

Novel *Bis*-Epoxides from Nitrophenacyl Bromides

E. Campaigne

Chemistry Laboratories of Indiana University, Bloomington, Indiana 47401

and

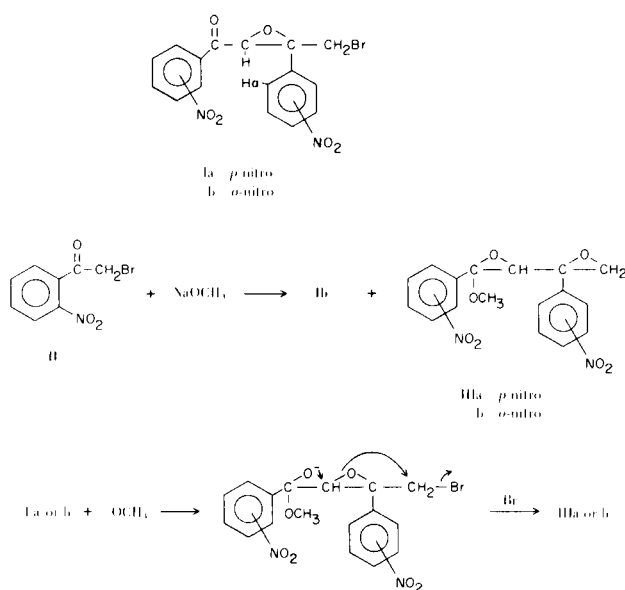
James H. Hutchinson (1)

Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37130

Received December 11, 1972

Charpentier-Morize *et al.*, (2) have reported the isolation of 4-oxo-2,3-epoxy-2,4-bis(*p*-nitrophenyl)-1-bromobutane (Ia) as the major product from the reaction of *p*-nitrophenacyl bromide and potassium carbonate in aqueous dioxane. We have now obtained a similar keto-epoxide (Ib) as one of two products isolated from the reaction of *o*-nitrophenacyl bromide (II) and sodium methoxide in absolute methanol. This type of structure has been previously reported (3-6). The other product isolated from this reaction has been identified as 1-methoxy-1,2,3,4-diepoxy-1,3-bis(*o*-nitrophenyl)butane (IIIb).

The mechanism for the formation of the keto-epoxide (Ia) has previously been discussed (2). However, we have found that when we treat Ia or b with a strong base, sodium methoxide, the corresponding *bis*-epoxides (IIIa or b) are formed. The *bis*-epoxide is evidently the result of methoxide anion attack on the carbonyl carbon of I and the subsequent double displacement giving III.



Interestingly, the nmr spectrum of Ib shows an unusual absorption for one of the ring protons—the Ha proton which is observed as a doublet at 6.41 ppm ($J = 8$ Hz). This abnormal upfield shift is probably due to the shielding of the Ha proton by the epoxide ring, due to hindrance to free rotation caused by the *ortho*-nitro group. This abnormal shift is not noted in the pmr spectrum of Ia.

EXPERIMENTAL

All melting points reported were determined with a Mel-Temp capillary melting point apparatus previously calibrated. The microanalyses were performed by either Midwest Microlab, Inc., Indianapolis, Indiana or Galbraith Laboratories, Knoxville, Tennessee. The ir spectra were recorded with a Beckman IR-20 spectrophotometer. The nmr spectra were recorded on a Varian T-60 or HA-100 spectrometer using TMS as internal standard. The following abbreviations are used in reporting the nmr data: s = singlet, d = doublet, m = multiplet.

1-Methoxy-1,2,3,4-diepoxy-1,3-bis(*o*-nitrophenyl)butane (IIIb).

A mixture of *o*-nitrophenacyl bromide (II) (6.0 g., 0.025 mole) and 25 ml. of absolute methanol was cooled to 0–5° in an ice bath and sodium methoxide (1.22 g., 0.025 mole) dissolved in 25 ml. of absolute methanol was added dropwise with stirring. After stirring at 5–25° for 3 hours, the mixture was heated to reflux for 3 hours and left to stir overnight at 25°. The precipitated product was collected and when recrystallized from benzene afforded 1 g. of colorless needles, m.p. 186–188°; ir λ max (potassium bromide): 1425 and 1345 (NO₂), 1290 and 875 cm⁻¹ (epoxy); nmr (deuteriochloroform): δ 7.3–8.2 (m, 8 aromatic H), 4.65 (d, $J = 12$ Hz, epoxy H), 4.4 (s, epoxy H), 4.3 (d, $J = 12$ Hz, epoxy H), 3.3 (s, -OCH₃).

Anal. Calcd. for C₁₇H₁₄N₂O₇: C, 56.98; H, 3.94; N, 7.82. Found: C, 56.53; H, 4.06; N, 7.80.

4-Oxo-2,3-epoxy-2,4-bis(*o*-nitrophenyl)-1-bromobutane (Ib).

After the removal of IIIb, the filtrate was poured over 400 g. of ice and the resulting precipitate was collected and when recrystallized from ethanol yielded 0.83 g. of colorless crystals, m.p. 135–136° dec.; ir λ max (potassium bromide): 1690 (C=O), 1520, and 1340 (NO₂), 1255, 860, and 795 cm⁻¹ (epoxy); nmr (deuteriochloroform): δ 8.16 (dd, $J = 8$ Hz, 1.8 Hz H *ortho* NO₂), 8.01 (dd, $J = 8$ Hz, 1.8 Hz H *ortho* NO₂), 7.1–7.6 (m, 5 aromatic H),

6.41 (dd, $J = 8$ Hz, 1.8 Hz Ha *ortho* epoxide), 4.47 (s, H epoxy), 3.85 (q, $J_{AB} = 12$ Hz $-\text{CH}_2$).

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}_6$: C, 47.37; H, 2.72; N, 6.87; Br, 19.62; Mol. Wt., 407. Found: C, 47.11; H, 2.94; N, 6.84; Br, 19.45; Mol. Wt., 403.

Reaction of Ib with Sodium Methoxide.

To a stirred suspension of Ib (0.215 g., 0.00052 mole) in 4 ml. of absolute methanol was added dropwise sodium methoxide (0.028 g., 0.00052 mole) dissolved in 4 ml. of methanol. After 24 hours, the precipitated product was collected and recrystallized from benzene yielding 0.11 g. (60%) of colorless crystals, m.p. 186-188°. Its ir spectrum was identical with the ir spectrum for IIIb.

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_7$: C, 56.98; H, 3.94; N, 7.82. Found: C, 57.25; H, 3.99; N, 7.76.

Reaction of Ia (7) with Sodium Methoxide.

To a stirred suspension of Ia (0.215 g., 0.00052 mole) in 4 ml. of absolute methanol was added dropwise sodium methoxide (0.028 g., 0.00052 mole) dissolved in 4 ml. of methanol. The colorless mixture quickly turned to dark orange and was allowed to stir at room temperature for 18 hours. The product was collected and when recrystallized from chloroform (decolorizing carbon) afforded 0.17 g. (92%) of a colorless powder, m.p. 215-217°; ir λ max (potassium bromide): 1520 and 1355

(NO_2), 1295, 1155, and 875 cm^{-1} (epoxy); nmr (deuteriochloroform): δ 7.3-8.5 (m, 8 aromatic H), 4.5 (s, 2 epoxy H), 3.9 (s, 1 epoxy H), 3.2 (s, $-\text{OCH}_3$).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_7$: C, 56.98; H, 3.94; N, 7.82. Found: C, 57.10; H, 3.89; N, 7.90.

Acknowledgement.

We are grateful to the U. S. Army Medical Research and Development Command, Department of the Army, contract No. DA-49-193-MD-3004 and to the Faculty Research Committee of Middle Tennessee State University, Murfreesboro, Tennessee for the support of this research.

REFERENCES

- (1) To whom correspondence should be directed.
- (2) M. Charpentier-Morize, R. Doukhan, and J. Sanaoulet, *Bull. Soc. Chem.*, 685 (1968).
- (3) J. A. Berson, *J. Am. Chem. Soc.*, 74, 5175 (1952).
- (4) H. H. Wasserman, N. E. Aubrey, and H. E. Zimmerman, *ibid.*, 75, 96 (1953).
- (5) C. L. Stevens, R. I. Church, and V. L. Tragnelis, *J. Org. Chem.*, 19, 522 (1954).
- (6) T. I. Temnikova, A. S. Dneprovskii, V. D. Barashkin, and A. I. Kobzeva, *Zh. Obshch. Khim.*, 6, 76 (1970).
- (7) We are indebted to Mr. James H. Scott of Sewanee Academy, Sewanee, Tennessee for providing a sample of this compound.