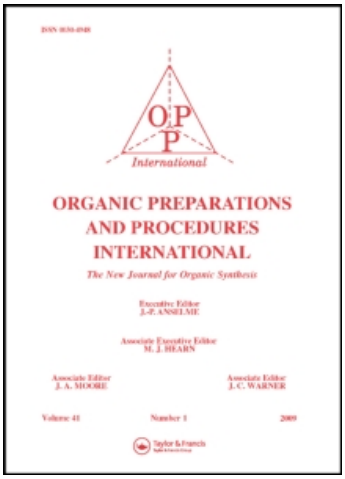

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AN IMPROVED SYNTHESIS OF 1,4-DIISOPROPENYLBENZENE VIA 1,4-BIS(1-BROMO-1-METHYLETHYL)BENZENE

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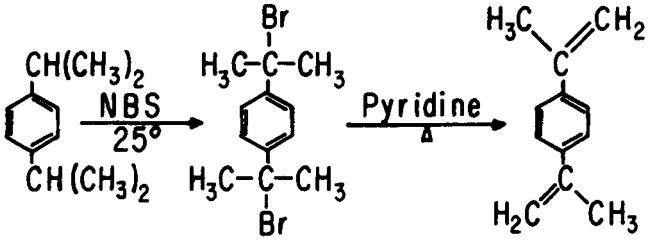
1,4-Diisopropenylbenzene has been found useful as a monomer in the synthesis of copolymers[1] and as a crosslinking agent for polystyrene and other polymers.[2] Previously the diene has been prepared in the laboratory by dehydration of the corresponding tertiary diol, the latter being prepared either by reaction of methylmagnesium bromide with terephthalate esters,[3,4] or by reaction of acetone with the dimagnesium derivative of p-dibromobenzene.[5] Overall yields are 40-50%. We have found that the diene may be more conveniently synthesized in an overall yield of 76% by the bromination of 1,4-diisopropylbenzene with N-bromosuccinimide to the previously unknown 1,4-bis(1-bromo-1-methylethyl)benzene, followed by dehydrobromination in boiling pyridine. It is



critical that the temperature be kept low during the bromination step in order to prevent thermal dehydrohalogenation and subsequent formation of unsaturated bromo compounds.[6] Presumably, this sequence should be applicable to other compounds of similar nature.

EXPERIMENTAL

1,4-Bis(1-bromo-1-methylethyl)benzene. - To a solution of 214 g (1.32 moles) of p-diisopropylbenzene (Aldrich Chemical Company) in 3500 ml of carbon tetrachloride in a nitrogen atmosphere was added 480 g (2.7 moles) of N-bromosuccinimide in portions over a 30 min. period. The stirred mixture was irradiated with a floodlight. The exothermic reaction began in 30 min. and cooling was applied to maintain the temperature at 25 ± 5°C. After 1.5 hr. the mixture was filtered and the filter cake (succinimide) was washed with carbon tetrachloride. The carbon tetrachloride was removed from the filtrate by distillation under reduced pressure below room temperature to give 402 g (95%) of crude 1,4-bis(1-bromo-1-methylethyl)benzene. The material may be used in the subsequent preparation without further purification. A recrystallized sample (pentane) had mp. 118-121°; nmr (CCl_4) τ 2.53 (s, 4, aromatic), 7.85 (s, 12, CH_3). Calcd. for $C_{12}H_{16}Br_2$: C, 45.1; H, 5.0; Br, 49.9. Found: C, 45.0; H, 4.9; Br, 50.0.

1,4-Diisopropenylbenzene. - 1,4-Bis(1-bromo-1-methylethyl)benzene, 402 g (1.25 moles), was dissolved in 1500 ml of pyridine and refluxed with stirring for 15 min. The cooled mixture was poured into 7500 ml of cold water. The

precipitate was collected by filtration and washed three times with water. Recrystallization of the filter cake from ethanol gave 203 g (80%) of 1,4-diisopropenylbenzene; mp. 64.5-65.0° (lit.[3] mp. 64.5°); nmr (CCl_4) τ 2.75 (s, 4, aromatic), 4.75 (m, 2, vinyl), 5.07 (m, 2, vinyl), and 7.95 (s, 6, CH_3).

REFERENCES

1. Scientific-Research Institute of Monomers for Synthetic Rubber, U.S.S.R. 191, 123, Jan. 14, 1967; Chem. Abstr., 68, 30875 (1968).
2. Esso Research and Engineering, Ger. 1,301,083, 14 Aug. 1969; Chem. Abstr., 71, 102667 (1969).
3. Yu. V. Mitin, Zhur. Obshchei Khim., 28, 3302 (1958).
4. I. H. Sadler, J. Chem. Soc., B, 1024 (1969).
5. N. V. Meiya and A. F. Nikolaev, Zhur. Organ. Khim., 1, 296 (1965); Chem. Abstr., 62, 16167 (1965).
6. Chemische Werke Heuls A.-G., Belg. 645,807, July 16, 1964; Chem. Abstr., 63, 9863 (1965).

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