

AN UNUSUAL DECOMPOSITION OF THE DIANION OF BENZOPHENONE AZINE

E. J. MacPherson and James G. Smith

University of Waterloo

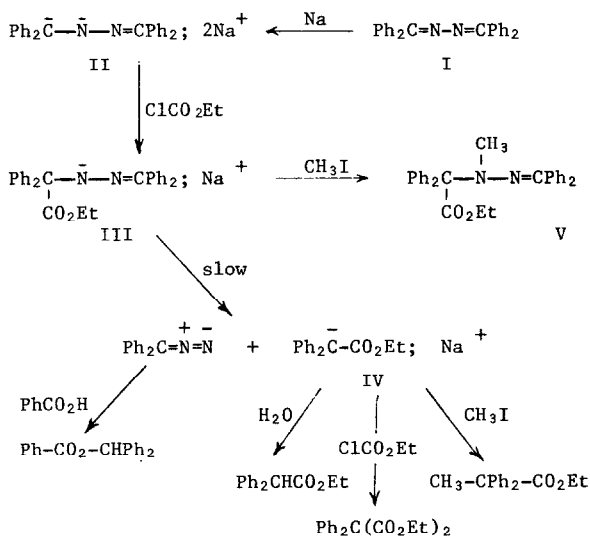
Department of Chemistry

Waterloo, Ontario

(Received in USA 2 June 1969; received in UK for publication 6 July 1969)

During the course of our investigations into the addition of alkali metals to carbon-nitrogen double bonds (1, 2, 3), we have examined the behaviour of benzophenone azine(I) since it contains two such bonds in conjugation. Our observations to date are incompatible with the earlier report of Schlenk and Bergmann (4) who suggested the formation of a tetra anion. Indeed, with sodium metal in ethyl ether or tetrahydrofuran, (I) clearly forms the dianion(II). One mode of reaction of this dianion(II) is sufficiently unusual that a preliminary report seemed warranted. Scheme I summarizes this decomposition and the experimental evidence which supports it.

SCHEME I



One mole of ethyl chloroformate (5) transformed the purple solution of the dianion(II) into a red solution whose colour remained unchanged on the addition of water. Evaporation of the solution gave a dark red oil whose infrared spectrum contained a strong band at 2050 cm^{-1} and from which ethyl diphenylacetate (6) crystallized. Addition of a mineral acid caused the red colour to disappear and a gas to be evolved.

Seemingly, the dianion(II) was converted initially to the monoanion(III) which underwent decomposition to diphenyldiazomethane and the monoanion(IV). The presence of diphenyldiazomethane, originally inferred by the presence of the band at 2050 cm^{-1} , was confirmed by treatment with benzoic acid and isolation of benzhydryl benzoate (7, 8). Anion(IV) was detected by its alkylation with methyl iodide (added 8 hours after the chloroformate) to produce ethyl α,α -diphenylpropionate (9).

However, the decomposition to diphenyl diazomethane and anion(IV) was not instantaneous. The two-step alkylation with ethyl chloroformate and methyl iodide, if performed with a 10 minute interval between additions, produced N-carbethoxydiphenylmethyl-N-methyl benzophenone hydrazone(V), (10).

Treatment of the dianion(II) with two moles of ethyl chloroformate produced, surprisingly, diethyl diphenylmalonate(6) and diphenyldiazomethane. Seemingly, reaction of the second mole of chloroformate with the intermediate(III) did not occur at a rate sufficiently fast to prevent its decomposition to (IV). The difference in behaviour of methyl iodide and ethyl chloroformate may be a reflection of the crowded nature of the reaction site on (III) and the difference in steric size of the two reagents.

ACKNOWLEDGEMENTS

The authors are indebted to the National Research Council of Canada for financial support and to the Ontario Government for a fellowship (E.J.M.).

REFERENCES

1. J. G. Smith, *Can. J. Chem.*, 46, 2271 (1968).
2. J. G. Smith and C. D. Veach, *Can. J. Chem.*, 44, 2245 (1966).
3. J. G. Smith and C. D. Veach, *Can. J. Chem.*, 45, 1785 (1967).
4. W. Schlenk and E. Bergmann, *Ann.*, 463, 281 (1928).
5. Added to the dianion(II) in tetrahydrofuran at -65°C .
6. Identified by comparison with an authentic sample.
7. H. Staudinger, *Eng. Anthes, F. Pfenninger, Ber.*, 49, 1928 (1916).
8. E. Hardegger et al., *Helv. Chim. Acta*, 31, 439 (1948).
9. Identified by the n.m.r. spectrum and hydrolysis to and comparison with the acid.
10. Satisfactory analyses and spectral data were obtained.