Experimental Section

The Photoaddition of *trans*-Stilbene to Dimethyl Fumarate. A solution of 1 (2.50 g, 0.014 mol) and 2 (20 g, 0.14 mol) in 500 ml of benzene was deaerated with a stream of dry, oxygen-free nitrogen and then irradiated (450-W Hanovia immersion lamp, Pyrex) for 24 hr while passing through nitrogen. The benzene was evaporated and the residue sublimed (bulb-to-bulb, on a Büchi rotary evaporator at 2 mm pressure; heating bath at 70–80°; collecting flask cooled in Dry Ice–2-propanol bath). The sublimate consisted of dimethyl fumarate and dimethyl maleate. The residue was chromatographed on 200 g of Merck 0.05–0.20 mm silica gel. Elution with 2% ethyl acetate in *n*-hexane gave traces of stilbene and stilbene dimers. Further elution gave a total of 1.1 g of oily material. Further elution with the same mixture of solvents gave 2.0 g (46% yield) of dimethyl-μ-truxinate (**3**) which was crystallized from methanol to give 1.6 g of analytically pure material: mp 121–123°; δ ($CDCl_3$) 7.21 (10 H, s, Ph), 4.5–4.7, 3.8–4.2 (4 H, AA′BB′ multiplet, cyclobutane hydrogens), and 3.33 (6 H, s, OCH_3).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.90; H, 6.11.

Elution with 3% and then 5% ethyl acetate in *n*-hexane afforded 0.20 g of oily material whose nmr spectrum and tlc chromatogram, by comparison with an authentic sample,[10] indicate the presence of a mixture containing dimethyl δ-truxinate (**5**). Elution with 10% ethyl acetate in *n*-hexane gave 0.28 g (6% yield) of dimethyl neotruxinate (**6**) which was crystallized from methanol to give 0.15 g of material with mp 131–132° (lit.[11] mp 127.5°): δ ($CDCl_3$) 6.71–7.35 (10 H, m, Ph), 3.91–4.43 (4 H, unsymmetrical m, cyclobutane hydrogens), 3.75 (3 H, s, CO_2CH_3 trans to β-Ph), and 3.28 (3 H, s, CO_2CH_3 *cis* to β-Ph). Further elution with increasing proportions of ethyl acetate afforded oily mixtures which were not investigated further.

Dimethyl μ-truxinate can also be isolated in lower yields directly after the sublimation step by several crystallizations from methanol. The first compound to crystallize is an unknown material with mp 218–220° (this substance can also be crystallized from the later chromatographic fractions) which is removed by filtration. The mother liquor then deposits dimethyl μ-truxinate.

μ-Truxinic Acid (4). A mixture of **3** (500 mg) and an aqueous HCl solution (75 ml, 1:2) was refluxed while stirring for 137 hr. The product was filtered (390 mg, 85% yield) and crystallized from aqueous acetic acid to give **4** (226 mg) with mp 252–254°: δ (DMSO) 7.20 (10 H, s, Ph), 4.58–4.26, 3.90–3.56 (4 H, AA′BB′, cyclobutane hydrogens).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.86; H, 5.52.

A mixture of the acid **4** (50 mg) in methanol (20 ml) was treated with several drops of thionyl chloride and warmed overnight. Evaporation of solvent left **3** having an nmr spectrum identical with that of the irradiation-derived sample. Crystallization from methanol gave 34 mg of **3**, mp 118–121°.

Acknowledgment. We are grateful to Miss Edna Gati for performing some preliminary experiments.

Registry No.—**1**, 103-30-0; **2**, 624-49-7; **3**, 52306-38-1; **4**, 528-35-8; **6**, 52305-39-2.

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(4) The nmr spectrum of the cyclobutane region of **3** is published [D. A. Ben Efraim and B. S. Green, *Tetrahedron*, **30**, 2357 (1974)] and in that paper the midpoint of the AA′BB′ cyclobutane multiplet is shown to be at the position expected for an isomer of cis-anti-cis configuration.
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(8) Compare with the *all-trans-* and *cis,anti,cis-*1,2,3,4-tetracarbomethoxycyclobutane isomers.[2a]
(9) See H. M. Rosenberg and M. P. Servé, *J. Org. Chem.*, **36**, 3015 (1971); F. D. Lewis and R. H. Hirsch, *Tetrahedron Lett.*, 4947 (1973).
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Facile Synthesis of *tert*-Butylacetylene

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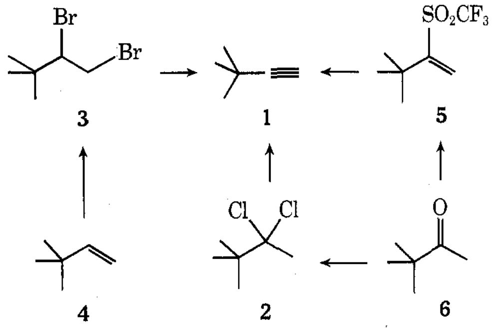
Until recently, *tert*-butylacetylene (**1**) was prepared by the method of Bartlett and Rosen[1] which entails the dehydrochlorination of pinacolone dichloride (**2**) in a sodium hydroxide melt. This reaction is difficult to control to the point of being hazardous on a large scale and affords only a moderate yield of **1**. With these limitations in mind, alternate preparations have recently appeared. Collier and Macomber[2] prepared the *vic*-dibromide **3** by the addition of Br_2 to *tert*-butylethylene (**4**) which was subsequently dehydrobrominated to **1**. However, the bromination must be carried out at −78° to avoid contamination of the product with substantial amounts of rearranged products. Hargrove and Stang[3] prepared the vinyl triflate **5** from pinacolone (**6**) and subsequently effected a base-catalyzed elimination of CF_3SO_3H to afford **1**. The latter procedure is disadvantaged by the expense of the $(CF_3SO_2)_2O$ required to prepare **5**.



With emphasis on experimental facility and economy, a modification of the Bartlett–Rosen procedure has been developed which permits the synthesis of **1** on a mole scale without recourse to low temperatures or expensive reagents. Pinacolone dichloride (**2**), readily prepared by reaction of pinacolone (**6**) with PCl_5,[1,4] was added to a mixture of *t*-BuOK in DMSO while maintaining the temperature below 40°. The product was isolated in 95% yield (from **2**) by direct distillation from the reaction mixture in ≥95% purity by vpc analysis. By this procedure, **1** has been prepared repeatedly in >90% yield in quantities ranging from 5–100 g.

Experimental Section

Boiling points are uncorrected. The nmr spectra were recorded on a Varian A-60A spectrometer using TMS as an internal standard; infrared spectra were recorded on a Perkin-Elmer 337 spectrometer in CCl_4 solution. Gas–liquid chromatographic analyses were performed on a Varian Model 90 chromatograph using ¼-in. × 12-ft columns packed with 10% SE-30 on Chrom W. Freshly opened bottles of *tert*-BuOK from MSA Corporation were employed and the DMSO, obtained from Fisher, was used without further purification.

***tert*-Butylacetylene.** A flame-dried 250-ml three-necked flask fitted with a thermometer, condenser, magnetic stirrer, and addition funnel was charged with 50 g (0.45 mol) of *t*-BuOK and 110 ml of DMSO. With magnetic stirring, pinacolone dichloride (35 g

0.22 mol) in 20 ml of DMSO was added at a rate sufficient to maintain the temperature below 40°. After addition was complete, the mixture was allowed to stir under nitrogen at ambient temperature for 2 hr. The reflux condenser was replaced by a distilling head and the reaction flask heated in an oil bath with the bath temperature gradually increased to 110° while material boiling up to 80° was collected. Redistillation through an 8-in. tantalum spiral column into a dry ice-acetone cooled receiver afforded 17.2 g (95%) of *tert*-butylacetylene, bp 36.5–38.5° (lit.[1] bp 36.4–37.8°) identical by ir, nmr, and vpc with an authentic sample prepared by the method of Bartlett and Rosen.[1]

Registry No.—**1**, 917-92-0; **2**, 594-84-3; *t*-BuOK, 865-47-4.

References and Notes

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(2) W. L. Collier and R. S. Macomber, *J. Org. Chem.*, **38**, 1367 (1973).
(3) R. J. Hargrove and P. J. Stang, *J. Org. Chem.*, **39**, 581 (1974).
(4) Insufficient care in maintaining efficient stirring and adequate temperature control is responsible for the fluctuating yields frequently observed in the preparation of the sensitive pinacolone dichloride (**2**) which undergoes facile monodehydrochlorination to the corresponding vinyl chloride. However, the vinyl chloride by-product can be used with equal success in the above procedure. In fact, we have frequently used mixtures of the vinyl chloride and dichloride to afford an overall yield of 70–75% of **1** from pinacolone.

Leaving Group Effect in the Reaction of 2-Thiophenesulfonyl Halides with Anilines in Methanol

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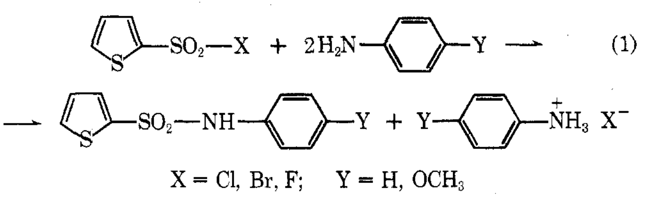
Previously the reaction kinetics of 2-thiophenesulfonyl chloride with several substituted anilines[1,2] was investigated and a study on the ultraviolet and infrared spectroscopic behavior of 2-thiophenesulfonanilides, reaction products, was carried out.[3]

The results of the kinetic measurements showed that 2-thiophenesulfonyl chloride is less reactive than the corresponding benzene derivative,[4] probably owing to the greater conjugative effect of the thiophene ring, but they gave no useful indications about the reaction mechanism.

The Hammett and Brϕnsted coefficient values for 2-thiophenesulfonyl chloride reactions with anilines in methanol[1] are almost coincident to those for the analogous reactions of benzenesulfonyl chloride.

For the latter reaction have been proposed both a one-step synchronous process, S_N2,[4] and a two-step addition–elimination mechanism involving the formation of a metastable intermediate, S_AN.[5]

In order to give a further contribution to this question, in this paper we report a kinetic study on the leaving group effect in the reaction of 2-thiophenesulfonyl halides with aniline and *p*-anisidine, eq 1.



(1)

X = Cl, Br, F; Y = H, OCH$_3$

Results and Discussion

The reaction of 2-thiophenesulfonyl halides with a large excess of aniline or *p*-anisidine in methanol solution is pseudo-first-order with respect to the sulfonyl halide. It was followed potentiometrically by titration of the acid produced with sodium hydroxide (see Experimental Section).

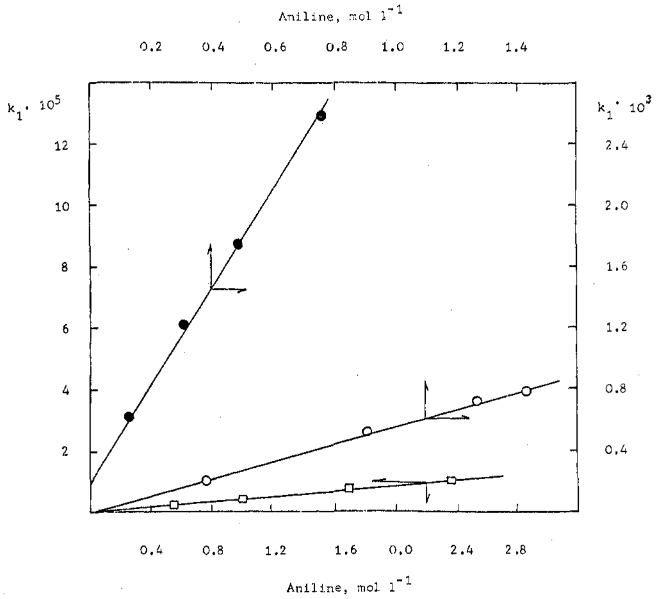


Figure 1. Pseudo-first-order rate constants at 25° against aniline concentration for the reaction of 2-thiophenesulfonyl halides: ●, 2-thiophenesulfonyl bromide; ○, 2-thiophenesulfonyl chloride; □, 2-thiophenesulfonyl fluoride.

The reaction of 2-thiophenesulfonyl bromide was followed to at least 80% completion, while that of 2-thiophenesulfonyl fluoride was followed to 25% completion, since it is very slow. The reaction yielded sulfonanilides, since the solvolysis of 2-thiophenesulfonyl halides in methanol is negligible.

Pseudo-first-order rate constants against aniline concentrations give linear plots, indicating that the reaction is first order also with respect to aniline (Figure 1).

The reactions were studied at different temperatures and the second-order rate constants, reported in Table I, together with the standard deviations and the linear correlation coefficients, were obtained by eq 2,[6] using the least-squares method.

$$k_{\mathrm{ps1}} = k_{\mathrm{solv}} + k_2[\text{aniline}] \qquad (2)$$

The value of k_{solv} is almost null for the reactions of 2-thiophenesulfonyl fluoride and chloride and negligible, with respect to k_2, for that of 2-thiophenesulfonyl bromide (Figure 1).

The activation parameters are reported in Table II, together with the linear correlation coefficients and the standard deviations.

2-Thiophenesulfonyl bromide reacts *ca.* five times faster than 2-thiophenesulfonyl chloride[1] with both aniline and *p*-anisidine, and respectively *ca.* 7200 and 35,700 times faster than 2-thiophenesulfonyl fluoride. The observed rate sequence follows the halogen polarizability sequence (Br > Cl ≫ F) and is inverse with respect to the S–Hal bond energy sequence.[7]

In order to distinguish between S_N2 and S_AN mechanisms we determined the relative amount of bond formation and bond breaking, respectively, for S–N and S–Hal bonds in the transition state, using the Brϕnsted coefficients[8] obtained from the plots of log k_2 against the pK_a of protonated anilines and hydrogen halides ones (Figure 2).

The Brϕnsted coefficient values (β) for the leaving group for the reactions of 2-thiophenesulfonyl halides are −0.31 and −0.38, respecitvely, with aniline and *p*-anisidine. The β