a modified Dean–Stark water separator. The mixture was poured into 10% sodium carbonate solution and the benzene layer separated. The aqueous layer was extracted several times with benzene. The combined benzene layers were washed with water and dried over sodium sulfate. The solvent was removed leaving 6.5 g of oil, presumably 2-(2-benzyl[1.3]dioxolan-2-yl)pyridine. To the crude product was added 4.3 g of benzyl bromide and 2 ml of tetramethylenesulfone. The mixture was kept at 50° for 4 days and the resulting viscous oil was washed with ethyl acetate and placed in 110 g of polyphosphoric acid. The mixture was heated at 115° for 12 hr, then poured on 110 g of ice. When the ice had melted, 100 ml of water was added and the mixture was heated on a steam bath for 4 hr. The solution was treated with charcoal and after cooling 25% perchloric acid was added until precipitation was complete. The gray-green precipitate was collected and recrystallized (charcoal) twice from absolute ethanol to yield 0.66 (5%) of yellow-green crystals, mp 215–223°. An analytical sample melted at 218–223°; the λ_{max} signals were at 242 mμ (log ε 4.45), 250 (4.46), 366 (3.82), 382 (3.83), 404 (3.78).

Anal. Calcd for $C_{20}H_{16}ClNO_4$: C, 64.95; H, 4.36; N, 3.79. Found: C, 64.86; H, 4.41; N, 3.90.

7,13-Dihydrobenz[*h*]acridizinium (12) Bromide.—The reduction of benz[*h*]acridizinium bromide[10] was carried out in 37% yield essentially as in the hydrogenation of acridizinium bromide. The product was colorless: mp 240–258°; λ_{max} 267 mμ (log ε 4.04); nmr (D_2O), δ 4.28 (S, 2, CH_2, C-7), 5.40 (S, 2, CH_2, C-13).

Anal. Calcd for $C_{17}H_{14}BrN$: C, 65.40; H, 4.52; N, 4.49. Found: C, 65.12; H, 4.50; N, 4.44.

The **perchlorate** had mp 167.5–171°.

Anal. Calcd for $C_{17}H_{14}ClNO_4$: C, 61.54; H, 4.25; N, 4.22. Found: C, 61.31; H, 4.19; N, 4.19.

Registry No.—**1,** X = Br, 15757-24-1; **1,** X = ClO_4, 15815-87-9; **2,** X = Br, 15757-25-2; **2,** X = ClO_4, 15815-88-0; **3,** X = ClO_4, 15815-89-1; **4,** X = Br, 15757-26-3; **4,** X = ClO_4, 15815-90-4; **5,** X = Br, 15757-27-4; **5,** X = ClO_4, 15892-89-4; **6,** X = Br, 15757-28-5; **7,** X = ClO_4, 15815-91-5; **8,** 260-61-7; **9,** 15815-92-6; **12,** X = Br, 15757-29-6; **12,** X = ClO_4, 15815-93-7; 11-benzylacridizinium perchlorate, 15815-94-8.

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Alkylation of Alkali Metal Salts of Pyrrole with Allyl and *n*-Propyl Tosylate

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In the course of a study of the factors affecting the position of alkylation of ambident anions, the reaction of alkali metal salts of pyrrole with allyl tosylate was investigated to evaluate the effectiveness of the latter as an alkylating agent.

TABLE I

REACTIONS OF PYRROLYLMETAL SALTS WITH ALLYL TOSYLATE AND ALLYL BROMIDE AT 65°

		Relative %					
		1-Allyl-pyrrole		2-Allyl-pyrrole		3-Allyl-pyrrole	
Cation	Solvent	*a*	*b*	*a*	*b*	*a*	*b*
K⁺	Dimethyl sulfoxide	99	89	0.50	8.0	0.50	3.0
K⁺	Tetrahydrofuran	86	80	11	18	3.0	2.0
K⁺	Benzene	66	14	25	80	9.0	6.0
Na⁺	Tetrahydrofuran	30	19	54	77	16	4.0
Na⁺	Tetrahydrofuran (inverse addition)	72	36	22	58	6.0	6.0
Li⁺	Tetrahydrofuran	24	1.0	59	90	17	9.0

[a] Reaction with allyl tosylate. [b] Reaction with allyl bromide (see ref 1 and 11).

The product of this reaction was a mixture of the isomeric allylpyrroles and higher boiling compounds which are presumed to be diallylpyrroles. In general, the composition of the product paralleled the one observed earlier in the reaction of alkali metal salts of pyrrole with allyl bromide.[1] In the present work, however, the N/C alkylation ratios, expressed in terms of the relative percentages of 1-, 2-, and 3-allylpyrrole, were considerably higher (Table I). It should be noted that the actual amount of carbon alkylation is higher than these numbers indicate, because of the further reaction of part of the initially formed 2- and 3-allylpyrrole to yield diallylpyrroles.[1,2] Nonetheless, there is a significant difference in selectivity between the two alkylating reagents allyl tosylate and allyl bromide.

The effect of the leaving group on the position of alkylation of ambident anions has been studied in relatively few cases and seems to vary. Thus, a change in the leaving group from Cl^- to Br^- to I^- has been reported to have no effect on product composition in the reaction of the sodium salt of 2,6-dimethylphenol with allyl and benzyl halides.[3] Similarly, no effect has been observed in the reaction of the lithium salt of 2-nitropropane with benzyl halides in dimethylformamide.[4] On the other hand, the same change in the leaving group has been found to decrease the yield of O-alkylated product in the reaction of the potassium, or sodium salt of ethyl acetoacetate with alkyl halides in dimethylformamide,[5] or dimethyl sulfoxide,[6] and in the reaction of the sodium salt of 2-carbethoxycoumaran-3-one with benzyl and *m*-nitrobenzyl halides in dimethylformamide.[7] In the same way, a change from Br^- to I^- causes a decrease in N alkylation in the reaction of the sodium salt of indole with alkyl halides.[2]

Tables I and II show that a change to more polar solvents increased the N/C alkylation ratio in the reaction of pyrrolylpotassium with allyl tosylate. This trend is in agreement with previous observations that aprotic solvents of higher ability to solvate cations favor

TABLE II

EFFECT OF TEMPERATURE ON THE REACTION OF PYRROLYLPOTASSIUM WITH ALLYL TOSYLATE

		Relative %		
Solvent	Temp, °C	1-Allyl-pyrrole	2-Allyl-pyrrole	3-Allyl-pyrrole
Dioxane	50	82	13	5.0
Dioxane	75	86	11	3.0
Dioxane	100	89	9.0	2.0
Toluene	50	47	37	16
Toluene	75	53	33	14
Toluene	100	62	25	13

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substitution at the more electronegative atom of the ambident anion.[1-3,8,9]

In the case of pyrrolylsodium, which is readily soluble in tetrahydrofuran, slow addition of a solution of the salt to a solution of the alkylating agent (inverse addition) increased markedly the relative amount of N-alkylated product in the present reaction with allyl tosylate, just as in the previously reported reaction with allyl bromide.[1]

When reactions were run in the same solvent (Table I, tetrahydrofuran), the position of substitution of the pyrrolyl anion was affected by the nature of the cation, in agreement with the findings that in aprotic solvents of low dielectric constant the proportion of alkylation at the more electronegative atom of the ambident anion increases as the cation is changed from Li^+ to Na^+ to K^+.[1,3,8,9] In this connection the fact should be noted that pyrrolylmagnesium halides are alkylated almost exclusively on carbon.[10]

Table II shows that in the treatment of pyrrolylpotassium with allyl tosylate an increase in the reaction temperature caused a small (dioxane) to moderate (toluene) increase of the relative percentage of N alkylation. The effect of temperature on the position of alkylation of ambident anions is not uniform. There was no clear-cut effect in the reaction of pyrrolylpotassium with allyl bromide,[11] but increased C alkylation was observed at a higher temperature with crotyl and benzyl halides.[1] A temperature increase has been reported to favor O alkylation of sodio-2-carbethoxycyclanones with isopropyl iodide in dimethyl sulfoxide,[12] O alkylation of ethyl acetoacetate with *n*-butyl chloride, and potassium carbonate in dimethyl sulfoxide, but C alkylation when the last reaction is run in N-methylpyrrolidine.[5]

The higher relative percentage of N-alkylated product generally obtained when *n*-propyl tosylate was substituted for allyl tosylate as the alkylating agent (Table III) is consistent with the greater selectivity of saturated alkyl halides, compared with allyl halides, in alkylating pyrrolylmetal salts[1] and indolylsodium[2] predominantly on the nitrogen atom, and salts of phenols,[3] or ethyl acetoacetate[6] predominantly on the oxygen atom. The effect of the cation on product composition is again significant in this case (Table III), as in the case with allyl tosylate (Table I).

TABLE III

REACTIONS OF PYRROLYLMETAL SALTS WITH *n*-PROPYL TOSYLATE AT 65°

		Relative %		
Cation	Solvent	1-*n*-Propylpyrrole	2-*n*-Propylpyrrole	3-*n*-Propylpyrrole
K^+	Tetrahydrofuran	97	2.5	0.50
K^+	Benzene	95	4.0	1.0
Na^+	Tetrahydrofuran	65	32	3.0
Li^+	Tetrahydrofuran	25	70	5.0

Experimental Section

The reactions were run under nitrogen at 65° for 8 hr, and the products were analyzed by gas-liquid partition chromatography. A 275-cm column packed with Chromosorb W 60/80, containing 20% silicone oil was used in a model 154 Perkin-Elmer vapor fractometer with helium as the carrier gas. Bromobenzene was the internal standard, and the peak areas were measured with a planimeter.

Procedure.—To a solution of 0.25 mol of pyrrole in 100 ml of dry solvent,[13] 0.20 g-atom of potassium[14] was added and the mixture was refluxed with stirring until completion of the reaction. After addition of 100 ml of solvent, the temperature was adjusted to the desired value, and 0.20 mol of the alkyl tosylate,[15] dissolved in 100 ml of solvent, was added dropwise over a period of 1 hr.[16] The reaction mixture was stirred at constant temperature for a further 8 hr; then it was cooled to room temperature and filtered. After the solid material had been washed with ether, it was dissolved in 100 ml of water, and the aqueous solution was extracted with ether. The combined filtrate, ether washings, and extracts were then dried over anhydrous magnesium sulfate. After removal of the solvents by distillation under reduced pressure, the residue was analyzed by gas-liquid partition chromatography.

Registry No.—Allyl tosylate, 4873-09-0; *n*-propyl tosylate, 599-91-7; pyrrolylpotassium, 16199-06-7.

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[14] Sodium hydride and lithium hydride were used for the preparation of the corresponding salts of pyrrole.

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The Benzene–Resorcinol–Phthaleinanhydride of v. Pechmann

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On heating *o*-benzoylbenzoic acid with resorcinol in sulfuric–acetic acid, v. Pechmann[1] obtained a compound of unestablished structure which he named benzene–resorcinol–phthaleinanhydride. This same compound (I) also resulted from the reaction of *o*-benzoylbenzoic acid with resorcinol in the presence of anhydrous zinc chloride.[2]

In this Note it is shown that I can also be obtained in high yields from 2 mol of *o*-benzoylbenzoyl chloride (II) and 1 mol of resorcinol by the method of Blicke[3] and in 94% yield and high purity in the reaction of equimolar quantities of II with 3-phenyl-3-(2,4-dihydroxyphenyl)-phthalide (III).

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