α-(Halomethyl)pyrroles as Alkylating Agents. A Study of the Alkylation of Methylbenzenes[1,2]

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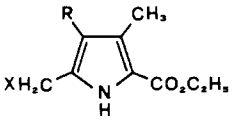
Due to the ease of their preparation[3,4] and to their high reactivity[5,6] α-(chloromethyl)- and α-(bromomethyl)-pyrroles are valuable intermediates for the synthesis of a number of pyrrole derivatives with functionalized α side chains. They have also been extensively used in alkylation reactions leading to dipyrrylmethanes,[7] dipyrrylmethenes,[8] and more complex polypyrrolic systems derived therefrom. Apart from a few papers dealing with the mechanism of dipyrrylmethane[9] and dipyrrylmethene[10] formation, detailed physical organic studies on these alkylation reactions are lacking. Furthermore, it does not seem that α-(halomethyl)pyrroles have ever been used for alkylating benzenoid substrates.

We now report on an investigation of the reaction of some α-(bromomethyl)- (**1–3**) and α-(chloromethyl)pyrroles (**4, 5**) with benzene derivatives in the absence of any added



1: X = Br, R = Cl
2: X = Br, R = Br
3: X = Br, R = $CO_2C_2H_5$
4: X = Cl, R = Br
5: X = Cl, R = $CO_2C_2H_5$
6: X = OH, R = $CO_2C_2H_5$
7: X = OH, R = Br
10: X = p-xylyl, R = $CO_2C_2H_5$
11: X = duryl, R = $CO_2C_2H_5$

alkylation catalyst. In order to avoid the formation of isomers, benzene and symmetrically substituted methylbenzenes (*p*-xylene and durene) were chosen as substrates. The structural features of the pyrrole derivatives were selected in such a way as to allow the study of the effect of the leaving halogen and the role, if any, of the β-R group on the course of the reaction.

Experimental Section

General Methods. Melting points are uncorrected. Unless otherwise stated, ^1H NMR spectra were obtained in $CDCl_3$ solution (internal standard tetramethylsilane) on a JEOL JNM-C60 HL apparatus. Thin-layer chromatographic (TLC) analyses were carried out on Merck F_{254} silica plates with 9:1 benzene–ethyl acetate as the eluent. Gas–liquid chromatographic analyses were performed on a Carlo Erba Fractovap Gl instrument equipped with a flame-ionization detector and connected to a Hewlett-Packard 18850 A integrator. The carrier gas was N_2. Microanalyses were performed at the Laboratorio di Microanalisi of the Istituto Superiore di Sanità, Roma.

Materials. Benzene and *p*-xylene (reagent grade) were purified and dried as usual and stored over sodium wire. For use in kinetic experiments, *p*-xylene was freshly distilled from sodium shortly before each experiment. Its isomeric purity was checked by GLC by using a 2-m Carbopack (100–200 mesh) column with 0.34% of tetranitrofluorene at 180 °C.[11] Durene was recrystallized from aqueous ethanol to a constant melting point. Ethyl 4-bromo-5-(bromomethyl)-3-methylpyrrole-2-carboxylate (**2**),[12] diethyl 5-(bromomethyl)-3-methylpyrrole-2,4-dicarboxylate (**3**),[13] and diethyl 5-(chloromethyl)-3-methylpyrrole-2,4-dicarboxylate (**5**)[14] were prepared and purified as described in the references given. Their structures were confirmed by ^1H NMR and their purity checked by quantitative determination[15] of the halide ion formed upon treatment with ethanolic sodium ethoxide. Diethyl 5-(hydroxymethyl)-3-methylpyrrole-2,4-dicarboxylate (**6**) was obtained in quantitative yield by hydrolysis of **5** in aqueous dioxane according to Corwin et al.;[14] mp 118–119 °C (lit.[14] mp 120–121 °C). 3,3′,5,5′-Tetrakis(ethoxycarbonyl)-4,4′-dimethyl-2,2′-dipyrrylmethane was prepared by melting **6** with $KHSO_4$;[14] mp 133–134 °C (lit.[14] mp 135 °C).

Ethyl 5-(Bromomethyl)-4-chloro-3-methylpyrrole-2-carboxylate (1). To a solution of ethyl 4-chloro-3,5-dimethylpyrrole-2-carboxylate[16] (0.135 g, 0.67 mmol) in 10 mL of CCl_4 was added 1.5 mL of a 0.5 M solution of bromine in the same solvent dropwise with stirring under nitrogen. After 1 h, a white solid began to separate. Stirring was continued until the evolution of hydrogen bromide had ended. The precipitate was collected, thoroughly washed with cold CCl_4, and recrystallized from CCl_4–petroleum ether (bp 40–70 °C): mp 140–141 °C; yield 0.14 g (74%). Upon evaporation of the filtrate, 0.03 g (22%) of starting material was recovered: ^1H NMR δ 1.42 (t, 3 H, $CO_2CH_2CH_3$), 2.27 (s, 3 H, CH_3), 4.44 (q, 2 H, $CO_2CH_2CH_3$), 4.52 (s, 2 H, CH_2Br), 9.9 (br s, 1 H, NH). Anal. Calcd for $C_9H_{11}BrClNO_2$: C, 38.52; H, 3.95; Br, 28.48; N, 4.99. Found: C, 37.98; H, 3.93; Br, 28.61; N, 4.98.

Ethyl 4-Bromo-5-(chloromethyl)-3-methylpyrrole-2-carboxylate (4). To a well-stirred suspension of ethyl 4-bromo-3,5-dimethylpyrrole-2-carboxylate[12] (0.48 g, 1.96 mmol) in 5 mL of dry ether was added freshly distilled SO_2Cl_2 (0.26 g, 1.95 mmol) dropwise at room temperature. The mixture became homogeneous, and shortly thereafter a white precipitate started to form. This was collected, washed with cold CCl_4, and recrystallized from the same solvent: mp 151 °C dec; yield 70%; ^1H NMR δ 1.38 (t, 3 H, $CO_2CH_2CH_3$), 2.30 (s, 3 H, CH_3), 4.34 (q, 2 H, $CO_2CH_2CH_3$), 4.61 (s, 2 H, CH_2Cl), 9.5 (br s, 1 H, NH). Anal. Calcd for $C_9H_{11}BrClNO_2$: C, 38.52; H, 3.95; Cl, 12.63; N, 4.99. Found: C, 38.29; H, 3.90; Cl, 12.80; N, 5.12.

Ethyl 4-Bromo-5-(hydroxymethyl)-3-methylpyrrole-2-carboxylate (7). A solution of **4** (0.25 g, 1.02 mmol) in 10 mL of peroxide-free dioxane, to which 0.2 mL of water had been added, was refluxed for 30 min. Any volatile material was then stripped off in vacuo and the crude product recrystallized from aqueous dioxane: yield 0.18 g (68%); mp 165 °C dec; ^1H NMR δ 1.35 (t, 3 H, $CO_2CH_2CH_3$), 2.25 (s, 3 H, CH_3), 4.03 (s, 2 H, CH_2OH), 4.16 (q, 2 H, $CO_2CH_2CH_3$), 10.3 (br s, 1 H, NH). Anal. Calcd for $C_9H_{12}BrNO_3$: C, 41.24; H, 4.61; Br, 30.49; N, 5.34. Found: C, 41.33; H, 4.55; Br, 30.35; N, 5.30.

Diethyl 5-Benzyl-3-methylpyrrole-2,4-dicarboxylate (8). To a stirred solution of 21 mmol of ethyl 2-(hydroxyimino)-3-oxobutanoate[17] and 6.62 g (21 mmol) of ethyl 3-oxo-4-phenyl-

(1) Dedicated to Professor Gabriello Illuminati on the occasion of his 60th birthday.
(2) Presented by A. Monaci at the 8th International Congress of Heterocyclic Chemistry, Graz, Austria, Aug 23–28, 1981.
(3) Gossauer, A. "Die Chemie der Pyrrole"; Springer-Verlag: West Berlin, 1974; p 327 ff.
(4) Jones, A. R.; Bean, G. P. "The Chemistry of Pyrroles"; Academic Press: London, 1977; p 353.
(5) Reference 3, pp 113, 265, 290, 331.
(6) Reference 4, pp 225, 349 ff.
(7) Fischer, H.; Orth, H. "Die Chemie des Pyrrols"; Akademische Verlagsgesellschaft: Leipzig, 1934; Vol I, p 331. Reference 3, p 112. Reference 4, p 149.
(8) Fischer, H.; Orth, H. "Die Chemie des Pyrrols"; Akademische Verlagsgesellschaft: Leipzig, 1937; Vol II, p 62. Reference 3, p 328. Reference 4, p 354.
(9) Melenteva, T. A.; Kazanskaya, L. V.; Berezovskii, V. M. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 1132. Kazanskaya, L. V.; Melenteva, T. A.; Berezovskii, V. M. *Zh. Obshch. Khim.* **1972**, *42*, 2523.
(10) Rattini, G. A.; Sleiter, G. *Justus Liebigs Ann. Chem.* **1975**, 1977.
(11) Di Corcia, A.; Liberti, A.; Samperi, R. *J. Chromatogr.* **1976**, *122*, 458.
(12) Fischer, H.; Ernst, P. *Justus Liebigs Ann. Chem.* **1926**, *447*, 139.
(13) Fischer, H.; Scheyer, H. *Justus Liebigs Ann. Chem.* **1923**, *434*, 237.
(14) Corwin, A. H.; Bailey, W. A.; Viohl, P. *J. Am. Chem. Soc.* **1942**, *64*, 1267.
(15) Angelini, G.; Illuminati, G.; Monaci, A.; Sleiter, G.; Speranza, M. *J. Am. Chem. Soc.* **1980**, *102*, 1377.
(16) Angelini, G.; Sleiter, G. *Gazz. Chim. Ital.* **1975**, *105*, 961.

0022-3263/82/1947-5217$01.25/0

Table I. Outcome of the Reaction of the α-(Halomethyl)pyrroles 1–5 with Benzene (B), p-Xylene (Xy), and Durene (D)[a]

pyrrole	R	X	ArH	reaction time, h	result
1	Cl	Br	B	24	no reaction
			Xy	24	*b*
2	Br	Br	B	24	no reaction
			Xy	22	*b*
3	CO_2Et	Br	B	24	no reaction
			Xy	144	40% **10**[c]
4	Br	Cl	B	24	no reaction
			Xy	68[d]	*e*
5	CO_2Et	Cl	B	24	no reaction
			Xy	3	100% **10**
			D[f]	24	99.6% **11**

[a] Experiments were performed in the dark at reflux temperature unless otherwise noted. [b] Complex reaction mixture, which contained only a trace (≤1%) of the p-xylyl derivative (GLC). [c] Pyrrole **10** was accompanied (TLC and comparison with authentic specimens) by diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate and 3,3′,5,5′-tetrakis(ethoxycarbonyl)-4,4′-dimethyl-2,2′-dipyrrylmethane. [d] At 94.3 °C. [e] Complex reaction mixture, which contained (^{1}H NMR and GLC) only a trace (≤1%) of the p-xylyl derivative, along with dipyrrylmethane **9** (12%), (hydroxymethyl)pyrrole **7** (1.7%), and other unidentified products. [f] In isooctane.

butanoate[18] in aqueous acetic acid was added zinc dust (2.75 g, 42 mmol) portionwise at such a rate as to keep the mixture refluxing gently. After the addition was complete, heating was continued for a further 90 min, and then the solution was decanted, while hot, from the excess of zinc into ca. 200 mL of ice-cold water. A gummy precipitate formed. After the mixture was allowed to stand 5 h, the liquid was decanted off and the precipitate taken up in ether. The ether solution was washed with water, aqueous $NaHCO_3$, and again with water and dried (anhydrous Na_2SO_4). Upon removal of the solvent, 2.32 g (35%) of **8** as snow-white scales was obtained, melting at 101–102 °C after recrystallization from aqueous ethanol: ^{1}H NMR (CCl_4) δ 1.30 (t, 6 H, α- and β-$CO_2CH_2CH_3$), 2.41 (s, 3 H, CH_3), 4.14 (q, 2 H, β-$CO_2CH_2CH_3$), 4.18 (q, 2 H, α-$CO_2CH_2CH_3$), 4.24 (s, 2 H, CH_2Ph), 7.14 (m, 5 H, C_6H_5), 9.4 (br s, 1 H, NH). Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.38; H, 6.87; N, 4.30.

3,3′-Dibromo-5,5′-bis(ethoxycarbonyl)-4,4′-dimethyl-2,2′-dipyrrylmethane (9). A mixture of **7** (0.26 g, 1 mmol) and powdered $KHSO_4$ was heated at 130–140 °C for ca. 40 min. The product, which was obtained by extracting the melt with boiling ethanol, melted at 175 °C dec after recrystallization from aqueous ethanol: yield 76%; ^{1}H NMR δ 1.25 (t, 6 H, 2 $CO_2CH_2CH_3$), 2.2 (s, 6 H, 2 CH_3), 4.03 (s, 2 H, CH_2), 4.07 (q, 4 H, 2 $CO_2CH_2CH_3$), 10.6 (br s, 2 H, 2 NH). Anal. Calcd for $C_{17}H_{20}Br_2N_2O_4$: C, 42.88; H, 4.23; Br, 33.56; N, 5.88. Found: C, 42.97; H, 4.11; Br, 33.68; N, 5.82.

Alkylation Experiments. These were performed by simply refluxing the α-(halomethyl)pyrrole in neat benzene or p-xylene for the time indicated in Table I. When durene was the substrate, a concentrated solution in dry isooctane was used. Due to the sensitivity of the α-(halomethyl)pyrroles both to light and to oxidation processes, all the experiments were carried out in the dark and under a dry nitrogen atmosphere. After the time stated in Table I had elapsed, any volatile material was removed in vacuo and the residue examined by both ^{1}H NMR and chromatographic techniques. Results are presented in Table I.

The following α-(arylmethyl)pyrroles were isolated and characterized.

Diethyl 3-methyl-5-(p-xylylmethyl)pyrrole-2,4-dicarboxylate (10): white crystals (from aqueous ethanol) melting at 110–111 °C; ^{1}H NMR δ 1.31 (t, 3 H, $CO_2CH_2CH_3$), 1.35 (t, 3 H, $CO_2CH_2CH_3$), 2.15 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 4.26 (s plus q, 4 H, p-xylyl CH_2 and $CO_2CH_2CH_3$), 4.31 (q, 2 H, $CO_2CH_2CH_3$), 6.89 (m, 2 H, arom), 7.04 (m, 2 H, arom), 8.4 (br s, 1 H, NH). Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.94; H, 7.28; N, 4.07. Found: C, 69.87; H, 7.20; N, 3.97.

Diethyl 3-methyl-5-(durylmethyl)pyrrole-2,4-dicarboxylate (11) was obtained from 0.6 g (2.19 mmol) of **5** and 7 g (52.3 mmol) of durene in 80 mL of isooctane: mp 99–100 °C (aqueous methanol); ^{1}H NMR δ 1.30 (t, 3 H, $CO_2CH_2CH_3$), 1.41 (t, 3 H, $CO_2CH_2CH_3$), 2.08 (s, 6 H, 2 CH_3), 2.24 (s, 6 H, 2 CH_3), 2.52 (s, 3 H, CH_3), 4.16 (q, 2 H, $CO_2CH_2CH_3$), 4.28 (s, 2 H, duryl CH_2), 4.32 (q, 2 H, $CO_2CH_2CH_3$), 6.48 (s, 1 H, duryl H), 8.1 (br s, 1 H, NH). Anal. Calcd for $C_{22}H_{29}NO_4$: C, 71.13; H, 7.87; N, 3.77. Found: C, 70.99; H, 7.81; N, 3.80.

Kinetic Measurements. The rates of the alkylation of p-xylene by the (chloromethyl)pyrrole **5** at 74.0 and 94.3 °C were measured by gas chromatography by determining the amount of pyrrole **10** as a function of time. The operating conditions were as follows: all-glass column (length 2 m, i.d. 3 mm) filled with 0.4% FFAP and 2% Methylsilicone SE-30 on silanized Chromosorb W 60-80; injector and column temperatures 250 and 200 °C, respectively; the internal standard was tetracosane (C. Erba GLC standard).

The kinetic runs were performed by dispensing (under a dry nitrogen atmosphere) ca. 3 mL of a ca. 3×10^{-3} M solution of **5** in p-xylene into an especially designed Teflon reaction vessel closed with a Mininert (Precision Sampling Corp.) valve, which was then immersed in the constant-temperature bath. The samples (10 μL) were withdrawn with a 25-μL Hamilton microsyringe, transferred into microtubes, and held at 0 °C until GLC analysis.

The stability of the p-xylyl derivative in the presence of the HCl formed was checked by heating 1 mL of a 1.8×10^{-3} M solution of **10** in p-xylene to which 50 μL of a 7×10^{-2} M solution of HCl in the same solvent has been added. GLC analysis of the reaction mixture after 3 h at 94.3 °C showed no variation of the concentration of **10**.

Results and Discussion

The results of the alkylation experiments of benzene, p-xylene, and durene with pyrroles **1–5** are presented in Table I. None of the halomethyl derivatives did react in neat benzene under the experimental conditions chosen, whereas all underwent reaction in neat p-xylene. However, the products formed varied, strongly depending on the nature of both the leaving halogen and the β-R substituent. (Bromomethyl)pyrroles **1–3** and (chloromethyl)pyrrole **4** reacted sluggishly, affording complex mixtures of products (arising from a number of not as yet clarified self-condensation and redox processes), from which only in the case of pyrrole **3** could substantial amounts of the alkylation product **10** be isolated. (Chloromethyl)pyrrole **5** proved instead to be an excellent alkylating agent, (arylmethyl)pyrroles **10** and **11** being obtained in practically quantitative yields. Unlike dipyrrylmethane derivatives, which are usually cleaved in the presence of strong acids, arylpyrrylmethane **10** proved to be remarkably stable toward the hydrogen chloride formed in the course of the reaction. The results obtained show that only those α-(halomethyl)pyrroles which bear an ethoxycarbonyl function at the β-position adjacent to the CH_2X group (viz., **3** and **5**) are able to alkylate moderately activated benzene derivatives.

A kinetic study of the reaction of **5** with p-xylene (neat) showed that the process is autocatalytic (see Figure 1). Since hydrogen chloride is formed during the alkylation, it was expected to be responsible for this behavior. Accordingly, the addition of HCl (up to $^1/_3$ mol with respect to the pyrrole) to the reaction mixture caused the S shape of the curve to disappear and the reaction to be speeded up (Figure 2). An attempt was also made to measure the rate of the uncatalyzed reaction by scavenging the hy-

(17) Fischer, H.; Noller, C. R. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 202.
(18) Breslow, D. S.; Baumgarten, E.; Hauser, C. R. *J. Am. Chem. Soc.* **1944**, *66*, 1286.

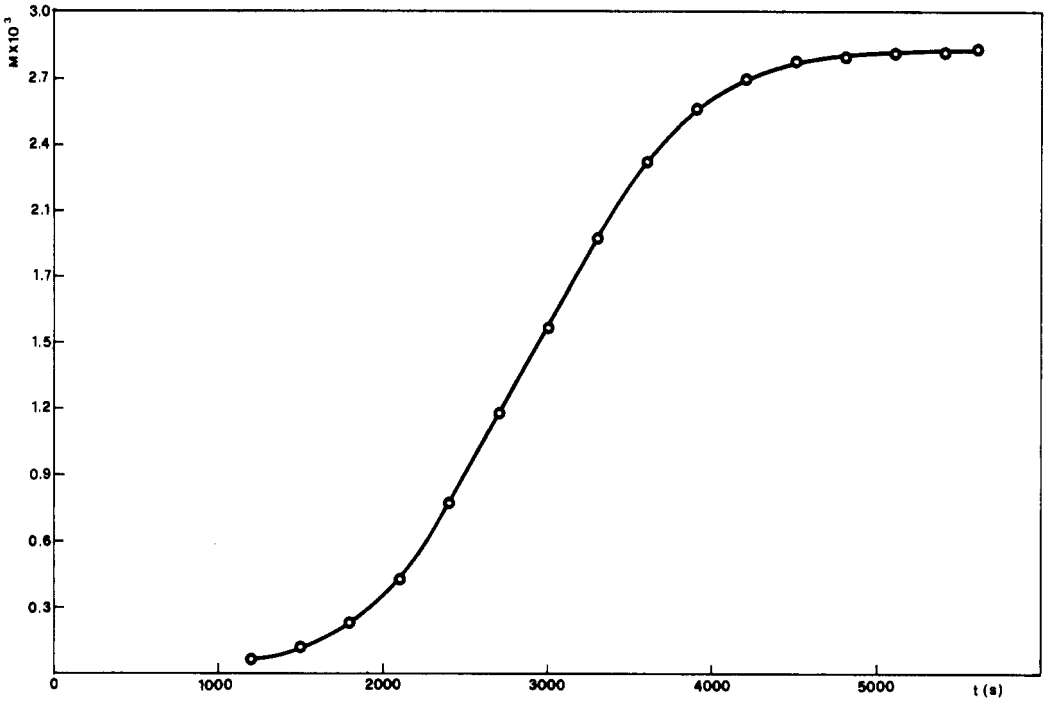
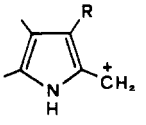


Figure 1. Plot of [10] vs. t (s) for the reaction of **5** with p-xylene (neat) at 94.3 °C, with [5] = 3.037×10^{-3} M.

drogen chloride with a nonnucleophilic tertiary amine (ethyldiisopropylamine) added in an equimolar amount with respect to the pyrrole. Surprisingly, even after 30 days of heating at 94.3 °C no **10** was formed at all, and the starting **5** was recovered unchanged. It would then appear to be unlikely that the so-called residual reaction[19] is the alkylation of the xylene nucleus. Therefore, the presence of the catalytically active species (HCl) at the beginning of the reaction should have a different origin.

It is well-known[20] that α-(halomethyl)pyrroles may readily undergo hydrolysis to the corresponding carbinols, which, in the presence of acids, easily give rise to the formation of dipyrrylmethanes and/or bis(pyrrylmethyl) ethers.[14,20,21] It thus appeared likely that HCl could be formed upon hydrolysis of the α-(chloromethyl)pyrrole by traces of water present in the "anhydrous" reaction system. This proved to be indeed the case. Careful examination of the chromatograms registered during the kinetic runs revealed the presence of a small peak, the area of which remained virtually constant up to ca. 75% reaction and which, by comparison with an authentic specimen,[14] could be ascribed to the presence of (hydroxymethyl)pyrrole **6** in the reaction mixture. The concentration of **6** was determined and found to be ca. 6×10^{-5} M, i.e., 2 orders of magnitude less than that of the (chloromethyl)pyrrole. The constancy of the concentration of **6** during nearly the whole process is consistent with the fact that water is continuously and rapidly regenerated upon the acid-catalyzed formation of the azafluvalenium ion **12**. We assume



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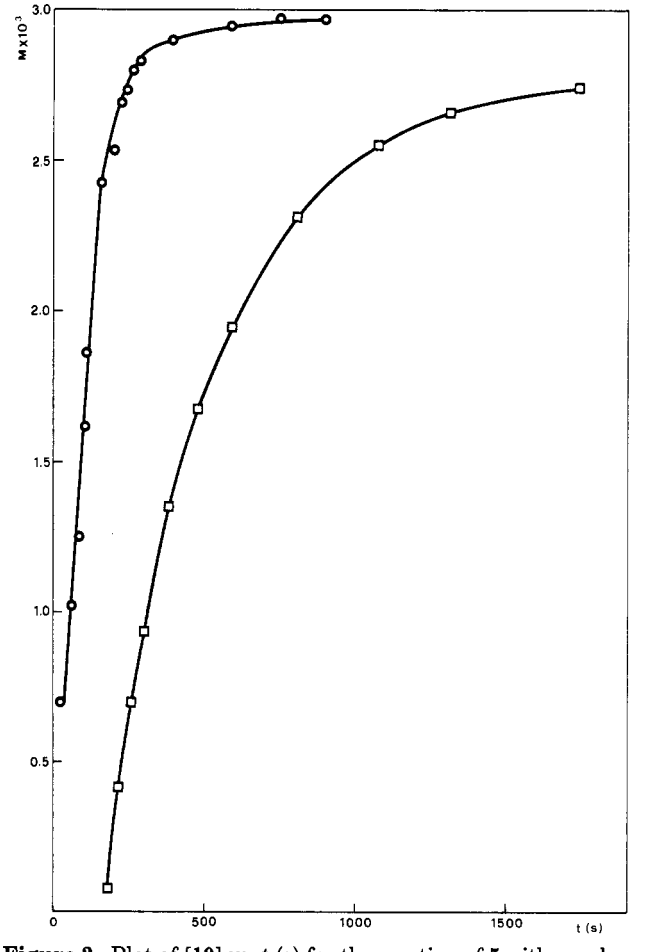


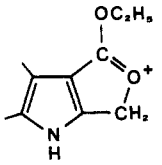
Figure 2. Plot of [10] vs. t (s) for the reaction of **5** with p-xylene (neat) in the presence of HCl with $[5]_0 = 3.037 \times 10^{-3}$ M: (○) [HCl] = 1.18×10^{-3} M, (□) [HCl] = 0.57×10^{-3} M; temperature = 94.3 °C.

12 to be the actual alkylating species. This is also supported by the very rapid alkylation of p-xylene by **6** in the presence of a trace of acid. Compared to that of **3**, the higher reactivity of **5** may be explained by the greater

(19) Boudart, M. "Kinetics of Chemical Processes"; Prentice-Hall: Englewood, Cliffs, NJ, 1968; p 125.
(20) Motekaitis, R. J.; Heinert, D. H.; Martell, A. E. *J. Org. Chem.* **1970**, *35*, 2504.
(21) Collier, G. L.; Jackson, A. H.; Kenner, G. W. *J. Chem. Soc. C* **1967**, 66.

polarization of the C–Cl bond which makes hydrolysis of the chloromethyl group easier.

Pyrroles **1**, **2**, and **4** undergo hydrolysis as easily as pyrroles **3** and **5**; the hydroxymethyl derivatives of the former are, however, unable to alkylate *p*-xylene in the presence of acids, giving rise instead to self-condensation products (Table I). An obvious conclusion is that the enhanced alkylating ability of the azafulvalenium ions deriving from pyrroles **3** and **5** depends on the presence of an ethoxycarbonyl function adjacent (β) to the methylene group. This specific neighboring-group effect would stabilize the positive charge through the contribution of acyloxonium-like structures[22] such as **13**, which strongly



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reduces the extent of its delocalization on the pyrrole nucleus, thus causing an overall increase in reactivity.

Registry No. **1**, 73018-14-1; **2**, 73018-12-9; **3**, 57745-26-3; **4**, 51740-95-5; **5**, 5408-12-8; **6**, 5422-89-9; **6** (cation), 83633-46-9; **7**, 83633-45-8; **8**, 83633-44-7; **9**, 7164-22-9; **10**, 83633-42-5; **11**, 83633-43-6; benzene, 71-43-2; *p*-xylene, 106-42-3; durene, 95-93-2; diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate, 2436-79-5; [3,3′,5,5′-tetrakis(ethoxycarbonyl)-4,4′-dimethyl-2,2′-dipyrryl]-methane, 5431-96-9; ethyl 4-bromo-3,5-dimethylpyrrole-2-carboxylate, 5408-07-1; ethyl 2-(hydroxyimino)-3-oxobutanoate, 5408-04-8; ethyl 3-oxo-4-phenylbutanoate, 718-08-1; ethyl 4-chloro-3,5-dimethylpyrrole-2-carboxylate, 58921-31-6.

(22) Gould, E. S. "Mechanismus und Struktur in der Organischen Chemie"; Verlag Chemie: Weinheim/Bergstr., Germany, 1964; p 679.

New Reaction of (Diethylamino)sulfur Trifluoride: Bis(diphenylmethyl) Ethers as Dehydration Products of (Diethylamino)sulfur Trifluoride and Diarylcarbinols†

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The use of (diethylaminosulfur)trifluoride [DAST, $(C_2H_5)_2NSF_3$] as a mild fluorinating agent has been described by Middleton[1a,b] and Markovskij.[1c] In particular, this reagent is useful for preparing monofluorides from alcohols and *gem*-difluorides from aldehydes and ketones under nonacidic conditions at low temperature. This represents an advance over the parent reagent, sulfur tetrafluoride (SF_4), which usually requires the presence of HF and higher temperatures than required for DAST for the successful replacement of oxygen functions by fluorine.[2]

In seeking a mild way to prepare fluorodiarylmethanes, I examined the reactions of some diarylcarbinols with DAST. As a result, I discovered a new reaction of DAST, namely, intermolecular dehydration of diarylcarbinols (**1**) to bis(diarylmethyl) ethers (**2**) in addition to, or instead of, replacement of OH by F to form fluorodiarylmethanes (**3**). The formation of ethers from aliphatic alcohols has been observed with SF_4[2b] and from halogenated acetaldehydes with both SF_4 and (dialkylamino)sulfur trifluorides at room temperature.[3] However, ether formation from diarylcarbinols and DAST occurs readily at −30 °C and represents a new and extremely simple way of forming these compounds from the parent alcohols. The ether-forming reaction appears to be limited to diarylcarbinols, both benzyl alcohol[1a] and triphenylcarbinol (see eq 1–3) giving the "normal" arylmethyl fluorides.

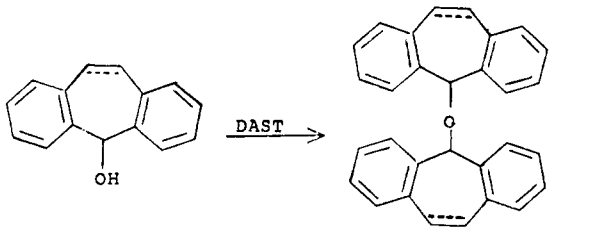
$$C_6H_5CH_2OH + (C_2H_5)_2NSF_3 \rightarrow C_6H_5CH_2F \quad (1)$$

$$\underset{\mathbf{1}}{Ar_2CHOH} + \underset{\text{DAST}}{(C_2H_5)_2NSF_3} \rightarrow \underset{\mathbf{2}}{Ar_2CHOCHAr_2} + \underset{\mathbf{3}}{Ar_2CHF} \quad (2)$$

$$(C_6H_5)_3COH + (C_2H_5)_2NSF_3 \rightarrow (C_6H_5)_3CF \quad (3)$$

Table I summarizes the overall results of four examples of this reaction which were examined in detail.

This reaction is an especially convenient way to prepare the ethers derived from dibenzsuberol and its 10,11-dehydro derivative, shown below. In the case of benzhydrol itself (**1d**; Ar = C_6H_5) essentially equal amounts of ether, **2d**, and fluoride, **3d**, are isolated after purification. 9-Fluorenol, **1c**, reacts in apparent good conversion to form a crude mixture of **2c** and **3c**, identified by NMR, but on further workup only **2c** was isolated pure in low yield, the fluoride fractions undergoing quite rapid decomposition at 25 °C.



1a 10,11-single bond
b 10,11-double bond

2a 10,11-single bond
b 10,11-double bond

The reaction is conveniently carried out by stirring the appropriate secondary alcohol, **1**, in dichloromethane at −30 °C and adding DAST dropwise in an equimolecular amount. In the case of **1b**, a transient magenta color was

Table I. Formation of Bis(diarylmethyl) Ethers Using DAST

example	diarylcarbinol **1**	product yield, % **2**	**3**
a	dibenzsuberol	48–64	0
b	dibenzcycloheptenol	67	0
c	9-fluorenol	13	48[a]
d	benzhydrol	44	40

[a] The indicated products were obtained pure in the yields shown except **3c**, for which the crude yield is reported, this compound being unstable to storage and purification.

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(1) (a) Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574. (b) Middleton, W. J.; Bingham, E. M. *Org. Synth.* **1977**, *57*, 50. (c) Markovskij, L. N.; Pashinnik, V. E.; Kirsanov, A. V. *Synthesis* **1973** 787.

(2) (a) Boswell, G. A.; Ripka, W. C.; Scribner, R. M.; Tullock, C. W. *Org. React.* **1974**, *21*, 1. (b) Hasek, W. R.; Smith, W. C.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1960**, *82*, 543.

(3) Siegemund, G. *Liebigs Ann. Chem.* **1979**, 1280–1290.

0022-3263/82/1947-5220$01.25/0