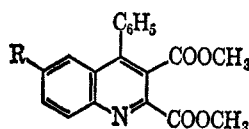


TABLE I
DIMETHYL 4-PHENYLACRIDINATES



R	Registry no.	Yield, %	Mp, °C	Formula	Anal., %					
					Calcd			Found		
					C	H	N	C	H	N
H	10039-67-5	76	129-130	C ₁₉ H ₁₅ NO ₄	71.02	4.71	4.36	70.76	4.86	4.40
Cl	10037-28-2	78	162.5-163	C ₁₉ H ₁₄ NO ₄ Cl	64.14	3.97	3.94	64.17	4.32	3.77
Br	10037-29-3	70	169.5-170.5	C ₁₉ H ₁₄ NO ₄ Br	57.01	3.53	3.50	56.79	3.09	3.58
NO ₂	10037-30-6	14	149-150	C ₁₉ H ₁₄ N ₂ O ₆	62.30	3.86	7.64	61.79	3.90	7.25

solution was filtered hot. Addition of cold hexane to the filtrate resulted in precipitation of 1.1 g (77%) of white flakes. The analytical sample, mp 97.5-99°, was prepared by recrystallization from benzene-hexane (1:1).

Anal. Calcd for C₁₄H₁₃NO₄: C, 64.86; H, 5.06; N, 5.40. Found: C, 64.60; H, 5.13; N, 5.29.

The nmr spectrum (CCl₄) showed the 4-methyl protons as a singlet at 2.67, the two ester methyl groups as singlets at 3.92 and 3.98, and the aromatic protons as a multiplet at 7.4-8.2 ppm (ratio 3:3:3:4).

8-Acetyl-2-carbomethoxy-4(1H)-quinolone was prepared from the above enamine adduct by fusion of 2.78 g in a test tube, followed by boiling of the melt for 5 min. The residual red oil was cooled, taken up in a minimum of hot methanol, and cooled to give 1.27 g of pink crystals. These were sublimed *in vacuo* to give 1.21 g (49%) of yellow crystals, mp 176-177°.

Anal. Calcd for C₁₃H₁₁NO₄: C, 63.66; H, 4.52; N, 5.71. Found: C, 63.75; H, 4.33; N, 5.62.

The nmr spectrum (DCCl₃) showed the acetyl methyl protons as a singlet at 2.80, the ester methyl protons as a singlet at 4.08, an aromatic multiplet at 7.2-8.6, the C-3 aromatic proton as a doublet (*J* = 2 cps, split by the N-H proton) at 6.92, and the N-H proton as a broad signal at 12.86 ppm (ratio 3:3:3:1:1).

2-Amino-5-bromobenzophenone was prepared from 5-bromo-isatoic anhydride,¹¹ benzene, and aluminum chloride according to the method described for the preparation of 2-aminobenzophenone.¹² Recrystallization of the crude product first from ethanol and then from petroleum ether (bp 30-60°)-benzene (1:1) gave the desired product in 21% yield, mp 109-110° (lit.¹³ mp 110°).

Registry No.—Dimethyl 4-methylacridinate, 10037-31-7; 8-acetyl-2-carbomethoxy-4(1H)-quinolone, 10037-32-8; enamine adduct, 10037-33-9.

(11) R. Adams and H. R. Snyder, *J. Am. Chem. Soc.*, **60**, 1411 (1938).

(12) F. S. Statham, *J. Chem. Soc.*, 213 (1951).

(13) J. F. J. Dippy and V. Moss, *ibid.*, 2205 (1952).

Butadiene from Vinyl Chloride. The Platinum(II)-Catalyzed Coupling of Vinyl Halides

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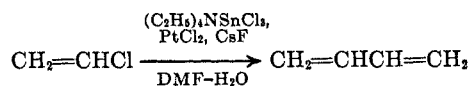
Vinyl halides having β hydrogens generally undergo β elimination to acetylenes in preference to coupling to conjugated dienes under Wurtz reaction conditions.^{1,2}

(1) A. Kirrmann and C. Moureu, *Compt. rend.*, **181**, 671 (1925).

(2) C. Prevost and C. Moureu, *ibid.*, **184**, 1460 (1927).

No method of converting vinyl halides to butadiene has been described.

We have found that reductive coupling of vinyl chloride to butadiene is effected at 25° by Sn(II) in solutions containing catalytic amounts of PtCl₂. The reaction is cocatalyzed by cesium fluoride. Under the best conditions, conversion to butadiene is nearly quantitative.



The coupling reaction is best performed by stirring a mixture of 2 molar equiv of (C₂H₅)₄NSnCl₂, 1 equiv of PtCl₂, and CsF in dimethylformamide (DMF) containing 2% water under an atmosphere of vinyl chloride. When (C₂H₅)₄NSnCl₂ is used in excess, the yield is 97% based on vinyl chloride in 40 hr at 25°. When water is omitted from the solvent, the reaction is slightly faster, but side reactions limit the yield of 85-90%. When CsF is omitted, the reaction is slow, being only 8% complete in 18 hr and 40% complete in 600 hr.

Besides DMF, the reaction can also be performed in acetonitrile or dimethyl sulfoxide (DMSO). The reaction is about as fast in acetonitrile as in DMF, but the latter is convenient because of its lower volatility. The reaction is slower in DMSO. Little or no coupling occurs when the solvent is ethanol, acetone, pyridine, or water. When tin(II) is introduced as stannous chloride dihydrate or as lithium trichlorostannite, yields are inferior.

A series of experiments was performed in which the Sn:Pt ratio was varied by changing the amount of PtCl₂ used. Cesium fluoride but not water was added to the reaction mixtures; the reactions were stopped after 18 hr at 25°. The conversions and yields are given in Table I. It is seen that the conversion to butadiene falls rapidly as the Sn:Pt ratio is increased above 5:1.

Mixtures of Pt(II) and Sn(II) chlorides in non-aqueous media are known to form intensely colored, labile coordination compounds in which the SnCl₃⁻ anion acts as a donor ligand. Salts of the [(SnCl₃)₂-PtCl₂]²⁻ and [(SnCl₃)₅Pt]³⁻ anions have been isolated from such solutions.³⁻⁵ The intensely red solutions in which the reductive coupling reaction occurs almost certainly contain substantial amounts of these species. The data in Table I indicate that conversion of most of

(3) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(4) A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963).

(5) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

TABLE I
VARIATION OF YIELD OF BUTADIENE WITH SN:PT RATIO

Molar ratio, Sn:Pt	Solvent	Temp, °C	Conversion ^a to C ₄ H ₆ , %	Yield ^b of C ₄ H ₆ , %
2:1	CH ₃ CN	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 C₄H₆ formed)/(moles of C₂H₃Cl introduced). ^b % yield = (200) (moles of C₄H₆ formed)/(moles of C₂H₃Cl consumed).

the platinum to [(SnCl₃)₅Pt]³⁻ impedes the coupling reaction. It seems likely, then, that an isomer of [(SnCl₃)₂PtCl₂]²⁻ is somehow involved in the coupling process.

The cage anion [Sn₃Pt₃Cl₂₀]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 [(C₂H₅)₄N]₄[Sn₃Pt₃Cl₂₀] 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 platinumous 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 platinumous 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).