Table I

Telomerization of *t*-Butyl Chloride with Butadiene[a]

Cat.	Yield of products, %			Reactants conversion, %
	$n = 1$	$n = 2$	$n > 2$	
$HClO_4$	. .	. .	100	21
$TiCl_4$	1	38	61	30
$AlCl_3$	9	6	85	60
$SnCl_4$	13	6	81	59
$ZnCl_2$	58	19	23	37
$BiCl_3$	60	22	18	64

[a] In these experiments, 0.45 mole of *t*-butyl chloride and 0.3 mole of butadiene in the presence of 0.5 g. of the halide catalyst were shaken for 5 days in pressure bottles at 20–25°.

reactants) zinc chloride or bismuth chloride and a reaction time of 120–130 hr. were necessary. A reaction time of more than 130 hr. at 20–25°, apart from being impractical, did not raise the conversion.

It has already been stated in the literature,[4,5] that concentrated hydrochloric acid suppresses the formation of high telomers. This is shown for the two most effective catalysts ($ZnCl_2$ and $BiCl_3$) in Table II.

Table II

Influence of Concentrated Aqueous Hydrochloric Acid on the Telomerization of *t*-Butyl Chloride and Butadiene Catalyzed by Zinc Chloride and Bismuth Trichloride[a]

Cat.	Concd. HCl, ml.	Yield of products, %				Reactants conversion, %
		$n = 1$	$n = 2$	$n > 1$	$n > 2$	
$ZnCl_2$	. . .	58	. . .	42	. . .	37
$ZnCl_2$	0.1	86	. . .	14	. . .	11
$ZnCl_2$	0.2	85	. . .	15	. . .	8
$ZnCl_2$	0.3	86	. . .	14	. . .	2
$ZnCl_2$	0.4	. . .	. . .	. . .	. . .	. .
$BiCl_3$	. . .	60	22	. . .	18	64
$BiCl_3$	0.05	61	18	. . .	21	64
$BiCl_3$	0.1	62	19	. . .	19	60
$BiCl_3$	0.2	82	14	. . .	4	46
$BiCl_3$	0.3	83	13	. . .	4	38
$BiCl_3$	1.2[b]	80.5	12.9	. . .	2.9	51

[a] In these experiments, 0.45 mole of *t*-butyl chloride and 0.3 mole of butadiene were shaken in the presence of 0.5 g. of the halide catalyst at 20–25° for 120 hr. [b] See large-scale preparation in the Experimental part.

In both reactions, 1-chloro-5,5-dimethyl-2-hexene can be prepared in 80–85% yield. However, in the zinc chloride catalyzed reaction, this is only possible at a conversion of 11%, compared with a 40–50% conversion in the case of $BiCl_3$. It is evident from the results of Table II that, for the preparation of the lower telomers, $BiCl_3$ is the catalyst of choice. The influence of different *t*-butyl chloride–butadiene molar ratios on the telomer distribution in telomerizations catalyzed by $BiCl_3$ and aqueous HCl (in amounts of 0.9 and 0.2%, respectively, based on the total weight of reactants) is shown in Table III.

Table III

Condensation of *t*-Butyl Chloride and Butadiene

Molar ratio[a]	Yield of products, %			Reactants conversion, %
	$n = 1$	$n = 2$	$n > 2$	
1:2	34	23	43	89
1:1.5	39	19	42	84
1:1	59	21	20	78
1:0.63[b]	81	15	4	63
1:0.4	93	5	2	40

[a] Molar ratios of *t*-butyl chloride to butadiene. [b] See ref. 4.

From these results it may be seen that favorable conditions for the preparation of 1-chloro-5,5-dimethyl-2-hexene exist when the molar ratio of *t*-butyl chloride to butadiene lies in the range of 1.6 to 2.2.

The last reaction parameter investigated was the effect of temperature on the *t*-butyl chloride–butadiene conversions and telomer distribution. It was found that at 40° the results shown in Table II could be obtained after only 15–17 hr. The telomer distribution remained almost unaltered, as can be seen from an optimized up-scaled run described in the Experimental part.

The chlorooctene and chlorododecadiene obtained in this telomerization process are all-*trans* compounds as evidenced by their infrared spectra.

Experimental

A. **Small-Scale Runs.**—A 250-ml. glass pressure bottle was cooled to −10°, filled with the required amounts of reactants and catalysts, and shaken at room temperature for a certain number of hours. Excess butadiene was vented off and the brown liquid was decanted into water; the mixture was well shaken, the organic layer was washed until neutral with water, separated, dried with calcium chloride, and distilled. 1-Chloro-5,5-dimethyl-2-hexene distilled at 65–68° (25 mm.), $n^{20}\text{D}$ 1.4447 (lit.[4] b.p. 46–47° at 10 mm., $n^{20}\text{D}$ 1.4456). The remaining higher boiling material consisted of chlorododecadiene distilling at 55–57° (0.1 mm.), $n^{20}\text{D}$ 1.4658 (lit.[5] 68–73° at 2.5 mm., $n^{20}\text{D}$ 1.4643) and higher telomers.

B. **Large-Scale Preparation.**—A mixture of 440 g. (4.75 moles) of redistilled *t*-butyl chloride, 162 g. (3 moles) of butadiene, 5.4 g. of bismuth chloride, and 1.2 ml. of concentrated aqueous HCl was charged in a glass autoclave. The reaction mixture was heated to 40° and stirred at this temperature for 15 hr. At this point the manometer showed that the pressure in the reaction vessel had fallen to 1 atm. or less. The crude reaction mixture was neutralized with diethylamine and distilled over a 50-cm. Vigreux column. After a forerun of unreacted *t*-butyl chloride and dissolved butadiene, 1-chloro-5,5-dimethyl-2-hexene distilled at 65–68° (25 mm.) to give 306 g. (80.5% yield at 51% conversion) of a pure product; chlorododecadiene distilled at 55–57° (0.1 mm.) to give 49 g. (12.9% yield), followed by a small amount of higher boiling material (b.p. 60–120° at 0.1 mm.), 11 g., corresponding to a 2.9% yield.

Pyridines from Cyanogen-Like Compounds and Unsymmetrical Dienes[1]

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The synthesis of pyridines at 350–450° by the thermally initiated reaction of cyanogen-like compounds with 1,3-butadiene was reported in the preceding paper.[3] With unsymmetrical dienes, a route to a series of new pyridines is apparent; the relative amounts of the isomeric pyridines from each unsymmetrical

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(2) Union Carbide Fellow in Chemistry, 1963–1964.

(3) G. J. Janz and A. R. Monahan, *J. Org. Chem.*, **29**, 569 (1964).

TABLE I

SYNTHESIS OF 2-CYANO- AND 2-PERFLUOROALKYLPICOLINES

RCN (moles)	Diene (moles)	Contact time, sec.	Total time, min.	Temp., ±1°C.	Material recovery, wt. %	Conversions per single pass, mole % Diene	Nitrile	Yields of pyridinic product, mole % *a*	*b*
CF_3CN (0.062)	Isoprene (0.058)	32.9	30	418.5	100	34.5	12.6	37.7	100
CF_3CN (0.200)	Pentadiene (0.385)	2770	300	400.0	99.0	62.0	60.0	50.2	100
$CF_3CF_2CF_2CN$ (0.101)	Isoprene (0.056)	49.9	60	420.5	100	46.8	11.4	44.2	100
$(CN)_2$ (0.132)	Isoprene (0.042)	36.6	48	412.9	93.1	83.3	12.9	11.1	22

[a] Yield of pyridinic products based on converted diene. [b] Yield of pyridinic products based on converted nitrile.

TABLE II

H^1 N.M.R. OF METHYL-GROUP PROTONS ON SOME SUBSTITUTED PICOLINES

Pyridines	δ (p.p.m. ±0.01, downfield from TMS external standard)
4-Methyl-2-heptafluoropropylpyridine	2.43[a]
5-Methyl-2-heptafluoropropylpyridine	2.37[a]
6-Methyl-2-cyanopyridine	3.19
4-Methyl-2-cyanopyridine	2.86[a]
5-Methyl-2-cyanopyridine	2.96[a]
3-Methyl-2-trifluoromethylpyridine	2.51
4-Methyl-2-trifluoromethylpyridine	2.18[a]
5-Methyl-2-trifluoromethylpyridine	2.12[a]
6-Methyl-2-trifluoromethylpyridine	2.42

[a] Isomeric mixture.

diene, furthermore, offers the prospect of a more penetrating insight in the reaction mechanism. The present communication reports on a series of experiments with isoprene and pentadiene in reaction with $(CN)_2$, CF_3CN, and $CF_3(CF_2)_2CN$.

Experimental

Cyanogen (99.5% minimum purity, b.p. -21.7°, American Cyanamid Co.) was vacuum degassed (−195°) in the conventional manner three times prior to use. The cyanogen-like compounds, CF_3CN and $CF_3(CF_2)_2CN$ (95% minimum purity, b.p. −64°; and 95% minimum purity, b.p. −5°, respectively; Peninsular Chemresearch, Inc.), were similarly vacuum degassed. The unsymmetrical dienes, $CH_2{=}C(CH_3){-}CH{=}CH_2$ and $CH_3{-}CH{=}CH{-}CH{=}CH_2$ (99% minimum purity, b.p. 34°; and 90% minimum *cis* isomer, b.p. 40°, respectively; Phillips Petroleum Co.), were distilled just prior to use. The purity of all samples was checked by gas chromatographic analysis.

The continuous flow reactor, recovery of materials, and monitoring of gaseous and liquid reactants have been described in the preceding paper[3] and were used without change. A summary of the experimental conditions, recoveries, and yields is in Table I. Quantitative separation of the pyridines was achieved by gas chromatography (Beckmann GC-2; 12-ft. di-*n*-decyl phthalate on firebrick column; 130–190°), and structural confirmation was by vibrational spectroscopy, mass spectra, and H^1 magnetic resonance data. The latter results are in Table II. The physical properties and microelemental analyses found for the new pyridines are given below.

3-Methyl-2-trifluoromethylpyridine had b.p. 174°, *d* 1.2402 g. ml.$^{-1}$, and n^{20}_D 1.466.

Anal. Calcd.: N, 8.70. Found: N, 8.51.

4-Methyl-2-trifluoromethylpyridine had b.p. 170°, *d* 1.2199, and n^{20}_D 1.4298.

Anal. Calcd.: N, 8.70. Found: N, 8.18.

5-Methyl-2-trifluoromethylpyridine had b.p. 171°, *d* 1.2202, and n^{20}_D 1.4298.

Anal. Calcd.: N, 8.70. Found: N, 8.48.

6-Methyl-2-trifluoromethylpyridine had b.p. 154°, *d* 1.2325, and n^{20}_D 1.4278.

Anal. Calcd.: N, 8.70. Found: N, 8.90.

4-Methyl-2-heptafluoropropylpyridine had b.p. 176°, *d* 1.3789, n^{25}_D 1.4040.

Anal. Calcd.: N, 5.36. Found: N, 5.46.

5-Methyl-2-heptafluoropropylpyridine had b.p. 181°, *d* 1.3792, and n^{25}_D 1.3934.

Anal. Calcd.: N, 5.36. Found: N, 5.90.

Isomer Ratios.—The relative amounts of the two isomeric pyridines in the products obtained by the techniques of gas chromatography and confirmed by H^1 magnetic resonance spectroscopy were as follows (for the experiments summarized in Table I).

RCN	Diene	4-CH_3: 5-CH_3 isomer ratio
CF_3CN	Isoprene	2.90:1.0
$CF_3(CF_2)_2CN$	Isoprene	2.52:1.0
$(CN)_2$	Isoprene	1.34:1.0

With pentadiene and CF_3CN, similarly, the ratio of the isomers (6-CH_3: 3-CH_3) in the pyridinic product was thus found to be 4.92:1.0.

Discussion

Inspection shows clearly that there is a correlation with the change in the electrophilic properties of the carbon in the C≡N group; as the electrophilicity of this center increases, there is an increase in the 4-CH_3 isomer in the pyridinic mixtures [*e.g.*, with CF_3CN, 74% 4-methyl-2-trifluoromethylpyridine; with $(CN)_2$, 57% 4-methyl-2-cyanopyridine]. That this is more probably due to the inductive effect rather than a volume factor[4] receives support from the near constancy of the isomer ratios when CF_3CN and $CF_3(CF_2)_2CN$, respectively, cyclize with isoprene. The isomer ratios further are found temperature invariant (400–420°) and independent of reaction time (30–300 min.), *i.e.*, that these are thermally isomerized equilibrium ratios appears improbable. The markedly smaller amounts of the 3-CH_3 isomer in the pentadiene–CF_3CN reaction undoubtedly relates to the influence of the terminal CH_3 of the diene; this may be attributed, in part, to a steric factor with *cis*-pentadiene. Further discussion of the secondary forces must await more detailed studies of the reaction mechanism. The present results underline the need to consider the role of polar structures in any complete account of this high temture gas phase Diels–Alder process.

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