

The nmr spectrum (CDCl_3) showed absorptions at δ 3.6–4.1 (m, 2 H, CH_2), 5.8–6.1 (m, 6.7 (broad, NH), and 7.1–7.7 (m, 3 H, $\text{C}_6\text{H}_5\text{S}^-$).

Anal. Calcd for $\text{C}_7\text{H}_7\text{NO}_2\text{S}$: C, 49.7; H, 4.1; N, 8.3. Found: C, 49.9; H, 4.3; N, 8.4.

5-(2-Thienyl)-3-nitroso-2-oxazolidone (5).—A mixture of 4.0 g (0.23 mol) of **4** in 40 ml of dry ether and 4.2 g of sodium bicarbonate was treated at -60° with 2.0 g of N_2O_4 . The mixture was allowed to come to room temperature and then filtered. The solvent was removed on a rotary evaporator and the yellow solid thus obtained was converted immediately into 2-ethynylthiophene.

A small sample of **5** was dried *in vacuo* for 20 min and gave a melting range of 60 – 65° with gas evolution. An nmr spectrum (CDCl_3) showed absorptions at δ 4.0–4.8 (CH_2), 6.1–6.4 (CH), and 7.3–7.9 ($\text{C}_6\text{H}_5\text{S}^-$).

2-Ethynylthiophene (1).—The product obtained from the previous reaction was dissolved in methanol (50 ml) and treated with sodium methoxide solution until gas evolution stopped. The mixture was poured into water, extracted with ether, and dried. The dried extracts from three runs were combined and distilled. The yield of **1** was 6.0 g (79%), bp 54 – 60° (20 mm), n_D^{25} 1.5882 (lit.^{2a} n_D^{25} 1.5886).

The infrared spectrum showed strong absorption at 3300 cm^{-1} ($\text{C}\equiv\text{CH}$) and medium absorption at 2100 cm^{-1} ($\text{C}\equiv\text{C}$). The nmr spectrum (CCl_4) showed absorption at δ 3.18 ($\text{C}\equiv\text{CH}$) and 6.8–7.4 ($\text{C}_6\text{H}_5\text{S}^-$).

2-Thienylpropionic Acid (6).—To a solution of 0.50 g (4.6 mmol) of **1** in dry ether was added 1.2 ml (6.7 mmol) of freshly prepared ethereal *n*-butyllithium (1.6 *N*). After 3 hr, 3 g of Dry Ice was added to the mixture with stirring. Water (5 ml) was added to the mixture and the contents were extracted with ether. The water layer was acidified to give 0.5 g (72%) of **6** which had mp 130 – 133° dec after drying (lit.^{2b} mp 130 – 133°). Unreacted **1** accounted for the balance of the material. The infrared spectrum (KBr) showed absorptions at 3000 (broad, acid), 2200 ($\text{C}\equiv\text{C}$), and 1675 cm^{-1} ($\text{C}=\text{O}$). The nmr spectrum (acetone- d_6) showed absorption at δ 7.4–7.6 (1 H), 7.8–8.2 (2 H, m, $\text{C}_6\text{H}_5\text{S}^-$), and 9.9 (s, 1 H, COOH).

Competitive Metalation of 2-Ethynylthiophene (1) and Phenylacetylene.—A freshly prepared ethereal solution of 1.6 *N* *n*-butyllithium (1.8 ml, 2.9 mequiv) was added under a dry nitrogen atmosphere to a solution of 0.32 g (3.0 mequiv) of **1** and 0.31 g (3.0 mequiv) of phenylacetylene in 10 ml of dry ether. After 3–4 hr, 1 g of powdered Dry Ice was added to the mixture. Water (5 ml) was added and the layers were separated. The acidified water layer was extracted with ether and worked up to give a mixture of **6** and phenylpropionic acid, δ 7.6–8.0 (m, 5 H, C_6H_5^-). A complete material balance was obtained.

Analysis of the mixture was accomplished by integration of the aromatic region of the nmr spectrum using the one-proton resonance of **6** at δ 7.4–7.6 as a standard. The ratio of **6** to phenylpropionic acid was determined to be 2.4:1 from an average of six experiments.

Registry No.—**1**, 4298-52-6; **3**, 20795-13-5; **4**, 20805-23-6; **5**, 36740-08-6.

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The Synthesis of Arylacetylenes. 3,5-Di-*tert*-butylphenylacetylene¹

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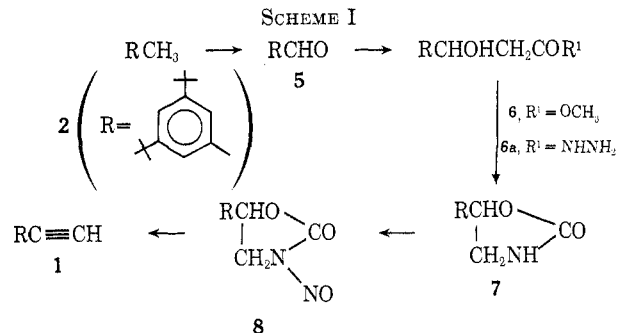
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In connection with a research program designed to provide molecules of the rotaxane type² we required a quantity of 3,5-di-*tert*-butylphenylacetylene (**1**). As

starting material 3,5-di-*tert*-butyltoluene (**2**) was readily available.³ Our first route involved oxidation of **2** to 3,5-di-*tert*-butylbenzoic acid (**3**), which was converted into 3,5-di-*tert*-butylacetophenone (**4**). Hopefully reaction of **4** with phosphorus pentachloride followed by treatment of the dichloride (or chloro olefin) produced with strong base should yield **1**. Although **4** was readily prepared, all attempts to convert **4** in good yield to **1** were unsuccessful. A similar failure to convert 2-acetylthiophene to 2-thienylacetylene in good yield is reported.⁴

The successful route is illustrated in Scheme I. The good overall yield of 41% (all yields of pure material)



from **2** to **1** indicates that this route deserves serious consideration for the synthesis of arylacetylenes.

The conversion of **5** to **8** was accomplished essentially as described.⁵ On treatment of **8** with butylamine⁶ a 95% yield of **1** was obtained. This reagent proved superior to the aqueous alcoholic alkali previously used for the synthesis of phenylacetylene.^{5,6a}

Experimental Section⁷

3,5-Di-*tert*-butylbenzaldehyde (5).—A solution of 228 g of **2**, 300 g of *N*-bromosuccinimide, and 1 g of benzoyl peroxide in 600 ml of CCl_4 was heated at reflux for 4 hr. After filtration the CCl_4 was removed on a rotary evaporator and the residue was added to a solution of 430 g of hexamethylenetetramine in 300 ml of water and 300 ml of ethanol. This solution was refluxed for 4 hr, 200 ml of concentrated HCl was added, and refluxing was continued for 30 min. The organic product was isolated as usual to yield a residue which was recrystallized from Skellysolve B [petroleum ether (bp 60 – 68°)] to yield 153 g (63% from **2**) of **5**,⁸ mp 84 – 85° .

(1) Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, U. S. Air Force, under Grant No. AFOSR-72-2237. The U. S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation hereon.

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(6a) NOTE ADDED IN PROOF.—Recently, **5** has been converted into **1** by the method of E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).

(7) All melting points are uncorrected. Analyses were performed by M-H-W Laboratory, Garden City, Mich. 48135. The phrase "worked up as usual" means that an ether-benzene solution of the products was washed with aqueous acid and/or alkali and saturated salt solution, and was filtered through anhydrous magnesium sulfate. The solvents were then removed on a rotary evaporator and the residue was treated as described. All experiments were repeated at least once. All new compounds gave ir, nmr, and mass spectra consistent with the assigned structures.

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Methyl β -(3,5-Di-*tert*-butylphenyl)- β -hydroxypropionate (6).—A mixture of 136 g (0.625 mol) of 5, 400 ml of benzene, and 44 g (0.705 g-atom) of activated zinc⁹ was heated until 200 ml of benzene had distilled. After 200 ml of dry ether was added, 96 g (0.634 mol) of methyl bromoacetate was added during 5 hr to the refluxing mixture. After refluxing for 10 hr more, the cooled reaction mixture was treated with 1 l. of NH_4OH and the organic products were isolated as usual. A small amount of the crude residue was crystallized from Skellysolve B to yield the analytical sample of 6, mp 66–67°. The remainder was treated as described below to yield 6a.

Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3$: C, 73.9; H, 9.7. Found: C, 73.9; H, 9.7.

β -(3,5-Di-*tert*-butylphenyl)- β -hydroxypropionic Acid Hydrazide (6a).—To a solution of 80.0 g of crude 6, obtained as above, in 60 ml of ethanol was added 10.0 g of anhydrous hydrazine. The mixture was heated until a clear solution resulted. After cooling, the resulting crystalline hydrazide was recrystallized from benzene-ethanol to yield 66.7 g (82.5% from 5) of pure 6a, mp 143–145°.

Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_2$: C, 69.8; H, 9.6; N, 9.6. Found: C, 69.5; H, 9.4; N, 9.8.

5-(3,5-Di-*tert*-butylphenyl)oxazolidone (7).—To a stirred mixture of 32.0 g of 6a, 200 ml of 6 *N* hydrochloric acid, and 50 ml of chloroform at 0–5° was added 12.0 g of sodium nitrite during 30 min. After stirring for 30 min the excess nitrous acid was destroyed with sodium sulfite. The organic product was taken into three 100-ml benzene extracts, which were washed with saturated salt solution and dried by pouring through magnesium sulfate. This benzene solution was added to 50 ml of refluxing benzene in a flask arranged so that the nitrogen evolved could be collected and measured over water. After nitrogen evolution had ceased the solvent was distilled and the residue was crystallized from Skellysolve B-ether to yield 27.1 g (90%) of 7, mp 167.5–168.5°.

Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}$: C, 74.1; H, 9.2; N, 5.1. Found: C, 74.1; H, 9.2; N, 5.1.

5-(3,5-Di-*tert*-butylphenyl)-3-nitrosooxazolidone (8).—By method B,⁵ 10.5 g of 7 in 50 ml of pyridine on treatment with 5.9 g of nitrosyl chloride in 30 ml of acetic anhydride was converted into 10.8 g (93.5%) of 8, mp 193–195° dec, after recrystallization of crude 8 from acetone.

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_3$: C, 67.1; H, 8.0; N, 9.2. Found: C, 67.1; H, 7.9; N, 8.9.

3,5-Di-*tert*-butylphenylacetylene (1).—To a refluxing solution of 4.90 g (0.066 mol) of butylamine in 100 ml of chloroform was added 20.0 g (0.066 mol) of 8 during 30 min. About 95% of the theoretical nitrogen was evolved. After removal of solvent, distillation yielded 13.4 g (95%) of 1, mp 87.0–88.5°. When a similar experiment was done in refluxing ether the yield was 78%.

Anal. Calcd for $\text{C}_{16}\text{H}_{22}$: C, 89.7; H, 10.4. Found: C, 89.7; H, 10.4.

Registry No.—1, 36720-94-2; 6, 36763-76-5; 6a, 36720-95-3; 7, 36720-96-4; 8, 36720-97-5.

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Reaction of Naphthalene Dianions with Tetrahydrofuran and Ethylene^{1a}

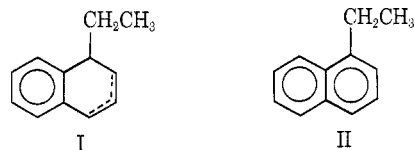
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In the course of our work with reactions of arene anion radicals, a frequently observed minor product from many reactions of sodium or lithium naphthalene in THF was identified as a mixture of 1-ethylidihydro-

naphthalenes (I). Identity was confirmed through aromatization to the known 1-ethylnaphthalene (II)



and conversion to its picrate complex. The recent work of Bates and coworkers on the cleavage of THF into ethylene and acetaldehyde enolate by strong bases² led us to consider this reaction as a source of the two-carbon fragment. The anion radical of naphthalene is not a particularly strong base,³ but the dianion should be considerably stronger. The observations that the amounts of ethylidihydro-naphthalene formed in THF solutions of potassium or sodium naphthalene were always very small at most, while lithium naphthalene solutions sometimes exhibited as much as 5% after standing for several days, coupled with the fact that the lithium anion radical is most prone to disproportionate to a mixture of dianion and neutral arene,⁴ strongly supported this hypothesis (see Table I). Warming a solution of naphthalene in

TABLE I
YIELDS OF 1-ETHYLIDIHYDRO- AND 1-ETHYLNAPHTHALENE^a

Solvent	Metal	Naphthalene/ metal ratio	Addend	Ethylated material, % yield ^b
THF	Li	0.22		54
Tetrahydropyran	Li	0.22		0
THF	Li	1.04		7
THF	K	0.33		~5
THF	Na	0.33		~5
1,2-Dimethoxy- ethane	Li	0.22		24
1,2-Dimethoxy- ethane	Li	0.22	750 mg of <i>n</i> -butyl vinyl ether	33
Tetrahydropyran	Li	0.29	750 mg of <i>n</i> -butyl vinyl ether	~10

^a See Experimental Section for details. ^b Relative to original naphthalene concentration.

THF containing a fourfold excess of lithium yielded ethylene, easily identified through its dibromide, and similar treatment of 2-methyltetrahydrofuran yielded ethylene and propylene in a 1:1.5 ratio. Bates observed only propylene formation from the "α-cleavage" reaction of 2-methyltetrahydrofuran with butyllithium.² (The "β-cleavage reaction" reported by Bates for this substrate² probably also occurred in our reaction, but we did not search for the 4-penten-1-ol product.)

Noting that solutions of excess lithium and naphthalene in THF readily give rise to a large amount of naphthalene dianion at 25°,⁵ we carried out the series of

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