gave 6.0 g (20% yield) of analytically pure *dl*-**5,7-dinitro-6,6-dimethyl-2,10-undecanedione** (Va), mp 81–82°.

Anal. Found for $C_{13}H_{22}O_6N_2$: C, 51.98; H, 7.49; N, 8.86.

The **disemicarbazones** VIa and VIb of compounds Va and Vb were prepared in the usual manner.[7]

Compound VIa was insoluble in common organic solvents. The analytical sample, mp 209–210° dec, was obtained after washing with water, 95% ethanol, and anhydrous ether.

Anal. Calcd for $C_{15}H_{28}O_6N_8$: C, 43.26; H, 6.78; N, 26.91. Found: C, 43.53; H, 6.86; N, 26.40.

Compound VIb after recrystallization from absolute ethanol had mp 204–205° dec.

Anal. Found for $C_{15}H_{28}O_6N_8$: C, 43.72; H, 6.71; N, 26.41.

B. Employing 5,7-Dinitro-6,6-dimethyl-2-heptanone (IV).—To a solution of compound IV (2.32 g, 0.01 mol) in 50 ml of 95% ethanol was added eight drops of 20% sodium hydroxide. After cooling to 5°, freshly distilled methyl vinyl ketone (3.5 g, 0.05 mol) was added slowly with stirring. Adjusting the reaction temperature to 40–45°, stirring the reaction mixture for 24 hr, cooling to −78°, and filtering afforded 2.5 g (83% yield) of compound V, mp 92–94°.

Partial Conversion of *meso*-5,7-Dinitro-6,6-dimethyl-2,10-undecanedione (Vb) into the *dl* isomer Va.—To a solution of 1.32 g (0.02 mol) of potassium hydroxide in 50 ml of anhydrous methanol was added pure Vb (3.02 g, 0.01 mol) with stirring at 0–5°. The clear solution was stirred 1 hr at 0–10° and concentrated *in vacuo*. Dissolving the solid residue in 50 ml of water adding acetic acid (1.20 g, 0.02 mol) with stirring at 0–5°, filtering, washing the residue with water, and drying *in vacuo* gave a mixture of Va and Vb, mp 71–91°.

Registry No.—I, 762-98-1; II, 16240-70-3; III, 16214-89-4; IV, 16200-44-5; IV-semicarbazone, 16200-45-6; Va, 16200-46-7; Vb, 16200-47-8; VIa, 16200-48-9; VIb, 16200-49-0.

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Chlorocarbonylation of Adamantane

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In a current study of free-radical substitution of adamantane, the authors observed that in various radical halogenating conditions, the ratio of formation of 1- and 2-adamantyl radicals from the parent hydrocarbon was rather normal (3–5, with statistical correction) and was not sensitive to the hydrogen abstracting reagents employed. However, when adamantane was treated with halogen compounds of relatively large bond dissociation energies (such as CCl_4 or $CHCl_3$) in the presence of initiators, a remarkably increased selectivity was observed.[1] We now wish to report the free-radical chlorocarbonylation of adamantane to give an additional example of competitive substitution on the 1 and 2 position of adamantane. Especially, the reaction affords a very convenient preparative route to 2-adamantanecarboxylic acid (and its derivatives) which can only be obtained *via* a multistep synthesis.[2] Radical chlorocarbonylation of alkyl,[3] cycloalkyl,[3] or aralkyl[4,5] was performed photochemically or thermally (peroxide induced) in the literature. In thermal chlorocarbonylation of adamantane, methyl 1- and 2-adamantanecarboxylates were obtained in good yield.

Adamantane was chlorocarbonylated with an equivalent molar amount of oxalyl chloride in the presence of benzoyl peroxide (Scheme I). On methanolysis of the products, methyl adamantanecarboxylates were obtained (consisted of 55% 1 and 45% 2 isomers; preparative yield 82%) which were easily separated by fractional distillation. The high yield of chlorocarbonylation and lack of cleavage product indicate that both 1- and 2-adamantyl radical are stable although the former is in nonplanar configuration. The reactivity ratio of the 1 to 2 position was calculated as 3.67 (with statistical correction) in good agreement with that of radical halogenation.[6]

Chlorocarbonylation of adamantane with fivefold excess of oxalyl chloride (as employed for paracyclophane)[5] gave on methanolysis only a small amount of the mixed (1- and 2-) monocarboxylates but also gave a mixture of the dicarboxylates in 53% yield (bp 160–170° (0.5 mm)), the major part of which was identified as dimethyl adamantane-1,3-dicarboxylate. Of interest was the chlorocarbonylation of 1-bromoadamantane (eq 1) which gave 1-chloroadamantane (*ca.* 41%) as the major product, methyl 3-chloroadamantane-1-carboxylate (*ca.* 24%) and 1,3-dichloroadamantane (*ca.* 8%) together with unidentified isomers of methyl chloro- and/or bromo adamantanecarboxylates.

Detailed description and mechanistic interpretation will be presented in a later paper.

Experimental Section

Chlorocarbonylation of Adamantane.—To a solution of 15 g of adamantane and 7.5 g of oxalyl chloride in 20 ml of chlorobenzene kept at 80–90° was added a mixture of 2.9 g of benzoyl peroxide, 7.5 g of oxalyl chloride, and 10 ml of chlorobenzene over a 3-hr period. The solution was further stirred at that temperature range for 20 hr. After cooling and addition of 50 ml of methanol, the combined solution was stirred for an additional 5 hr. Distillation gave 6.1 g of recovered adamantane (it sublimed) and 10.4 g (82% yield) of methyl adamantanecarboxylate (bp 92–97° (9 mm)) which comprised 55% of the 1 and 45% of the 2 isomer. Separation of these was accomplished by fractional distillation with a rotatory band (No. 25 plate) at 135–139.5° (25 mm); pure methyl adamantane-1-carboxylate distilled first and the pure 2 isomer distilled last. Identification of the esters was made by vpc of the esters and the corresponding carboxylic acids and by a mixture melting point determination of the 1-carboxylic acid with an authentic sample (by nmr) of the 2-carboxylate (CCl_4, TMS; τ 6.36 singlet (3 H), 7.47 broad (1 H), 7.70 broad (2 H on β position[7] and 8.17 broad (12 H)). The index of refraction for the 2-ester was $n^{28}D$ 1.4970.

Anal. Calcd for the 2-ester: H, 9.28; C, 74.23. Found: H, 9.13; C, 74.01.

The melting point of the corresponding 2-carboxylic acid was 143° (lit.[2] 143.5–144.5°).

Chlorocarbonylation of 1-Bromoadamantane.—To a solution of 1 g of 1-bromoadamantane and 0.6 g of oxalyl chloride in 5 ml of chlorobenzene kept at 80–90° was added a mixture of 0.25 g of benzoylperoxide, 0.6 g of oxalyl chloride, and 3 ml of chlorobenzene over a 1-hr period. The solution was then stirred at 80–95° for 12 hr. After cooling and addition of 30 ml of meth-

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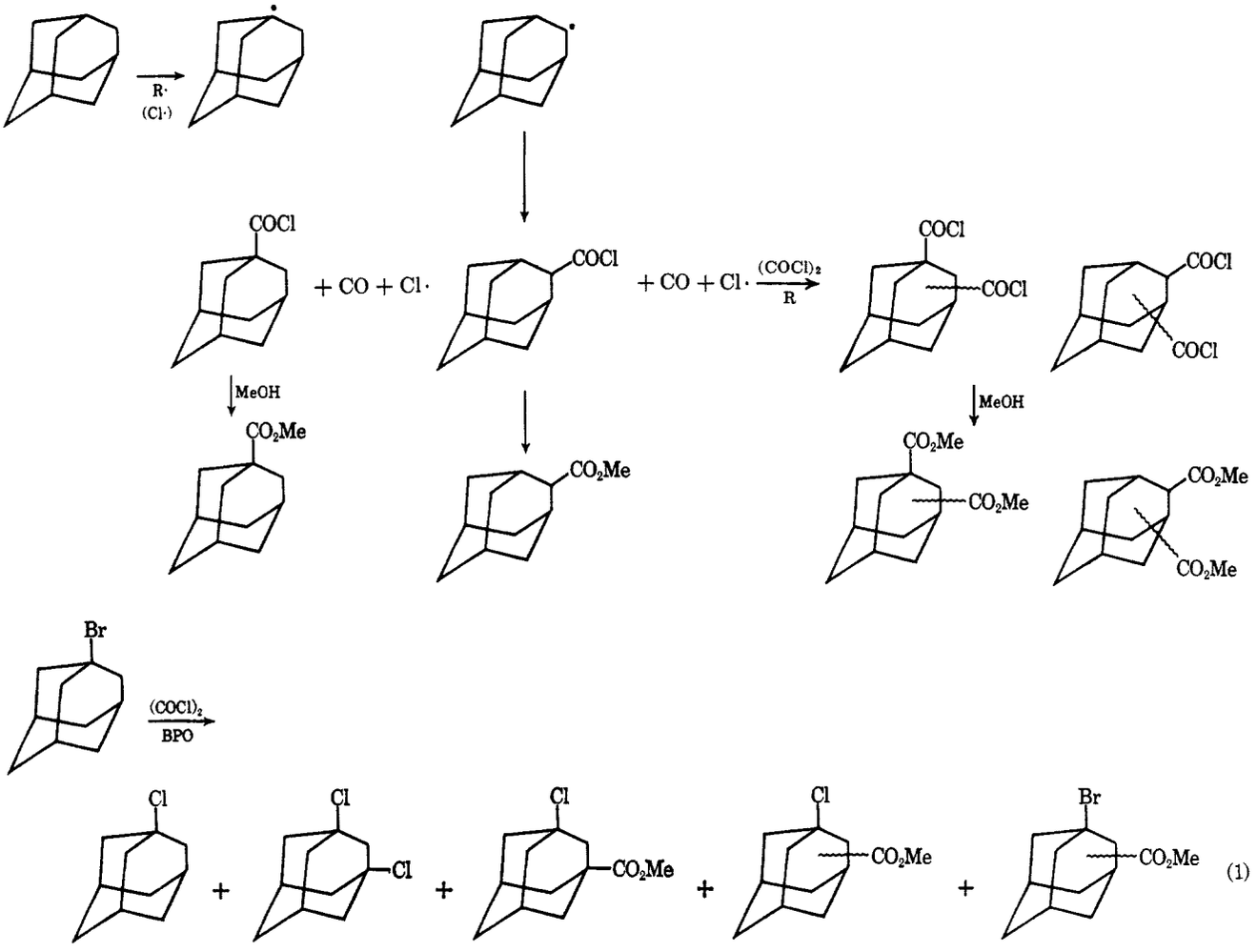
(6) See ref 1 and also G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961), for autoxidation and photochlorination.

(7) Nmr spectra of some 2-substituted adamantanes were reported where α and β hydrogens shifted considerably, supporting our assignment. See C. R. Fort, Jr., and P. von R. Schleyer, *ibid.*, **30**, 789 (1965).

SCHEME I



anol, the combined solution was stirred for 7 hr and then volatile compounds were distilled off. The residual products were analyzed by vpc.

The conversion was about 80% on the basis of recovered 1-bromoadamantane and at least eight products were formed. The main product was 1-chloroadamantane (*ca.* 41%) (identified with an authentic sample by PEG 20,000 and Silicone D.C. 550 columns) and two of the others were identified as 1,3-dichloroadamantane (*ca.* 8%) and methyl 3-chloro-admantane-1-carboxylate (24%) (identified by vpc). Structure of other minor five products were not yet determined. Presumably they were methyl halo- (chloro- and/or bromo-) adamantanecarboxylates. Methyl adamantanecarboxylate, and dimethyl adamantanedicarboxylates were not found.

Registry No.—Adamantane, 281-23-2; 1-bromoadamantane, 768-90-1.

Synthesis and Reactions of Cyclic Amidines[1-3]

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In a recent article, Kwok and Pranc[4] reported the synthesis and nmr spectra of some N-substituted 2-iminopyrrolidines prepared from a variety of primary amines and 4-chlorobutyronitrile (**2c**). In this note, we summarize an independent study which supports their conclusions, corrects older literature, and expands the general reaction to include other ω-halonitriles (**2a–f**).

In 1927, Kiel reported that the reaction of excess ammonia or methylamine with **2c** in ethanol led to the hydrochlorides of 4-amino- (**3b**) and 4-methylaminobutyronitrile (**3c**), respectively.[5] Further, he structured the reduction product of his **3c** as N-methyl-1,4-diaminobutane (**5b**). Our spectral and chemical evidence, coupled with that of Kwok and Pranc,[4] decisively establish Kiel's amination product to be instead the hydrochlorides of 2-imino- (**4a**) and 1-methyl-2-methyliminopyrrolidine (**4c**), while lithium aluminum hydride or sodium in ethanol (Kiel's procedure)[5] reduction of **4c**, and the more stable hydrobromide **4d**, produces only N,N′-dimethyl-1,4-diaminobutane (**5d**). Further, mild but prolonged alkaline hydrolysis of **4c** and **4d** led to 1-methylpyrrolidone (**6a**) and methylamine.

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(2) Presented at the Second Middle Atlantic Regional Meeting of the American Chemical Society, New York, N. Y., Feb 7, 1967.

(3) Taken from the Ph.D. Thesis of A. A. Cevasco, 1967.

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