TABLE I

VARIATION OF YIELD OF BUTADIENE WITH Sn:Pt RATIO

Molar ratio, Sn:Pt	Solvent	Temp, °C	Conversion[a] to C_4H_6, %	Yield[b] of C_4H_6, %
2:1	CH_3CN	25	88	88
3:1	DMF	25	82	85
8:3	DMF	25	82	85
4:1	DMF	25	77	89
5:1	DMF	25	55	85
6:1	DMF	25	20	71
7:1	DMF	25	5	31
8:1	DMF	25	0.1	...
30:1	DMF	77	9	48
No $PtCl_2$	DMF	25	0.00	0.00

[a] % conversion = (200) (moles of C_4H_6 formed)/(moles of C_2H_3Cl introduced). [b] % yield = (200) (moles of C_4H_6 formed)/(moles of C_2H_3Cl consumed).

the platinum to $[(SnCl_3)_5Pt]^{3-}$ impedes the coupling reaction. It seems likely, then, that an isomer of $[(SnCl_3)_2PtCl_2]^{2-}$ is somehow involved in the coupling process.

The cage anion $[Sn_8Pt_3Cl_{20}]^{4-}$, which forms readily in acetone,[6] was shown not to be involved in the reductive coupling process. An attempt to effect the reaction in acetonitrile using preformed $[(C_2H_5)_4N]_4[Sn_8Pt_3Cl_{20}]$ with CsF added gave only a 2% conversion to butadiene. Formation of this anion may explain why the reductive coupling does not occur in acetone.

The cocatalytic effect of CsF is not understood; very little of the CsF appears to dissolve in the reaction media. Neither CsCl nor NaF was found to have a cocatalytic effect.

The possibility of coupling other vinylic halides to conjugated dienes by this method was examined. Vinyl fluoride was coupled to butadiene about as readily as was vinyl chloride. Coupling of β-bromostyrene was effected in 25% yield at 140°; α-chlorostyrene gave 2,3-diphenylbutadiene, isolated as the bromine adduct, in 11% yield at 110°.

Coupling of nonvinylic halides by this method was also briefly studied. Allyl chloride was coupled to 1,5-hexadiene in 50% conversion in 72 hr at 25°. Ethyl chloride gave no butane under these conditions.

Experimental Section

Coupling of Vinyl Chloride to Butadiene.—In a 150-ml Kjeldahl flask having a ball joint were placed 1.5 g (5.65 mmoles) of platinous chloride, 4.0 g (0.0113 mole) of tetraethylammonium trichlorostannite, about 5 g of cesium fluoride, 12 ml of dimethylformamide containing 2% water, 0.01 g of hydroquinone, and a magnetic stirring bar. The flask was attached to a vacuum train having a manometer; the total volume was about 240 ml. The system was quickly evacuated to a pressure of about 2 mm, and vinyl chloride (330 ml at 498 mm and 25°, 0.0134 mole) was condensed into the reaction flask. The intensely red reaction mixture was stirred at ambient temperature. The pressure in the system did not change for about 3 hr. It then fell steadily for about 15 hr and more slowly for about 15 hr more. After 40 hr, the product gas mixture was distilled from the solvent. It occupied 330 ml at 246 mm and 25°. Gas chromatography showed this gas to be 98.8% butadiene, 0.5% air, 0.1% diethyl ether, and traces of other gases, including vinyl chloride. Thus, the conversion was 97%. The infrared spectrum of the gas confirmed that this analysis was substantially correct.

(6) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *Inorg. Chem.*, **5**, 109 (1966).

This procedure with appropriate variations was used for all vinyl chloride and vinyl fluoride coupling experiments described above.

Coupling of β-Bromostyrene to *trans,trans*-Bistyrene.—A mixture of 2.0 g (7.5 mmoles) of platinous chloride, 8.0 g (0.0226 mole) of tetraethylammonium trichlorostannite, 8.3 g (0.045 mole) of β-bromostyrene, about 5 g of cesium fluoride, a trace of hydroquinone, and 25 ml of anhydrous dimethylformamide was stirred in a nitrogen atmosphere at 135–140° for 18 hr. The solvent was distilled at 60° and 0.1 mm. The residue was extracted with ether. The extract was concentrated and recrystallized from a mixture of benzene and ethanol to give, in two crops, 1.14 g (25%) of *trans,trans*-bistyrene, mp 151–152°, lit.[7] mp 152.5–153.5°. The nuclear magnetic resonance (nmr) spectrum was consistent with the proposed structure.

Coupling of α-Chlorostyrene.[8]—A similar procedure was used except that the reaction was effected in refluxing propionitrile (bp 97°). An extract of the crude product in chloroform was treated with bromine; recrystallization from a mixture of chloroform and hexane gave 0.60 g (11% over-all) of 1,4-dibromo-2,3-diphenyl-2-butene, mp 144–144.5°, lit.[9] mp 144–147°. The nmr spectrum was consistent with the proposed structure.

Coupling of Allyl Chloride to 1,5-Hexadiene.—Essentially the procedure described above for the coupling of vinyl chloride was used except that the allyl chloride was introduced as a liquid. The reaction mixture was stirred for 72 hr at 25°. Gas chromatography showed that about 50% of the allyl chloride had been converted to 1,5-hexadiene.

Tetraethylammonium Trichlorostannite.[10]—Warm, clear solutions of 22.6 g (0.1 mole) of fresh stannous chloride dihydrate and of 16.6 g of tetraethylammonium chloride in the minimum amounts of 0.5 *N* HCl were thoroughly mixed. The mixture was cooled to 0° to complete crystallization of the product. The product was collected, dried at a pressure of 1 mm, and recrystallized by slow addition of ether to a filtered solution in ethanol to give 23.0 g (65%) of product, mp 78–78.5°. The solid and its solutions decompose slowly in air.

Registry No.—Butadiene, 106-99-0; vinyl chloride, 75-01-4; β-bromostyrene, 103-64-0; *trans,trans*-bistyrene, 538-81-8; α-chlorostyrene, 618-34-8; 1,4-dibromo-2,3-diphenyl-2-butene, 7781-70-6; allyl chloride, 107-05-1; 1,5-hexadiene, 529-42-7; tetraethylammonium trichlorostannite, 7781-71-7.

(7) B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, 229.

(8) Prepared as described by C. Dufraisse and J. E. Viel, *Bull Soc. Chim. France*, **37**, 874 (1925).

(9) C. F. H. Allen, C. G. Eliot, and A. Bell, *Can. J. Chem.*, **17B**, 75 (1939).

(10) This substance was first prepared and characterized by Drs. R. V. Lindsey and U. G. Stolberg in this laboratory.

The Condensation of Azlactones with N-Acylpyridinium Ion

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The γ condensation of N-acylpyridinium ions with carbon nucleophiles has been observed in a number of instances including dimethylaniline,[1] acenaphthenone, acetophenone, and cyclohexanone.[2]

In examining the formation of azlactones from N-formylamino acids by means of acetic anhydride in

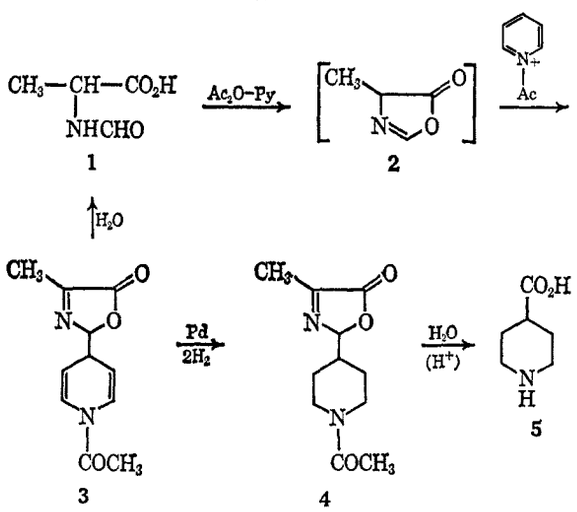
(1) E. Koenigs and E. Ruppelt, *Ann.*, **509**, 142 (1934).

(2) W. von E. Doering, *J. Am. Chem. Soc.*, **73**, 2104 (1951); see also E. Ghigi, *Ber.*, **73**, 677 (1940); **75**, 764 (1942); *Gazz. Chim. Ital.*, **76**, 352 (1946).

pyridine we observed that N-formylalanine (1) produced a yellow, crystalline product, mp 111–112° dec. This compound absorbed in the ultraviolet at 250 mμ (ε 14,000) and exhibited a band in the infrared at 5.65 rather than at 5.55 μ characteristic of the azlactone system. These data as well as the elemental analyses excluded from consideration the possibility of the simple azlactone 2 anticipated. That this substance was a coupled product arising from the anticipated azlactone (2) with N-acetylpyridinium ion became evident on neutral, aqueous hydrolysis. On warming with water the new substance was smoothly cleaved to N-formylalanine (1) isolated as such, together with pyridine identified as its picrate salt, mp 145–150° dec. These findings indicated that the substance at hand most probably had structure **3**, the product of γ coupling of azlactone 2 with N-acetylpyridinium ion. The ultraviolet of the new compound, moreover, with λ_{max} 250 mμ excluded a homoannular diene system that would have arisen from α coupling[3] or alternatively a bond rearrangement product of **3**. Isolated disposition of the double bonds was further supported by the failure of the coupled product to undergo Diels–Alder addition with either maleic anhydride or N-phenylmaleimide.[3] The nmr spectrum in chloroform-*d* provided confirmation of **3** exhibiting the acylmethyl singlet at τ 7.8 and the 4-methyl, seen as a doublet centered at τ 7.75 owing to homoallylic coupling with the 2 proton. The vinyl proton pattern with bands at τ 2.73, 3.45, and 5.05 also closely paralleled that reported for 1,1′-diacetyl-1,1′,4,4′-tetrahydro-4,4′-bipyridyl.[4]

Final proof of the point of attachment of the azlactone moiety at the γ position of the pyridine ring was provided by hydrogenation of **3** to the tetrahydro system (**4**), mp 125–127°, followed by acid hydrolysis to piperidine-4-carboxylic acid (**5**). The formation of

SCHEME I



2-[4-(1-acetyl-1,4-dihydropyridinyl)]-3-oxazolin-5-ones may be a general reaction for simple N-formylamino acids. Although with N-formylphenylalanine, N-formylglycine, and N-formyltryptophane, noncrystalline products are produced which are correspondingly unstable, nonetheless spectroscopically they conform in large measure to the characteristics determined in the case of **3**.

Experimental Section

2-[4-(1-Acetyl-1,4-dihydropyridinyl)]-3-oxazolin-5-one (3).—A 5-g sample of N-formylalanine was dissolved in 20 cc of pyridine, treated with an equal volume of acetic anhydride, and allowed to stand for 24 hr at room temperature. At the end of this period the solvents were evaporated *in vacuo* and the residue was crystallized from acetone–ether to give **3** as yellow needles: mp 110–112°, wt 1.6 g, $\lambda_{max}^{CH_3OH}$ 250 mμ (ε 14,000); $\lambda_{max}^{CHCl_3}$ 5.65 μ.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.95; H, 5.49; N, 12.71. Found: C, 60.10; H, 5.48; N, 12.67.

An additional 0.60 g of **3** was obtained from the mother liquors of crystallization by chromatography on silica gel. Elution was effected with ethyl acetate.

2-[4-(1-Acetylpiperidyl)]-3-oxazolin-5-one (4).—A solution of 500 mg of **3** in 25 cc of ethyl acetate was slurried with 150 mg of 5% rhodium-on-alumina catalyst and filtered. The filtrate was subsequently treated with 250 mg of the same catalyst and hydrogenated. The hydrogen uptake was 2 mole equiv. The reaction mixture was filtered, concentrated, and crystallized from acetone–ether to give 340 mg of **4**: ultraviolet showed no maximum; $\lambda_{max}^{CHCl_3}$ 5.65 μ.

Anal. Calcd for $C_{11}H_{16}N_2O_3$: C, 58.90; H, 7.18; N, 12.47. Found: C, 59.18; H, 7.13; N, 12.86.

Hydrolysis of 4 to Piperidine-4-carboxylic Acid 5.—A 100-mg sample of the hydrogenation product (**4**) in 3 cc of water was treated with potassium bicarbonate until a pH of 8–9 was maintained. The reaction mixture was warmed briefly on the steam bath and then allowed to stand at room temperature for 30 min. At the end of this time the reaction mixture was concentrated to dryness *in vacuo* followed by treatment with 5 cc of 50% aqueous hydrochloric acid and refluxing for 1 hr. The hydrolysate was diluted with water and extracted with chloroform followed by ether. The aqueous layer was evaporated *in vacuo* and the residue was extracted with hot alcohol. The alcohol extract was concentrated to a gum which was redissolved in isopropyl alcohol. Addition of acetone to the isopropyl alcohol solution deposited solid material that was separated and recrystallized to give alanine hydrochloride. The isopropyl alcohol filtrate was concentrated to yield 10–15 mg of piperidine-4-carboxylic acid hydrochloride, mp 255–265° dec. The infrared of this material was identical with that of an authentic specimen.

Registry No.—**3**, 10036-55-2; **4**, 10036-56-3; piperidene-4-carboxylic acid hydrochloride, 5984-56-5.

(3) M. Saunders and E. Gold, *J. Org. Chem.*, **27**, 1439 (1962).
(4) A. T. Nielsen, D. W. Moore, G. M. Muha, and K. H. Berry, *ibid.*, **29**, 2175 (1964).

The Acylation of Cyclooctene and 1,5-Cyclooctadiene

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The stannic chloride catalyzed reaction of cyclooctene with acetyl chloride was found by Ruzicka to yield 1-acetylcyclooctene as the major product.[1] Later Jones, Taylor, and Rudd reported that addition of cyclooctene to the aluminum chloride–acetyl chloride complex in methylene chloride at −15° gave 1-acetylcyclooctene in 48% yield.[2] Nenitzescu and co-workers have reported that acetylation of cyclooctene in iso-

(1) L. Ruzicka and H. A. Boekenhoogen, *Helv. Chim. Acta*, **14**, 1319 (1931).
(2) N. Jones, H. T. Taylor, and E. Rudd, *J. Chem. Soc.*, 1342 (1961).