Asian Journal of Chemistry Vol. 8, No. 3 (1996), 357–360

Studies on Complex Arylhydrazones, Part XIII—Action of Bromine on 2,3-Dioxo-2-Phenylhydrazono Butyric Acid

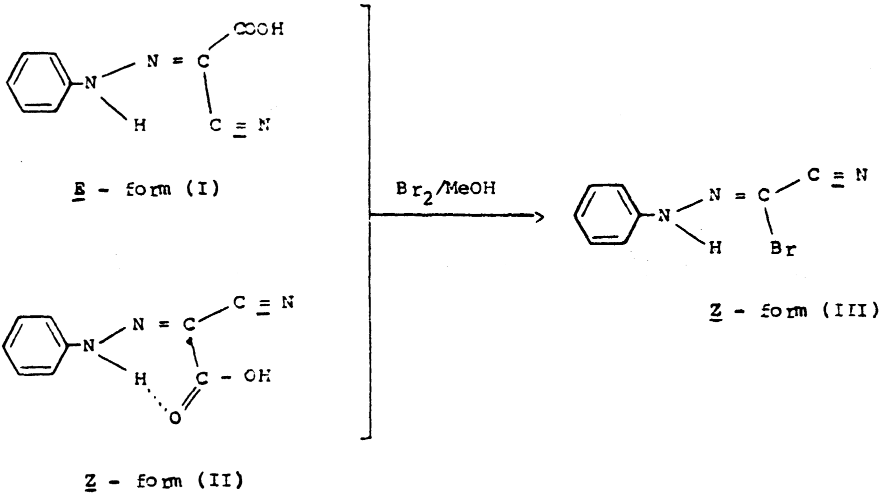
N. PRASAD*, A. SAHAY†, J. PRASAD‡ and K.R.K. SINGH††
Department of Chemistry
Bihar University, Muzaffarpur–842 001, India.

The nature of brominated product is dependent on the amount of bromine and time of reaction in the bromination of acid ketone. The products identified as *z*-form. When the reaction was carried out in NaOAc medium, the main product was dibrominated product; on the other hand, tribrominated product was the main product in acetic acid medium.

INTRODUCTION

Earlier work[1] shows that *E*-(I) and *Z*-(II) forms of cyanoacetic acid phenylhydrazone on bromination in methanol afford only one isomer *i.e.*, *Z*-(III) form of monobrominated product.

Bromination of ethylhydrogen mesoxalate phenylhydrazones has also been reported by us in an earlier communication.[2] It has been observed[2] that electron withdrawing groups in aromatic nucleus deactivated the ring to such an extent that bromination in the nucleus did not take place even with excess of bromine in presence of sunlight and on increasing the temperature. On the other hand electron releasing groups in the aromatic nucleus activated the ring and nuclear



---

†Deptt. of Chemistry, S.R.S. College, Patna-14, India.
‡Deptt. of Chemistry, M.S. College, Motihari, India.
††Deptt. of Chemistry, St. Paul's School, Darjeeling, India.

bromination was observed with excess of bromine in sunlight. In continuation of our earlier report,[2] the present paper describes the action of bromine on 2,3-dioxo -2-phenylhydrazone butyric acid.

EXPERIMENTAL

2,3-Dioxo-2-phenylhydrazono butyric acid was prepared in our laboratory by known procedure.[3] Bromine solution in acetic acid was prepared by dissolving 6 mL of bromine in 44 mL of glacial acetic acid.

Preparation of compound (VI):

0.001 Mol of 2,3-dioxo-2-phenylhydrazono butyric acid was warmed with acetic acid (10 mL) and then mixed with sodium acetate (100 mg). The contents were treated with bromine solution in acetic acid (2 mL). A pale yellow compound was obtained which was crystallised from aq. acetic acid in 50% yield having m.p. 130°C.

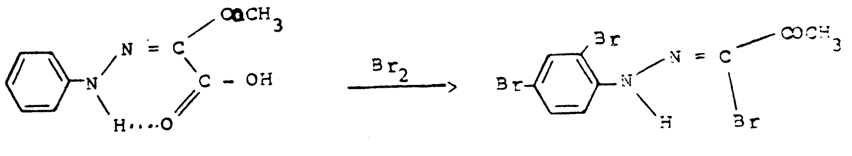
Preparation of compounds (V) and (VII)

0.001 Mol of 2,3-dioxo-phenylhydrazono butyric acid (2-methoxy derivative in case of VII) was dissolved by warming with acetic acid (10 mL). The cooled solution was treated with 2 mL of bromine solution in acetic acid at room temperature in sunlight. A pale yellow solid was separated immediately which was crystallised from acetic acid in 60% yield.

Purity of all the compounds was checked on silica gel G plates using iodine vapour as the detecting agent.

RESULTS AND DISCUSSION

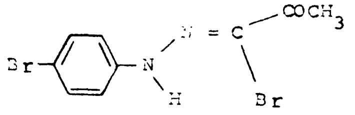
2,3-Dioxo-2-phenylhydrazono butyric acid (IV), on bromination in acetic acid at room temperature in sunlight gave the tribrominated product (V) (m.p. 110°C).



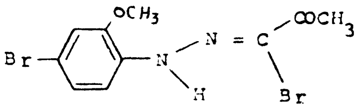
(IV) (V)

Bromination in the presence of sodium acetate gave a compound, m.p. 130°C, which was proved to be dibrominated product (VI) and the mother liquor again deposited the compound (V). Further *o*-methoxy derivative of compound (IV) on treatment with excess of bromine in acetic acid in sunlight gave compound (VII).

The characterisation of the compounds (V), (VI) and (VII) has been done during the present course of investigation on the basis of elemental analysis and



(VI)



(VII)

IR spectral data. The identity of the compound (V) was also confirmed on the basis of ^{13}C NMR and ^{1}H NMR spectral data.

In IR spectra, bromo derivatives (V, VI and VII) display a medium band in the region 3280 cm^{-1} which may be assigned to ν(N—H) vibration.[4] A very sharp band at around 1680 cm^{-1} occurs due to $\nu(>C{=}O)$ of carbonyl group while a strong or medium band at around 1580 cm^{-1} may be assigned to ν(N=C). The strong bands at 1060 ± 10 cm^{-1} and 1000 ± 10 cm^{-1} show the aromatic C—H in-plane bending while those at around 780 cm^{-1}, 810 cm^{-1} and 880 cm^{-1} corresponds to the aromatic C—H out-of-plane bending. The absorptions below 700 cm^{-1} occur because of skeletal vibrations.

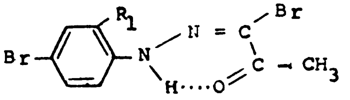
The ^{13}C NMR spectra of compound (V) showed resonances at δ 188, 137.5, 134, 131.5, 123, 116.5, 114, 108 and 24. Out of the five low intensity peaks (intensity of ipso and quarternary carbon resonances are known to be lower[5, 6]) at δ 188, 137.5, 134, 123 and 108, the one at δ 188 is obviously assignable to carbonyl carbon. The resonances at δ 137.5, 134 and 108 can safely be assigned to the ipso carbons (C-1 C-2 and C-4 respectively). We have assigned the remaining one at δ 123 to imino carbon[5, 6] Out of the four high intensity peaks at δ 131.5, 116.5, 114 and 24, the one at δ 24 is assignable to the methyl carbon. The remaining three high intensity peaks at δ 131.5, 116.5 and 114 can be assignable to the remaining three aromatic carbons.

The ^{1}H NMR spectrum of the compound (V) also confirms the structure[5, 6] as it showed resonances at δ 11.0 (1H, S) for—NH proton, δ 7.43–7.45 (3H, m) for aromatic protons and δ 3.25 (3H, S) for methyl protons.

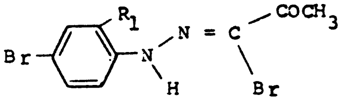
The ^{13}C NMR spectrum of the compound (VII) showed resonances at δ 185, 145, 128, 124, 123, 115, 114, 55 and 24. The peaks at δ 185, 145, 128 and 123 of small intensities were assigned to carbonyl carbon, ipso carbon (C-2 and C-1) and imino carbon respectively.[5, 6] The resonance of ipso carbon C-4 was probably buried under the peaks of other aromatic carbons. The methoxyl carbon resonance was assigned at δ 55 and methyl carbon at δ 24. The aromatic carbons C-3, C-5 and C-6 of large intensities were assigned respectively at δ 114, 124 and 115 on the basis of literature values.[5, 6]

The ^{1}H NMR spectrum of the compound (VII) is consistent with the structure as it showed resonances at δ 10.97 (1H, S) for imino proton, δ 8.4–9 (3H, m) for aromatic protons, δ 3.76 (3H, S) for methoxyl protons and δ 3.125 (3H, S) for methyl protons.[5,6]

The bromo products (V, VI and VII) could exist in two geometrical isomers (E- and Z-).



(E-form)



(Z-form)

(where R_1 = Br, H and OMe)

Considering the difference in the environment of carbonyl and methyl carbon (as one is the part of chelated ketomethyl and the other free ketomethyl), we expected two resonances in ^{13}C NMR spectrum for both carbonyl and methyl carbon. The appearance of only one signal for each carbon suggests that the bromo products (V, VI and VII) exist in only one isomer. The bromo products (V, VI and VII) seem to be *Z*-isomers. In IR spectra, when intramolecular H-bonding occurs in such type of compounds, the N—H stretching frequency vibration suffers a characteristic red shift and observed at around 3080 cm^{-1} .[4, 7–8] In the present case the higher shift in N—H (observed at around 3280 cm^{-1}) stretching frequency can be attributed to absence of intramolecular H-bonding. Thus on the basis of these evidences, the bromo products (V, VI and VII) can be deduced to exist in *Z*-form.

ACKNOWLEDGEMENT

The authors are thankful to Prof. R.J. Ferrier, Victoria University, Wellington, New Zealand for ^{13}C NMR and ^{1}H NMR spectral measurements.

REFERENCES

1. Brecknell, Carman, Death and Kirby, *Aust. J. Chem.*, **22**, 1915 (1969).
2. N. Prasad, A. Sahay, J. Prasad and K.R.K. Singh, *Asian. J. Chem.*, **8**, 65 (1996).
3. N. Prasad, R.M. Prasad, A. Sahay, A.K. Srivastava and J. Prasad, *Asian J. Chem.*, **6**, 901 (1994).
4. A. Sahay, *Asian J. Chem.*, **6**, 476 (1994).
5. R.M. Prasad, Ph.D. Thesis, Bihar University, Muzaffarpur (1985).
6. D. Prasad, N. Prasad, R.M. Prasad, R.J. Ferrier, and S.M. Milgate, *J. Chem. Soc., Perkin Trans.*, **1**, 1397 (1984).
7. H.C. Yao, *J. Org. Chem.*, **29**, 2959 (1979).
8. A. Mitchell and D.C. Nonhebel, *Tetrahedron*, **35**, 2013 (1979).

(*Received*: 12 June 1995; *Accepted:* January 1996) AJC-1055