

Journal of Organometallic Chemistry, 139 (1977) C51-C55
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

HYDRODESULFURIZATION AND RING CONTRACTION OF SULFUR HETEROCYCLES BY
NICKEL(0) COMPLEXES

JOHN J. EISCH and KYOUNG R. IM

Department of Chemistry, State University of New York at Binghamton, Binghamton
New York 13901 (U.S.A.)

(Received June 9th, 1977)

Summary

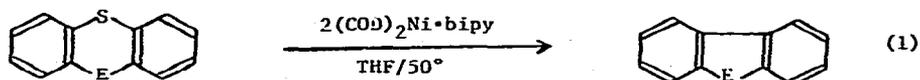
Sulfur heterocycles, such as dibenzothiophene, phenoxathiin and phenothiazine, have been shown to undergo desulfurization with soluble, nickel(0)-derived reagents in either of two ways: (1) simple ring contraction; or (2) complete substitution of hydrogen for the sulfur. Thus, when treated with two equivalents of a 1:1 mixture of bis(1,5-cyclooctadiene)nickel(0) and 2,2'-bipyridyl, phenoxathiin yields dibenzofuran. If, however, one equivalent of LiAlH_4 is employed with the two equivalents of $(\text{COD})_2\text{Ni}$ and 2,2'-bipyridyl, this heterocycle gives a high yield of diphenyl ether.

The cleavage of carbon-sulfur bonds in heterogeneous media containing alkali metals [1-8] or Raney nickel [9-11] is a most useful reaction in organic synthesis and in organic structure determination, as for example, of coal and petroleum derivatives [4]. Such cleavages proceed especially smoothly when the reductant can function in an homogeneous medium, such as with sodium in liquid ammonia [12] or with the dilithium adduct of biphenyl in tetrahydrofuran [13].

Therefore, we have examined the efficacy of soluble nickel(0) complexes in cleaving the carbon-sulfur bonds of certain heterocyclic systems by means of oxidative addition. By varying the ligands on the nickel we have now observed that such desulfurizations can be made to proceed smoothly in either

*Part IV of the series: "Organic Chemistry of Subvalent Transition Metal Complexes" (previous parts, *J. Organometal. Chem.*, **96** (1975) C19, C23; **139** (1977) C45.

of two ways: 1) simple ring contraction; or 2) complete substitution of hydrogen for the sulfur. Thus, for example, although dibenzothiophene (I), phenoxathiin (II), phenothiazine (III) or thianthrene (IV) do not react with bis(1,5-cyclooctadiene)nickel(0) in benzene or THF, they do undergo cleavage in warm THF when treated with two equivalents of a 1:1 mixture of $(\text{COD})_2\text{Ni}$ and 2,2'-bipyridyl. Work-up with conc. HCl or with LiAlH_4 gives 50-70% yields of the ring-contracted heterocycle in the case of II, III and IV; I gives biphenyl and a small amount of 2-biphenylthiol:



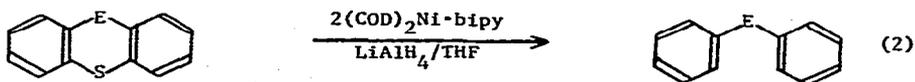
II, E = O

III, E = N-H

IV, E = S

In the reaction of dibenzothiophene, which yields only biphenyl and no detectable biphenylene when treated with 2 equivalents of $(\text{COD})_2\text{Ni}$ and bipyridyl, it remains to be ascertained whether ring contraction occurs first and then the biphenylene intermediate is subsequently cleaved by nickel(0).

On the other hand, when one equivalent of each of the sulfur heterocycles was added to 2 equivalents of $(\text{COD})_2\text{Ni}$, 2 equivalents of 2,2'-bipyridyl and one molar equivalent of LiAlH_4 in THF, a hydrodesulfurization of I-III occurred in yields of 80-100%*:



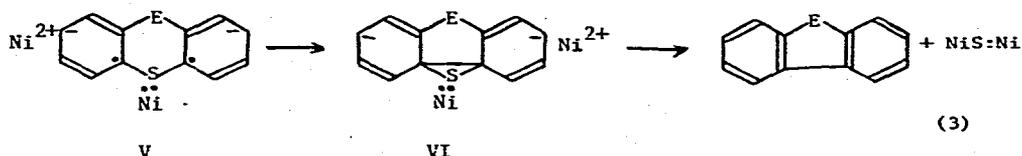
I, E = σ -bond

II, E = O

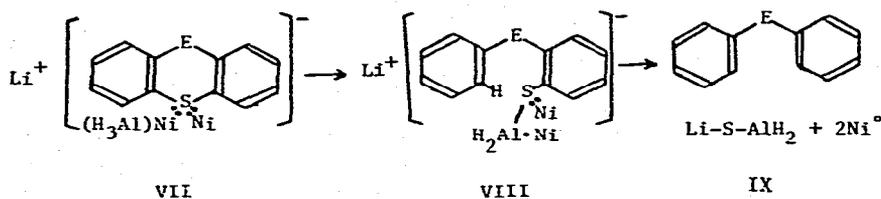
III, E = NH

* $(\text{COD})_2\text{Ni}$ is reported to react with LiAlH_4 with the formation of H_2 and $\text{Li}_2[\text{H}_3\text{Al-Ni-AlH}_3]$ [14]. In the present case a 2:1 ratio of $(\text{COD})_2\text{Ni}$ and LiAlH_4 yields the more reactive reagent. In unpublished studies in this Laboratory diisobutylaluminum hydride has been found to react with tetrakis(trisubstituted phosphine)nickel(0) and platinum(0) complexes to yield H_2 and presumably complexes of the type $(\text{R}_3\text{P})_2\text{M}(\text{Al-i-Bu}_2)_2$ [15].

The necessity of two equivalents of nickel(0) for both modes of desulfurization suggests that one nickel coordinates with the sulfur heterocycle, while the second nickel ruptures the ring. For the ring contraction the second nickel probably functions as an electron-transfer agent (V-VI) as in the case of nickel(0) cleavages of epoxides and ethers [16] (eq. 3):



The active reagent in the hydrodesulfurization is apparently some form of hydroaluminum nickelide* that, similar to V, attacks a nickel complex of the heterocycle (VII + VIII + IX):



Typical experimental procedures for the cleavages and ring contractions are the following (yields not yet optimal):

Hydrodesulfurization of dibenzothiophene

A solution of 4.0 mmol each of (COD)₂Ni and 2,2'-bipyridyl in 20 ml of anhydrous tetrahydrofuran was stirred under an argon atmosphere for 40 min at room temperature. Then 2.2 mmol of lithium aluminum hydride was added and after 10 min of stirring, 1.9 mmol of dibenzothiophene. After a reaction time of 20 h at 60°, treatment with water and ether, followed by extraction of the organic layer with 6 N aqueous HCl, gave after solvent removal and GLPC, an 80% yield of biphenyl (mp, IR and NMR).

Under similar conditions, phenoxathiin gave >90% of diphenyl ether and phenothazine, 80 % of diphenylamine.

Desulfurization with ring contraction

A solution of 4.0 mmol each of (COD)₂Ni and 2,2'-bipyridyl in 20 ml of

anhydrous THF was treated with 1.9 mmol of phenoxathiin and the mixture stirred at 50° for 40 h. Work-up by hydrolysis with 6 N aqueous HCl in the air yielded, after usual extraction, drying and solvent removal, 50-60% of dibenzofuran (mp, IR and NMR).

An alternative work-up, namely the addition of 4.0 mmol of LiAlH₄ to the reaction mixture and a 30-min reflux period under argon, gave upon subsequent hydrolysis (as above) a faster and better-yielding purification; the yields ranged up to 70% of dibenzofuran.

Under analogous conditions, thianthrene gave a 60% yield of dibenzothiophene and 10% of biphenyl, and phenothiazine only carbazole, but dibenzothiophene yielded 70% of biphenyl and a trace of 2-biphenylthiol.

Control experiments with lithium aluminum hydride. When solutions of 1.9 mmol of either dibenzothiophene or phenoxathiin in 20 ml of anhydrous tetrahydrofuran were heated with 2.2 mmol of lithium aluminum hydride for 20 h at 60°, hydrolytic work-up showed the presence of only a trace of biphenyl (<0.4%).

Acknowledgements

The authors are indebted to the National Science Foundation for the support of this research by Grant CHE76-10119.

References

1. N. L. Holy, Chem. Rev., 74 (1974) 243.
2. J. F. Garst, Acc. Chem. Res., 4 (1971) 400.
3. a) H. W. Sternberg, C. L. Delle Donne, P. Pantages, E. C. Moroni and R. E. Markby, Fuel, 50 (1971) 432; b) H. W. Sternberg and C. L. Delle Donne, ibid., 53 (1974) 172.
4. T. Ignasiak, A. V. Kemp-Jones and O. P. Strausz, J. Org. Chem., 42, (1977) 312.
5. H. Gilman and D. L. Esmay, J. Amer. Chem. Soc., 75 (1953) 2947.
6. H. Gilman and J. J. Dietrich, J. Org. Chem., 22 (1957) 850.
7. H. Gilman and J. J. Dietrich, J. Amer. Chem. Soc., 80 (1958) 380.

8. E. Lieber and S. Somasekhara, *Chem. Ind.*, (1958) 1367.
9. F. F. Blicke and D. G. Sheets, *J. Amer. Chem. Soc.*, 70 (1948) 3768.
10. F. F. Blicke and D. G. Sheets, *J. Amer. Chem. Soc.*, 71 (1949) 4010.
11. W. A. Bonner and R. A. Grimm, *Org. Sulfur Compounds*, (1966) 35.
12. W. O. House, "Modern Synthetic Reactions," 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, pp. 213-216.
13. J. J. Eisch, *J. Org. Chem.*, 28 (1963) 707.
14. H. O. House and G. Wilke, unpublished studies, cited in P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel," Vol. I, Academic Press, New York, N.Y., 1974, p. 261-262.
15. J. J. Eisch and M. Akhtar, unpublished studies, 1973.
16. J. J. Eisch and K. R. Im, *J. Organometal. Chem.*, 139 (1977) C45.