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A NEW SYNTHESIS OF 4-BROMOMETHYLBENZAL BROMIDE AND 1,4-bis(DIBROMOMETHYL)-BENZENE

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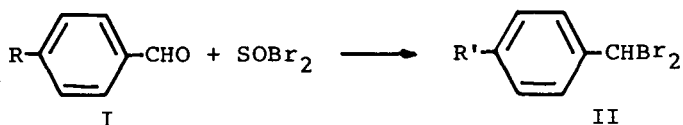
3. N. P. Peet and S. Sunder, *J. Org. Chem.*, 40, 1909 (1975).
4. F. M. Julien and H. T. Seifen, U.S.2,974,163 (1961); *Chem. Abstr.*, 55, 14381 (1961).

A NEW SYNTHESIS OF 4-BROMOMETHYLBENZAL BROMIDE
AND 1,4-bis(DIBROMOMETHYL)-BENZENE

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(1/12/81)

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Although two different methods for the preparation of 4-bromomethylbenzal bromide IIa have been studied, a one-step synthesis of this compound in good yield has yet to be achieved. In one such method, *p*-xylene was brominated at 130° to yield a mixture of brominated products from which IIa was isolated in 23% yield.^{1,2} Drefahl and Plotner³ isolated the same product after treatment of *p*-tolualdehyde with phosphorous tri-bromide in carbon disulphide followed by bromination of the intermediate product, 4-methylbenzal bromide, at 140° in the presence of a powerful source of light.



a) R = CH₃ b) R = CHO

a) R' = CH₂Br b) R' = CHBr₂

The other compound 1,4-bis(dibromomethyl)benzene (IIb) has been synthesized by various research groups, but a high yield synthesis of this compound under ordinary conditions is yet to be realized. In one such method^{4,5} dry bromine was

added to *p*-xylene at 150° followed by heating the reaction mixture at 170° for a short time, yielding a mixture of products from which IIb was isolated in low yield. Russian workers^{6,7} prepared the same compound by treatment of *p*-xylene with bromine at 140-60° in the presence of cumene hydroperoxide or benzoyl peroxide as an initiator (20% solution in pentachloroethane). Using an equimolar mixture of bromine and chlorine at 120-140°, Kasimov *et al.*⁷ have reported a better yield of the product. Plander and Zahalka⁹ have used an irradiation technique for the preparation of same compound.

In our hands thionyl bromide reacted with *p*-tolualdehyde (Ia) and terephthalaldehyde (Ib) within 2.5 hrs yielding IIa and IIb respectively in very high yields.

EXPERIMENTAL SECTION

4-Bromomethylbenzal Bromide.— Addition of thionyl bromide (8 ml) to *p*-tolualdehyde (6.0 g, 0.05 mol) at room temperature followed by heating the red solution at 100-110° for 2.5 hrs led to copious evolution of sulphur dioxide and hydrogen bromide. The solution was then cooled and the solid residue dissolved in carbon tetrachloride. The slightly pink solid which separated was filtered and dried. Sublimation at 95°/10 mm. followed by recrystallization from carbon tetrachloride (120 ml) gave 14.0 g (80%) of 4-bromomethylbenzal bromide as white plates, mp. 116°. IR (KBr): 1600 (aromatic), 840 (*p*-substitution) cm⁻¹. NMR (CDCl₃): τ 2.3 to 2.8 (4H, m, aromatic), 3.5 (1H, s, CHBr₂), 6.55 (2H, s, CH₂Br).

Anal. Calcd. for C₈H₇Br₃: C, 27.98, H, 2.04; Br, 69.97.

Found: C, 27.94; H, 2.05; Br, 69.80.

1,4-bis(Dibromomethyl)benzene.- Addition of freshly distilled thionyl bromide (15 ml) to terephthalaldehyde (10.0 g, 0.07 mol) at room temperature followed by heating the mixture at 100-120° for 2 hrs resulted in copious evolution of SO₂. After about 20 minutes, the aldehyde dissolved to yield a red solution and within two hours of heating, the red solution turned to a solid mass. It was cooled and dissolved in carbon tetrachloride (600 ml). The clear solution thus obtained was allowed to stand at room temperature overnight. The product, 1,4-bis(dibromomethyl)benzene, was obtained in quantitative yield as colorless needles, mp. 168°. IR (KBr): 1600 (aromatic), 850, 790 (p-substitution) cm⁻¹. NMR (CCl₄): τ 2.5 (4H, s, aromatic), 3.4 ppm (2H, s, CHBr₂).

Anal. Calcd for C₈H₆Br₄: C, 22.7; H, 1.42; Br, 75.8

Found: C, 22.68; H, 1.33; Br, 75.85

REFERENCES

1. A. LeCanu, *Compt. Rend.*, 118, 534 (1887).
2. E. F. J. Atkinson and J. F. Thorpe, *J. Chem. Soc.*, 91, 1687 (1907).
3. G. Drefahl and G. Plotner, *Chem. Ber.*, 94, 907 (1961).
4. L. Honig, *Monatsh. Chem.*, 9, 1150 (1909).
5. T. Gunther, *Ann.*, 347, 110 (1905).
6. R. G. Kasimov, A. V. Fomichev, S. Ya. Livshits, and V. V. Oleinik, *USSR*, 170, 934 (1965); *Chem. Abstr.* 63, 9863a (1965).
7. R. G. Kasimov, A. V. Fomichev, S. Ya. Livshits, Z. N. Zubareva and V. V. Oleinik, *USSR*, 173, 731 (1965); *Chem. Abstr.* 64, 2002f (1966).
8. A. M. Mezheritskii, V. V. Oleinik, Z. N. Zubareva, O. I. Lykova, and V. G. Sezhnev, *USSR*, 344, 716 (1976); *Chem. Abstr.* 84, 121,409h (1976).
9. E. Plander and J. Zahalka, *Radioisotopy (Czech.)* 13, 371 (1972).