Tetrahedron Letters No.49, pp. 6157-6161, 1966. Pergamon Press Ltd.
Printed in Great Britain.

AZO AND HYDRAZO COMPOUNDS. III[1,2]
BIS(ETHOXYCARBONYL)SULFURDIIMINE AND ETHYL N-SULFINYL CARBAMATE

John Hancock and Alan R. Markert
Department of Chemistry, Reed College
Portland, Oregon 97202

(Received 22 September 1966)

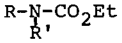
Acyclic compounds of the type I were not well known when this work was begun; until 1965 only two examples had been reported -- Ia[3] and Ib[4] -- but in that year the

$R\text{-}N{=}S{=}N\text{-}R'$

I

$EtO_2C\text{-}N{=}S{=}O$

II



$R\text{-}N(R')\text{-}CO_2Et$

III

Ia: R=R'= n-butyl
Ib: R=R'= phenyl
Ic: R=R'= t-butyl
Id: R=R'= t-octyl
Ie: R=R'= p-chlorophenyl
If: R=R'= ethoxycarbonyl

IIIa: R=R'=Cl
IIIb: R=H, R'=Cl

members Ic-Ie were also characterized.[5] We wish to add If to the list, and to relate it to II, the inclusion of which is timely in view of the work of Wucherpfennig and Kresse.[6]

Consideration of new routes to azo compounds led to the investigation of the reaction of sulfur with ethyl N,N-dichlorocarbamate (IIIa);[7] in benzene at reflux temperature (4 hours) the reaction yielded various sulfur chlorides and a yellowish-orange oil, b.p. 80°/0.25 mm. (80% yield). The oil analyzes correctly for If and shows the properties to be expected for that compound, including great sensitivity to moisture (giving sulfur dioxide and ethyl carbamate). More interesting, however, are the dehydrogenating properties of If; reaction with hydrazobenzene (warm benzene solution) gave almost immediately azobenzene and bis(ethoxycarbonylamino)sulfide (IV)[8] in high yields. Compound IV was also produced in the reaction of IIIb with sulfur under the same conditions, but the reaction has not yet been fully investigated.

Ethyl N-sulfinyl carbamate (II), a colorless liquid, b.p. ≤30°/0.1 mm., prepared for the first time[9] from thionyl chloride, ethyl carbamate, and pyridine in benzene solution at room temperature, also shows extraordinary sensitivity to water and appears to be hydrolyzed even more rapidly than thionyl chloride. Rapid hydrolysis produces sulfur dioxide and ethyl carbamate, but slow hydrolysis (in air) gives a 1:1 complex[10] of IV and VI,[11] instead of V, which might have been expected. When II is

$EtO_2C\text{-}NH\text{-}S\text{-}NH\text{-}CO_2Et$
IV

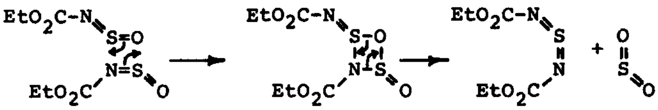
$EtO_2C\text{-}NH\text{-}SO\text{-}NH\text{-}CO_2Et$
V

$EtO_2C\text{-}NH\text{-}SO_2\text{-}NH\text{-}CO_2Et$
VI

$RSO_2N{=}S{=}NSO_2R$
VII

$RSO_2N{=}S{=}O$
VIII

heated, If and SO_2 are formed, presumably by a mechanism of the following type, analogous to that by which VIII is converted to VII.[6]



Further investigations into the reactions of If and II are in progress; the authors are indebted to the donors of the Petroleum Research Fund (American Chemical Society) and to the National Science Foundation (NSF-GE-6381) for financial support.

REFERENCES

1) Part II. J. Hancock, <u>Tetrahedron Letters</u>, 1585 (1964).
2) From the B.A. thesis of Alan R. Markert, Reed College, 1966.
3) M. Becke-Goehring and G. Weis, <u>Angew. Chem.</u>, <u>68</u>, 678 (1956).
4) R. Cramer, <u>J. Org. Chem.</u>, <u>26</u>, 3476 (1961). Compare (i) G. Leandri and P. Rebora, <u>Gazz. Chim. Ital.</u>, <u>87</u>, 503 (1957); (ii) A. Foffani, G. Leandri, I. Zanon, and C. Carpanelli, <u>Tetrahedron Letters</u>, 21 (1959).
5) D.H. Clemens, A.J. Bell, and J.L. O'Brien, <u>Tetrahedron Letters</u>, 1487 and 1491 (1965).

6) W. Wucherpfennig and G. Kresse, *Tetrahedron Letters*, 1671 (1966).

7) Fr. Patent 56,285 (*Chem. Abs.*, *52*, 11115^h (1958)). Yield (this work), 79%. The compound often explodes when distilled at atmospheric pressure (J. Houben, *J. prakt. Chem.*, [2], *105*, 19 (1922)), but we have distilled it safely *in vacuo* (b.p. 54-55°/11 mm., λ_{max,CCl_4} 315 mμ, $\epsilon = 290$).
The compound decomposes slowly at room temperature to give $CH_3CH(NHCO_2Et)_2$ and is best stored at -20° or below (unpublished work with R.H. Higer, R.S. Knutson, J. Woronsberg, and H.G. Rosenthal, Reed College).

8) K. Hafner and W. Kaiser, *Tetrahedron Letters*, 2185 (1964). The authors are indebted to Prof. Hafner for a copy of the infrared spectrum of IV.

9) Yield, 20% without taking into account recovered ethyl carbamate. Use of a more volatile solvent should improve the yield, since some II was detected in the benzene used. For a review on organic N-sulfinyl compounds, see G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H.P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem. Intl. Ed.*, *1*, 89 (1962).

10) KBr pellets of IV and VI, made separately and mounted together, give a composite spectrum (A) which is not identical with one (B) made by mixing IV and VI in

the same pellet. Evaporation of ether from a 1:1 solution of IV and VI gives a solid, the infrared spectrum of which is identical to B. The differences appear in the NH stretch region and in the carbonyl stretch region.

11) E.F. Degering, G.L. Jenkins, and B.E. Sanders, *J. Am. Pharm. Assoc.*, *39*, 624 (1950).