloride. None of these experiments require the formation of cumyl radicals.

EXPERIMENTAL

All reagents and solvents were of reagent grade and they were used as obtained except as noted. Tetrahydrofuran was further purified by distillation from benzophenone ketyl under nitrogen. Chlorotrimethylsilane was purified by distillation under nitrogen just prior to use. All reactions were conducted under nitrogen using air-sensitive techniques. Gas chromatography was carried out on a Hewlett-Packard HP-5890 gas chromatograph equipped with a 15 meter x 0.54 mm Alltech non-packed AT-1000 (formerly Superox-FA) polyethylene glycol ester column and a Series II HP-3396 integrator. A temperature ramp of 10°/min was utilized. Mass spectra were obtained using a HP-5970 mass-selective detector interfaced to a HP-5890 Series II gas chromatograph equipped with a 12m x 0.2mm crosslinked methyl silicone column. Analytical thin layer chromatography was performed with Merck F-254 plates and column chromatography with Aldrich neutral alumina. Proton and carbon NMR spectra were measured in $CDCl_3$ solution by using a Varian VXR-200 or Gemini instruments operating at 200 and 75 MHz respectively. Brucker AC-250, AM-330 and DPX-400 spectrometers were also used in obtaining proton spectra. Infrared spectra were recorded with a Perkin-Elmer 1600 Series FTIR.

The analyses of product mixtures was carried out by GC/MS with special emphasis on quantitation by gas chromatography. The identity of each component was verified by comparison to authentic standards. Calibration standards were prepared by making serial dilutions to stock solutions of known concentration, thereby ensuring linear detector response over a broad range. Multipoint calibrations were carried out in units of milligrams/gram so that the molar amount of each component present could be calculated by simply knowing the total weight of the product mixture. Tetradecane was used as the internal standard in aliquots that were analyzed using absolute calibration. Peak area percents were normalized to represent a given component, the percent of the component is equal to its area divided by the total areas and then further corrected for detector response.

Preparation of Sodium Naphthalenide: In a typical preparation, a 100 ml multineck flask fitted with a magnetic stirrer, thermometer, reflux condenser and under a positive pressure of nitrogen, was charged with 2.56g (0.02 mol) of sublimed naphthalene and 80 ml of THF. There was then added 0.46g (0.02 g-atom) of freshly cut sodium. The resulting deep green solution was stirred overnight at room temperature. a 2 ml aliquot was withdrawn and added to a solution prepared from 20 ml of methanol and 5 ml of distilled water. Titration with 0.01 N HCl indicated the solution was 0.24 mole/liter in base.

α-Nitrocumene: This substance was prepared by a modified literature procedure.[14]

α-Chlorocumene: This material was prepared by the addition of hydrogen chloride gas to α-methylstyrene

A Representative Reaction of Sodium Naphthalenide with α-Nitrocumene: To a 50 ml multinecked flask fitted with a reflux condenser, thermometer, magnetic stirrer under a positive pressure of nitrogen, was charged with 0.718 g (0.00435 mol) of freshly distilled α-nitrocumene and 2.2 ml of tetrahydrofuran. To this stirred solution was added, dropwise at 25°C, a solution of sodium naphthalenide prepared from 0.100 g (0.00435 g-atom) of freshly cut sodium, 0.557 g (0.00435 mol) of naphthalene and 17.6 ml of tetrahydrofuran. The resulting mixture was stirred at room temperature. The course of the reaction was monitored by gas chromatography. In fact, the reactions were over i.e. the sodium naphthalenide was consumed as fast as it was added. The GC results were the same if the reaction mixtures were quenched with methanol or directly injected into the chromatograph.

A Representative Reaction of Sodium Naphthalenide with α-Chlorocumene: To a 50 ml multinecked flask fitted with a reflux condenser, thermometer, magnetic stirrer and under a positive pressure of nitrogen, was charged 0.605 g (0.00392 mol) of freshly distilled α-chlorocumene and 3 ml of tetrahydrofuran. To this stirred solution was added a solution of sodium naphthalenide prepared from 0.09 g (0.00392 g-atom) of freshly cut sodium and 0.502 g (0.00392 mol) of naphthalene and 15.6 ml of tetrahydrofuran. The gas chromatographic analysis was the same as used for α-nitrocumene.

REFERENCES

1. Lund, H. and Baizer, M., Ed. "Organic Electrochemistry", M. Dekker Inc., New York, NY, 1991, 3rd Ed., Chpt. 8 and 9.

2. "The Chemistry of the Carbon-Halogen Bond", Patai, S. Ed., John Wiley and Sons, New York NY 1973, Parts 1 and 2.

3. For reviews see (A) Kornblum, N., Angewandte Chem., Int Ed., 1975, 14, 734 (B) Kornblum, N., "The Chemistry of Functional Groups, Supplement 7: The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives", Patai, S., Ed., John Wiley and Sons, New York NY 1982, pp 361-393.

4. Hoffmann, A. K., Hodgson, W. G., Maride, D.L. and Jura, W. H., J. Am. Chem. Soc., 1964, 86, 631.

5. Wu, F., Guarr, T. F., and Guthrie, R. D., J. Phys. Org. Chem., 1992, 5, 7.

6. Bazier, M. M. and Chvma, J. L., J. Org. Chem., 1972, 37, 1951.

7. Bank, S. and Bank, J. F., Tet. Letts., 1971, 4581.

8. Russell, G. A., Mudryk, B., Ros, F. and Jawdosiuk M.,, Tetrahedron, 1982, 38, 1059.

9. Denney, D. B. and Denney, D. Z., ibid., 1991, 47, 6577.

10. Denney, D. B., Denney, D. Z. and Perez, A. J., ibid, 1993, 49, 4463.

11. Extensive ab initio calculations, S. P. Fenelli, Thesis Rutgers University 1996, support this conclusion and they will be reported separately.

12. Russell, G. and Metcalfe, A. R., J. Am. Chem. Soc., 1979, 101, 2359.

13. Skinner, K. J., Hochester, H. S. and McBride, J., J. Am. Chem. Soc., 1974, 96, 4301.

14. Kosower, E. M. and Severn, O. J., J. Am. Chem. Soc., 1969, 91, 1710.

(*Received in USA* 3 *January* 1997; *revised* 3 *March* 1997; *accepted* 4 *March* 1997)