same conditions, gave a white product in 35% yield that furnished analytical data consistent with the structure of 1,3-diphenyl-3-*p*-toluenesulfonyl-1-propene (XIV).

1-*p*-Toluenesulfonyl-1,3-diphenylpropen-2-one *p*-Toluenesulfonylhydrazone (XV).—XV had mp 160–162° from methanol. Ir spectrum showed bands at 3200 (s), 3020 (w), 2880 (w), 1640 (w), 1600 (s), 1480 (s), 1400 (vs), 1335 (vs), 1315 (vs), 1230 (m), 1162 (vs), 1130 (vs), 1080 (vs), 1050 (s), 925 (s), 885 (s), 845 (m), 812 (vs), 790 (s), 760 (s), 740 (m), 705 (vs), and 675 cm^{-1} (vs) in KBr. Nmr ($CDCl_3$) signals appeared at δ 8.14 (singlet, 1 H) for the NH proton, 7.85–6.5 (multiplet, 14 H) for aromatic protons, 4.7 (singlet, 1 H) for the proton on C bearing *p*-toluenesulfonyl, 3.38 (singlet, 2 H) for benzilic protons, and 2.34 and 2.18 (two singlets, 6 H) for the two methyls of *p*-toluenesulfonyl.

Anal. Calcd for $C_{29}H_{26}N_2O_4S_2$: C, 65.4; H, 5.30; N, 5.26. Found: C, 64.8; H, 5.12; N, 5.31.

1,3-Diphenylallene (XII).—XII had mp 47–50° from *n*-pentane. Ir and uv spectra were in good agreement with the data reported in the literature.[11] Nmr spectrum (C_6D_6) showed signals at δ 7.5–7.1 (multiplet, 10 H) for aromatic protons and at 6.58 (singlet, 2 H) assigned to allenic protons.

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29; mol wt, 192.25. Found: C, 94.12; H, 6.35; mol wt (mass spectroscopy), 192.

1,3-Diphenylpropyne (XI).—The pale yellow oil distilled at 151–155° (4 mm). Ir and uv spectra were in good agreement with the data reported in the literature.[12] Nmr spectrum (C_6D_6) showed signals at δ 7.5–7.0 (multiplet, 10 H) for aromatic protons and 3.78 (singlet, 2 H) for benzilic protons.

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29; mol wt, 192.25. Found: C, 94.2; H, 6.05; mol wt (mass spectroscopy), 192.

1,3-Diphenyl-3-*p*-toluenesulfonyl-1-propene (XIV).—XIV had mp 150–153° from CH_2Cl_2–pentane. Ir spectrum showed bands at 3020 (w), 1580 (m), 1480 (m), 1450 (m), 1310 (vs), 1140 (vs), 1080 (m), 1020 (vw), 975 (m), 920 (w), 875 (vw), 810 (m), 780 (m), 750 (vs), 715 (m), and 665 cm^{-1} (m) in KBr. Nmr ($CDCl_3$) signals appeared at δ 7.5–6.9 (multiplet, 14 H) for aromatic protons, 6.42 (multiplet, 2 H) assigned to vinylic protons, 4.65 (multiplet, 1 H) for the proton on C bearing *p*-toluenesulfonyl, and 2.25 (singlet, 3 H) assigned to the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.84; H, 5.79; S, 9.18. Found: C, 75.9; H, 5.65; S, 9.15.

Decomposition of 2-*p*-Toluenesulfonylazo-1,3-diphenylpropene. Route B.—II (3.0 g, 0.8 × 10^{-3} mol) in 150 ml of dry chloroform was allowed to stand for several hours until the red color of the solution disappeared. After removal of solvent by evaporation under reduced pressure at room temperature, the mixture was treated as indicated for route A. Compounds XI, XII, XIV, and XV were obtained in yields which were not substantially changed from those observed in route A.

Registry No.—I, 29127-96-6; II, 29127-97-7; IV, 29127-98-8; VII, 29119-39-9; VIII, 29119-40-2; XI, 4980-70-5; XII, 19753-98-1; XIV, 29128-01-6; XV, 29128-02-7; α-acetoxydeoxybenzoin *p*-toluenesulfonylhydrazone, 24854-36-2; α-acetoxy-1,3-diphenylpropan-2-one *p*-toluenesulfonylhydrazone, 29128-04-9.

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Meisenheimer-Type Compounds from Heteroaromatic Substrates. The Reaction of Methoxide Ion with 2-Methoxy-3,5-dinitrothiophene[1]

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The formation and isolation of a Meisenheimer-type adduct from 2-methoxy-3,5-dinitrothiophene and methoxide ion are described. Addition of the nucleophile occurs at the 2 position only, to yield the 2,2-dimethoxy-3,5-dinitrothiacyclopentenate ion. The specific rate and, particularly, the equilibrium constant for the formation of this adduct at 25° are larger than the corresponding values for the formation of the adduct between 2,4,6-trinitroanisole and methoxide ion at the same temperature.

Meisenheimer-type adducts formed from nitro-substituted homocyclic aromatic substrates and methoxide ion have been intensively studied.[2] The formation of similar adducts from pyridine and pyrimidine derivatives has been reported[3–8] and compared with the corresponding reactions of homocyclic compounds. We are now considering the behavior of suitable five-membered ring substrates in order to evaluate the role of the ring size and of the heteroatom in the formation of the adducts. Following a preliminary communication,[9] we report detailed results and additional data for the reaction of 2-methoxy-3,5-dinitrothiophene with methoxide ion.

Experimental Section

Materials.—The methanol used for the rate measurements was purified as described;[3] however, since methanol distilled over magnesium methoxide may still contain traces of basic impurities,[10] that used in the experiments carried out in the presence of sodium acetate was redistilled over *p*-nitrobenzoic acid. 2-Methoxy-3,5-dinitrothiophene ($\epsilon_{max} = 0.92 \times 10^4\ M^{-1}\ cm^{-1}$ at 243 nm; $\epsilon_{max} = 1.04 \times 10^4\ M^{-1}\ cm^{-1}$ at 343 nm, in methanol) was prepared by a known procedure[11] and by nitration of 2-methoxy-5-nitrothiophene[12] with 99% nitric acid in acetic anhydride at 0°. Attempts to obtain it by methoxy dechlorination of 2-chloro-3,5-dinitrothiophene were unsuccessful. Other materials used and the analytical and nmr and uv visible spectral

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procedures were as described previously.[3,4] Chemical shifts are approximate to ±0.02 ppm. Ir spectra were determined in KBr disks on a Perkin-Elmer 257 spectrophotometer.

Isolation and Characterization of the Adduct.—2-Methoxy-3,5-dinitrothiophene (40 mg) was dissolved in the least amount of methanol. Nearly 1 equiv of methanolic sodium methoxide (0.7 M) was added with a microsyringe. The solution immediately turned reddish purple. The solvent was removed at 10^{-1} Torr at 25°, and the residue, a purple microcrystalline solid, was washed repeatedly with dry benzene and dried to constant weight in order to eliminate any associated solvent.

Anal. Calcd for $C_6H_7N_2NaO_6S$: C, 27.9; H, 2.7; N, 10.85; Na, 8.9. Found:[13] C, 27.8; H. 2.6; N, 10.8; Na, 9.0.

The adduct was characterized through its nmr, ir, and electronic spectra (Results and Discussion). In MeOH solution the adduct was characterized spectrophotometrically as the species obtained when sodium methoxide was added to a solution (2×10^{-5} M) of the substrate in methanol. When the concentration of methoxide ion was 4×10^{-4} M, the conversion of the substrate into the adduct was complete at 25°. The time required for this was *ca.* 5 min. At concentrations of methoxide greater than 5×10^{-3} M, the adduct appeared to be unstable, since the pink color of the solution faded. The rate of fading increased as the concentration of the nucleophile was increased. This behavior was not investigated further; probably the strong excess of the nucleophile is responsible for a ring-opening reaction similar to that undergone by nitrofurans[14] in the presence of strong bases or by 3,4-dinitrofurans with amines.[15]

Rate Measurements. A. Sodium Methoxide as Reagent.—The formation of the adduct is a relatively fast reaction. In order to follow the kinetics at 25°, solutions of the substrate ($2\text{–}3 \times 10^{-5}$ M) and of sodium methoxide ($3\text{–}6 \times 10^{-4}$ M) in methanol were placed in the separate compartments of a Y-shaped, thermostated tube. At zero time the solutions were mixed and rapidly poured into a thermostated 1-cm cell. The increase in optical density at 531 nm with time was recorded. The rate data are reported in Table I.

TABLE I

REACTION OF 2-METHOXY-3,5-DINITROTHIOPHENE (MDNT) WITH METHOXIDE ION IN METHANOL SOLUTION AT 25°[a]

[MDNT], $\times 10^5$ M	$[MeO^-]$ $\times 10^4$ M	k_{obsd}, $sec^{-1} \times 10^2$	k_{II}, M^{-1} sec^{-1}
2.00	3.93	1.35	34.4
2.00	3.93	1.37	35.0
3.01	5.89	2.16	36.7
3.01	4.71	1.84	38.1
3.01	4.71	1.67	35.5
			Av 36

[a] For comparison, literature data are reported (references quoted in parenthesis) of k_{II} and K_f values for the reaction of trinitroanisole with methanolic methoxide ion at 25°: k_{II} = 7–10 (ref 3), 4 (ref 21), 4.55 [T. Abe, T. Kumai, and H. Arai, *Bull. Chem. Soc. Jap.*, **38**, 1526 (1965)], 16–20 M^{-1} sec^{-1} (ref 24a); K_f = 10,000–20,000 (ref 3), 7700 (ref 21), 2260 [T. Abe, T. Kumai, and H. Arai, *Bull. Chem. Soc. Jap.*, **38**, 1526 (1965)], 17,000 M^{-1} (ref 24a).

B. Sodium Acetate as Reagent.—A small amount of methoxide ions is present when sodium acetate is dissolved in methanol. A 0.1 M solution of acetate has a limited buffer capacity so that the interaction of the substrate slightly modifies the methoxide ion concentration. It has been found that the kinetics of formation of the adduct follow a pseudo-first-order law for the first 70–80% of reaction both in the reaction of 2,4,6-trinitroanisole and of 2-methoxy-3,5-dinitrothiophene. Second-order rate constants, k_{II}, were obtained from the equation[3]

$$k_{II} = k_{obsd}/([MeO^-] + K_f^{-1})$$

where k_{obsd} is the experimentally found pseudo-first-order rate constant and K_f is the equilibrium constant for the formation of the adduct. In the experiments using methoxide ion as reagent, the value of K_f^{-1} was negligible compared to that of the concentration of methoxide ion. For the experiments using sodium acetate, K_f was determined as described in the next section. The rate data are reported in Table II.

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR THE FORMATION OF THE ADDUCTS IN METHANOLIC SODIUM ACETATE (0.1 M) AT 25°

Substrate	Concn, 10^5 M	K_f, M^{-1}	k_{obsd}, sec^{-1}	k_{II}, $M^{-1} \times sec^{-1}$
2,4,6-Trinitroanisole[a]	2–3	8.8×10^3	7.75×10^{-4}	4.25
2-Methoxy-3,5-dinitrothiophene[b]	0.9–2.6	4×10^5	9.14×10^{-4}	13

[a] Average value from two determinations; uncertainty is 9% for K_f, 1% for k_{obsd}, and 5% for k_{II}. [b] Average value from two determinations; uncertainty is 8% for K_f, 8% for k_{obsd}, and 7% for k_{II}.

Equilibrium Measurements.—The equilibrium constants

$$K_b = \frac{[AcOH][MeO^-]}{[AcO^-][MeOH]};\quad K_f = \frac{[adduct]}{[MeO^-][ArOMe]}$$

$$K_{MeOH} = [MeO^-][MeOH_2^+]$$

were combined to give the following relations, neglecting the concentration of $MeOH_2^+$.

$$[MeO^-] = K_b\frac{[AcO^-]}{[AcOH]};\quad [AcOH] = [MeO^-] + [adduct]$$

Taking the value[16] of K_{MeOH} at 25° as 1.2×10^{-17} and the value[17] of K_a (*i.e.*, K_{MeOH}/K_b) as 2.63×10^{-10} at ionic strength 0.1 M and using the experimentally found concentrations of the adduct, the value of K_f was determined (Table II).

Results and Discussion

In deuterated DMSO, 2-methoxy-3,5-dinitrothiophene shows two singlets in the nmr spectrum at τ 1.53 and 5.63 (relative area 1:3). Upon addition of 1 equiv of 5 M methanolic sodium methoxide to a 0.5 M solution of the substrate, both peaks are shifted upfield. The weaker peak is shifted to τ 2.14 with its intensity almost unchanged; the exact chemical shift of the stronger peak cannot be clearly observed because of an intense signal from methanol in the same region.

A red solid, found to be a 1:1 adduct by elemental analysis, can be isolated from the methanolic solution of the reagents; its nmr spectrum in deuterated DMSO shows two peaks of relative intensity 1:6 at τ 2.13 and 6.71. The former coincides with that observed for the reaction product formed *in situ;* the latter is attributed to two equivalent methoxyl groups. This indicates that the adduct results from a nucleophilic attack by methoxide ion at the carbon atom originally bound to the methoxyl group.

In accordance with a *gem*-dialkoxy structure,[18] the ir spectrum of the solid (2940 w, 1560 m, 1501 s, 1420 s, 1332 s, 1277 vs, 1247 vs, 1216 s, 1173 s, 1127 vs, 1092 sh, 1061 s, 1027 cm^{-1} s) shows strong absorptions in the ketal region[19] (1000–1250 cm^{-1}).

The electronic spectra of a methanolic solution of the isolated adduct and of the product of interaction between the reagents in methanol are identical and display two maxima at 312 nm (ϵ 7.5×10^3 M^{-1} cm^{-1}) and 531

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nm (ϵ 2.3 × 10^4 M^{-1} cm^{-1}), whereas a freshly prepared methanolic solution of the substrate does not absorb in the visible region. This fact might have allowed K_f to be determined directly by recording the change in optical density at equilibrium in solutions containing the same amount of substrate and the nucleophile at different concentrations.[3] However, it was found that at 25° when the concentration of methoxide ion was as low as 4×10^{-4} M, and that of the substrate was 2×10^{-5} M, the substrate was entirely changed to the corresponding adduct. The value of K_f was then considerably higher than the corresponding value for the adduct of trinitroanisole (K_f = 1–2 × 10^4 M^{-1} at 25°).[3] It was not thought convenient to decrease the concentration of methoxide further, since unavoidable traces of water (10^{-4}–10^{-5} M) and carbon dioxide could hydrolyze and neutralize a certain amount of methoxide ion and introduce inaccuracy in the calculated value of its concentration.

A lower limiting value for K_f at 25° was calculated by assuming that, at the lowest concentration of methoxide, only $^1/_{100}$th of the original amount of 2-methoxy-3,5-dinitrothiophene had not been converted into the adduct. The value obtained (2.7 × 10^5 M^{-1}) is at least ten times higher than the value reported for trinitroanisole.

The kinetics of formation of the adduct were followed at 25° by measuring the increase in optical density at 531 nm; pseudo-first-order kinetics were observed. Both the pseudo-first-order rate constants and the second-order rate constants calculated from them are reported in Table I.

A comparison with the rate constants found for the formation of the adduct of trinitroanisole at the same temperature (7–10 M^{-1} sec^{-1}) shows that the thiophene derivative reacts faster by a factor of about 4 only.

The data obtained in methanolic sodium methoxide indicated that the K_f value was too high for determination. Therefore, it was thought that, because of the high thermodynamic stability of the adduct, the reaction could also be studied in methanolic sodium acetate at a very low concentration of methoxide ion. This salt is solvolyzed in methanol according to the equation

$$\text{AcO}^- + \text{MeOH} \rightleftharpoons \text{AcOH} + \text{MeO}^-$$

Since the autoprotolysis constant of methanol[18] and the acidity constant of acetic acid in methanol are known (although literature values for the latter vary somewhat), it is possible to calculate the concentration of the methoxide ion formed from the methanolysis of sodium acetate with reasonable accuracy.

The electronic spectra of 2-methoxy-3,5-dinitrothiophene and 2,4,6-trinitroanisole in methanolic sodium acetate were found to be identical with those observed in methanolic sodium methoxide. In view of the much greater nucleophilicity of the methoxide ion relative to acetate, it is assumed that the acetate ions are responsible for the formation of methoxide ions but do not compete with the latter for the attack on the ring carbon. It must be emphasized that, owing to uncertainties in the $\text{p}K_a$ value of acetic acid in methanol, this method provides reliable results in terms of relative rates and equilibrium constants rather than absolute values for each individual substrate.

As to the determination of the constant K_f in the presence of sodium acetate, the concentration of the adduct is conveniently measured spectrophotometrically after the reaction has attained equilibrium (see Experimental Section). The adduct from the thiophene derivative was thus found to be thermodynamically more stable than the adduct of trinitroanisole by a factor of about 40 (Table II). The high K_f value explains why a colorless methanolic solution of 2-methoxy-3,5-dinitrothiophene (10^{-3} M) slowly becomes faintly pink with a small maximum of absorption at 531 nm; the amount of methoxide ion present in pure methanol (*ca.* 10^{-8} M) is sufficient to convert a very small portion of the substrate into the adduct. A noteworthy example of a similar formation of a Meisenheimer-type adduct by reaction of a neutral molecule with the conjugate base of a neutral solvent is the reaction of 4,6-dinitrofuroxan in water; in this case the formation of the adduct is almost complete.[20]

Since the concentrations of the substrates are always much lower than that of the acetate, throughout the reaction the concentration of methoxide ion is expected to remain almost unchanged. Accordingly, the observed kinetics of formation of the adducts follow a pseudo-first-order law up to 70–80% of reaction. The second-order rate constants reported in Table II were obtained by dividing the observed pseudo-first-order rate constants by the methoxide ion concentration which was calculated using Bunnett's[19] value for the $\text{p}K_a$ of acetic acid in methanol. The rate constants obtained in acetate solution are comparable to those obtained when methoxide ion was used as reagent. Good agreement is also found for the reactivity ratio between 2-methoxy-3,5-dinitrothiophene and 2,4,6-trinitroanisole.

Several factors have been suggested in order to explain the stability of Meisenheimer-type adducts. First of all, the presence of powerful electron-attracting groups ortho and para to the reaction center is required, so that the negative charge of the nucleophile can be effectively delocalized. Secondly, relief of steric strain and of steric inhibition of resonance with respect to the initial aromatic systems[21] may also contribute to the stability of those adducts characterized by a carbon atom bearing two alkoxy groups and having two adjacent nitro groups. The reality of this effect was shown by X-ray crystallographic analysis of 2,4,6-trinitrophenetole[22] and of its adduct with ethoxide ion.[23] In the adduct, the two nitro groups at the 2 and 6 position were found to be almost coplanar with the ring, whereas in the initial aromatic system they are twisted by 33 and 62° out of the plane and are not allowed to attain full conjugation.

The relatively low reactivity of the alkoxy-bearing position, as compared to that of a hydrogen-bearing position, was interpreted[21] by assuming that the steric crowding in the transition state leading to the 1,1-dialkoxy adduct is larger than in the transition state leading to the 1,3-dialkoxy adduct. This view has been criticized[24] and an alternative explanation has been offered[24b] to this kinetic effect by taking into account

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the influence of multiple alkoxy substitution at a tetrahedral carbon[25] and direct conjugation phenomena between methoxy and nitro substituents.

We may now ask what connection, if any, can be established between the factors affecting the adduct formation in six-membered rings and that in the thiophene system under investigation. In the latter case we have observed a comparable rate of formation and a much higher stability constant relative to the 2,4,6-trinitroanisole system. A comparison in terms of geometrical parameters is not strictly correct since too many changes are involved altogether on passing from one system to another. An important point to keep in mind is that the observed overall stability constant for the five-membered ring system depends not only on the stability of the resulting adduct but also on that of the starting heteroaromatic system. It is likely that the energy content of the thiophene system is higher than that of 2,4,6-trinitroanisole. It is of interest to note that calculations of the localization energy at the 2 position of thiophene,[26] for electrophilic as well as nucleophilic reactions, indicate that the formation of a σ complex at this position is clearly favored with respect to benzene.

There are, however, two points of structural comparison which must be made despite the difficulties of assessment just mentioned. The first point concerns the steric situation of the nitro groups in the thiophene derivative. Because of the lower steric compression between vicinal groups in the five-membered ring and the presence of only one flanking nitro group, the steric factor, *i.e.*, reduced steric inhibition of resonance, cannot account for the stability of the complex. The second point concerns the *relative* change in geometry of the two systems under comparison.

The C(2)–C(1)–C(6) angle in trinitroanisole is almost 120°, while the S–C(2)–C(3) angle of the thiophene derivative should be near to 111.5°.[27] When the C(1) atom in the former compound forms a new bond with methoxide ion, the C(2)–C(1)–C(6) angle in the adduct is forced to a value close to that of a tetrahedral carbon atom (109.5°), and, therefore, a certain amount of strain affects the six-membered ring. As to the adduct of the thiophene derivative, a tetrahedral value can also be expected for the S–C(2)–C(3) angle, but this is much closer to that of the original substrate. It is then to be expected that the formation of the adduct involves less bond strain in the five-membered than in the six-membered ring system.

Although the adduct from 2-methoxy-3,5-dinitrothiophene is thermodynamically stable, it is easily destroyed by a strong excess of nucleophilic reagents (see Experimental Section). Also, in agreement with other workers,[11] we have found that the yield in the methoxy dechlorination of 2-methoxy-3,5-dinitrothiophene is very low. These facts could be reconciled with the generally accepted two-step mechanism of aromatic substitution provided that the intermediate σ complex having a Meisenheimer-type structure in some cases is diverted to a decomposition path other than the one leading to the conventional substitution product.

Registry No.—MDNT, 27357-00-2; methoxide ion, 3315-60-4; 2,2-dimethoxy-3,5-dinitrothiacyclopentenate ion, 29152-91-8.

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Substituent Effects in the Reaction of Sodium 4-Nitrophenoxide with 2-Bromoacetanilides

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The kinetics of the reaction of sodium 4-nitrophenoxide with ten 3′- and 4′-substituted 2-bromoacetanilides in 2-methoxyethanol solvent have been examined at 45.3, 55.3, and 65.3°. Second-order kinetics were found, and the rate constants were fit to a Hammett-type equation using van Bekkum, Verkade, and Wepster normal σ values to yield a ρ value of $+0.65 \pm 0.02$, independent of temperature. The amide link is transmitting substituent effects relatively efficiently in this process. Apparently normal activation parameters were encountered.

The transmission of activation effects through acyl links in compounds of the type XCH_nCOZY from Y to a reactive site X adjacent to the carbonyl group has been little studied; Z is taken to be an atom with an unshared electron pair, nitrogen in the present case. A considerable body of information relates the effect of a change at X with reactivity or equilibria at the carbonyl group or at atom Z; examples are of the pK_a's of substituted amino acids[3] and phenylacetic acids,[4] the infrared frequencies of substituted anilides,[5] the hydrolysis reactions of phenylacetates,[6] as well as many other reactions which could be cited. On the other hand, when this work was begun virtually no work had been reported which dealt with transmission of effects from Y to X; for example, no measurements of pK_B of substituted glycine anilides have been reported. It is clear that

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