

cipitate is filtered off and the filtrate is evaporated to remove solvent; the oily residue is distilled at 140°C/0.4 torr [yield of (6): 0.20 g (64%); colorless stable oil].

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[1] *Immonium Chemistry, Part 5.-Part 4: H. G. Viehe, Th. van Vyve, and Z. Janousek, Angew. Chem.* 84, 991 (1972). *Angew. Chem. internat. Edit.* 11, 916 (1972).

[2] J. H. Ottenheim and J. W. Garritsen, British Pat. 901 169, (1962); *Chem. Abstr.* 58, 6810, (1963); H. Ulrich: *The Chemistry of Imidoyl Halides*. Plenum Press, New York 1968 p. 207.

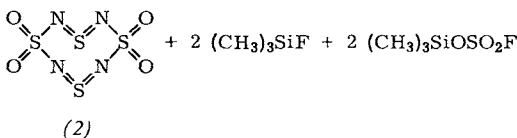
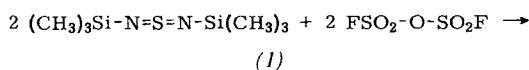
[3] H. G. Viehe, Lecture at the Nottingham Symposium on Acetylenes, July 1971; E. Goffin and Y. Legrand, *Dissertations, Université de Louvain*, in preparation.

Synthesis of the First Oxide of Tetrasulfur Tetranitride

By Herbert W. Roesky and Olaf Petersen^[*]

We reported recently the synthesis of S₃N₃O₃Cl, the S,S,S'-trioxide of a six-membered sulfur-nitrogen ring^[1]. We have now succeeded in isolating the first oxide of the S₄N₄ ring.

N,N'-Bis(trimethylsilyl)sulfur diimide (1)^[2] reacts with the anhydride of fluorosulfuric acid with cleavage of trimethylfluorosilane and trimethylsilyl fluorosulfate to give S₄N₄O₄ (2).



(2) is a yellow solid which sublimes at 80–90°C under oil-pump vacuum. Decomposition point: 115 to 120°C. The compound is not formed on reaction of (1) with SO₂Cl₂. In the presence of moisture it decomposes with loss of SO₂ and turns brown in color. The given structure follows from complete elemental analysis and the MS and IR data.

The mass spectrum contains the molecular ion at *m/e* = 248 with a relative intensity of only 0.1%. This is accompanied by the following characteristic ions: *m/e* = 216, S₄N₄O₂ (16%); 184, S₄N₄ (1%); 170, S₃N₃O₂ (13%); 138, S₃N₃ (1%); 124, S₃N₂ (4%); 110, S₃N (1.5%); 92, S₂N₂ (8%); 78, S₂N (14%); 64, SO₂ (17%); 48, SO (16%); 46, NS (100%); 32, S (9%); 28, N₂ (17%).

In the IR spectrum absorptions occur at (cm⁻¹): 1420 (s), 1400 (s), 1328 (vs), 1280 (w), 1218 (m), 1202 (m), 1175 (s), 1137 (vs), 1115 (vs), 1072 (w), 1018 (w), 980 (w), 895 (w), 850 (w), 830 (w), 715 (s), and 704 (s). The bands at 1420 and 1400 cm⁻¹ are assigned to asymmetric S=O stretching vibrations.

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Experimental:

To a solution of (1) (0.1 mol) in CCl₄ (200 ml) in a 500-ml two-necked flask fitted with dropping funnel is added dropwise over 3h a solution of F₂S₂O₅ (0.1 mol) in CCl₄ (100 ml). The mixture is then boiled under reflux for 4h and the solvent and volatile products subsequently removed by evaporation and condensation into a trap under vacuum. The residue remaining in the flask is sublimed under oil-pump vacuum. Four sublimations are required for complete purification of the product. Yield 2.5 g (5%).

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[1] H. W. Roesky, *Angew. Chem.* 83, 253 (1971); *Angew. Chem. internat. Edit.* 10, 266 (1971).

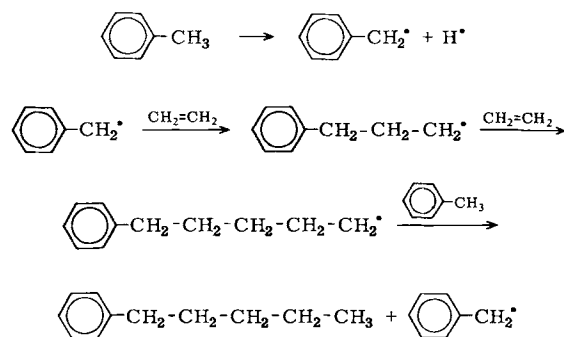
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Side-Chain Alkylation of Toluene with Ethylene^[1]

By Ernst Oltay, Johannes M. L. Penninger, and Hendrik Maatman^[*]

In the presence of metallic Na or K as a catalyst, with or without promoter, the three hydrogen atoms of the methyl group in toluene can be stepwise alkylated with ethylene, the most highly alkylated product formed being 3-ethyl-3-phenylpentane^[2–4]. In the presence of butyl-Li and a di-tertiary amine, toluene reacts with ethylene to give a straight-chain homologous series^[5, 6].

We have found that toluene reacts with ethylene in the absence of a catalyst even at as low a temperature as ≈ 400°C and a pressure of 50 atm to give alkylbenzenes having straight alkyl chains (for instance, *n*-propylbenzene and *n*-pentylbenzene). The reaction proceeds *via* free radicals.



Compounds yielding benzyl radicals catalyze the reaction. Thus the conversion of toluene and the selectivity of the side-chain alkylation to give straight-chain alkylbenzenes are favored by addition of benzyl chloride and benzyl bromide (Table 1).

All compounds were isolated by preparative gas chromatography and identified by NMR, IR, and MS, as well as by their gas-chromatographic retention times. The new reaction is of general applicability.

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Table 1. Side-chain alkylation of toluene with ethylene. Cr-Ni-Mo steel autoclave (314 cm³), 20 g (217 mmol) toluene, 7 g (250 mmol) ethylene, 380°C, 55 atm, 2 h.

C ₆ H ₅ CH ₂ Br [wt.-%]	Toluene conversion [%]	Yield [mol.-%]		all straight chain alkyl- benzenes
		<i>n</i> -propyl- benzene	<i>n</i> -pentyl- benzene	
—	10.6	32.7	12.4	45.1
0.1	13.3	42.1	25.1	67.2
0.5 [7]	19.3	56.7	25.5	82.2
1.0	24.0	60.9	14.5	75.4

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German version: Angew. Chem. 84, 947 (1972)

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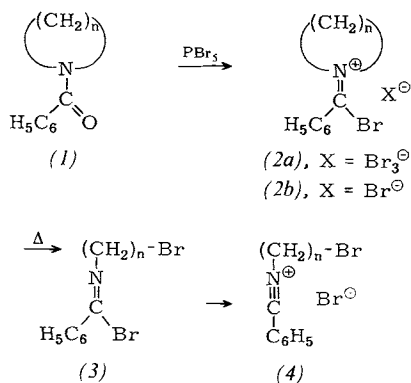
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[7] We obtained almost identical results with an equivalent amount of benzyl chloride.

The Mechanism of the Bischler-Napieralski Reaction^[1]

By Gábor Fodor, J. Gal, and B. A. Phillips^[*]

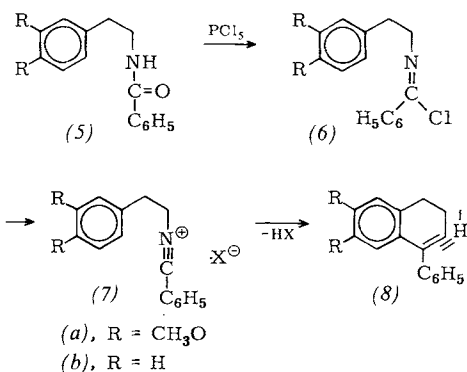
The fragmentation of cyclic benzamides of type (1) upon the action of phosphorus pentabromide^[2] leads to α , ω -dibromoalkanes and benzonitrile. Our recent studies have revealed that the first step of this reaction is in fact the formation of the α -bromoiminium tribromide (2a) which can be isolated^[3] in more than 90% yield. Reduction of this compound with an olefin (e.g. cyclohexene) results in the quantitative formation of the monobromide (2b)^[4]. Mild heating of (2b) gave the *N*-(ω -bromoalkyl)imidoyl bromide (with $n = 5$) which was also synthesized *via* its hydrobromide from *N*-(5-bromoamyl)benzamide and carbonyl bromide^[4] (or phosphorus pentabromide) followed by reduction of Br₃⁻ to Br⁻, and mild heating.



Imidoyl bromides—unlike imidoyl chlorides^[5]—have not been previously known in pure form. We have found that imidoyl bromides equilibrate with nitrilium bromides (4) and hence are the intermediates which occur after the bromoiminium bromide in the degradation of the amide (1)^[6].

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However, if unlike in the amide degradation there is an internal nucleophile present, it should react with the carbon of the nitrilium group. This is the case in the Bischler-Napieralski ring closure reaction of *N*-acyl-2-arylethylamines (5) under the influence of P₂O₅, POCl₃ or ZnCl₂ to give the 3,4-dihydroisoquinolines (8). To prove this we have converted *N*-[2-(3,4-dimethoxyphenyl)ethyl]benzamide (5a) at room temperature with phosphorus pentachloride in CCl₄ into the crystalline hydrochloride of the benzimidoyl chloride (6a) (80% yield). This salt loses hydrogen chloride slowly at room temperature (more rapidly at 85°C) and gives quantitatively the cyclized product, i.e. 6,7-dimethoxy-1-phenyl-3,4-dihydroisoquinoline hydrochloride (8a).



The reaction can be followed with NMR using CDCl₃ as solvent: (6a) shows a singlet at 3.82 ppm for the six methoxy protons which is converted to two singlets at 3.80 and 4.09 ppm as the cyclization to (8a) proceeds. The aromatic region is also informative in that the original peak at 6.82 ppm integrating for three protons changes to two singlets at 6.94 and 7.13 ppm which integrate for one proton each.

Addition of a Lewis acid (ZnCl₂, SnCl₄, etc.) enhanced the rate of cyclization. This could be explained through a push-pull displacement of chlorine from the imide carbon in (6) by the nucleophilic arene carbon, synchronously with attack of the Lewis acid upon the chloride ion. Alternatively, one can suppose intermediary formation of the nitrilium ion (7a), which could then react very fast^[7] with the aromatic carbon.

In order to slow down the cyclization, and detect the nitrilium ion, *N*-(2-phenylethyl)benzamide (5b) was converted into the crystalline imidoyl chloride hydrochloride^[8] and then into the base (6b), which was distilled at 132°C/0.045 torr. If stannic chloride is added to a solution of (6b) in a NMR tube, the triplet at 4.02 ppm of the methylene adjacent to nitrogen disappears and a new CH₂ triplet appears at 4.68 ppm, indicating nitrilium ion (7b) formation. Upon standing at 25°C this triplet is slowly (faster upon heating) displaced to 4.20 ppm, which is the chemical shift of the methylene protons at C-3 in the hydrochloride of the 3,4-dihydroisoquinoline (8b). Moreover, the *N*-(2-phenylethyl)benzonitrilium ion could also be trapped as the crystalline hexafluoroantimonate. It reacts subsequently in solution to give the dihydroisoquinolinium hexafluoroantimonate.

N-(2-Phenylethyl)benzonitrilium complexes have previously been obtained from a metal halide complex of the nitrile and 2-phenylethyl chloride^[9], reminiscent of the Ritter reaction^[10]. The product was also cyclized into the