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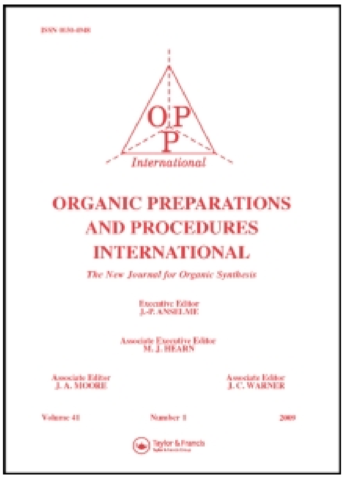

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LARGE SCALE PREPARATION OF 1, 3-DIMETHYLADAMANTANE

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LARGE SCALE PREPARATION OF 1,3-DIMETHYLADAMANTANE

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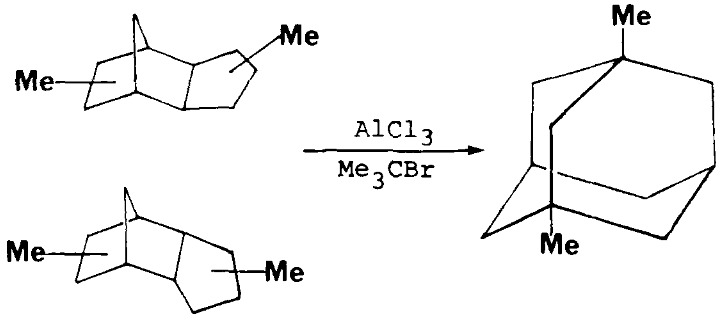
1,3-Dimethyladamantane (DMA) can be produced inexpensively in kilogram quantities from RJ4 (Ashland Chemical Co.), a high density jet fuel composed largely of the various isomers of the tetrahydromethylcyclopentadiene dimer (TCPD).[1] The conversion of RJ4 to DMA was carried in methylene chloride with aluminum chloride and tert-butyl bromide.[2] After work-up, the crude product was fractionated to give a 48-52% yield of a product containing 88-91% of 1,3-dimethyladamantane; this level of purity was adequate for other syntheses.[3] Further purification gave a sample which was identical to an authentic sample of 1,3-dimethyladamantane (Aldrich).



TCPD DMA

EXPERMENTAL SECTION

1,3-Dimethyladamantane.- Aluminum chloride (3113 g, 23.35 moles) was stirred in 3 l of methylene chloride. After cooling to 5°, 2680 g of

RJ4[91.65% of TCPD, 2456 g, 14.95 moles] was added over one hr. (temp. ≤10°). A solution of 504 ml of 96% <u>tert</u>-butyl bromide (575 g, 4.20 moles) in 500 ml of methylene chloride was then added over the course of 1.5 hr. An exotherm to 15-20° occurred. Afterwards, the reaction was stirred for 0.5 hr. at 10° then heated to reflux over 2-3 hrs. During the heating step at reaction temperature of 30-38°, a material distilled which was discarded and a small amount of HCl was evolved. The reaction was refluxed for 7 hrs. After cooling, the reaction mixture was added (0.5 hr) to a mixture of 8 l of 20% HCl and 3 kg of ice. Ice was added as needed to keep the temperature from rising above 25-30°. The aqueous layer was removed and extracted once with 1 l of methylene chloride. The organic layers were combined and were washed successively with 4 l of water, twice with 4 l of 10% HCl, once with 4 l of water and finally twice with 4 l of 10% $NaHCO_3$ Soln. The organic layer was dried on 200 g of anhydrous sodium sulfate and 50 g of anhydrous sodium carbonate. After filteration, the solvent was distilled and then, using a 15.0 cm. Vigreux column (N_2 atmosphere), the crude 1,3-dimethyladamantane was distilled at 195-215°, amounting to 1620 g (78% DMA). This material was fractionated (N_2 atmosphere) through a heated column (45 cm x 1.9 cm) which was packed with Rashig rings (6 x 6 mm) to give 1343 g of product, bp. 201-205°, lit. bp. 205°. This fraction was shown to contain 90.46% DMA (50% yield) by glc [10% SE-30 on 80/100 Supelcoport (6' x 1/8")].

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A CONVENIENT SYNTHESIS OF 10,10'-DIMETHYL-9,9'-BIACRIDYLIDENE

Submitted by
(02/27/87)

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Recent interest[1,2] in 10,10'-dimethyl-9,9'-biacridylidene (DBA) has prompted our investigation into a more convenient synthesis and extensive characterization of DBA. Lemstead and Hundertmark reported the first synthesis of DBA from N-methylacridone (NMA) using zinc and acetic acid.[3] While Kormendy[4] and Decker[5] were apparently able to repeat this procedure,