

TABLE I  
ACETYLATION OF ALKYL BENZENES AT 0 AND 40°

Hydrocarbon	Temp, °C	Yield of ketone fraction, %		
		Acetophenone	<i>p</i> -Alkylacetophenone	Dialkylacetophenone
Ethylbenzene	0	3.0	91.3	3.0
	40	2.6	96.3	
Propylbenzene	0	4.8	84.7	
	40	2.9	89.3	
Isopropylbenzene	0	22.7	46.2	20.2
	40	24.5	51.8	18.5
<i>sec</i> -Butylbenzene	0	32.8	40.4	28.2
	40	33.9	37.4	29.0
<i>tert</i> -Butylbenzene	0	14.7	55.2	23.5
	40	17.3	50.4	24.2

No anomalous behavior was noted between Friedel-Crafts acetylations run at 0 and 40° under conditions specified by Nightingale, Huckler, and Wright. Normal monoalkylbenzenes showed little or no tendency to disproportionate even at 40° (Table I) and consequently gave high yields of the corresponding *p*-alkylacetophenone. In the case of secondary and tertiary monoalkylbenzenes, however, disproportionation was competitive with acetylation and resulted in significant yields of the corresponding dialkylacetophenones (20–30%) and acetophenone. These data suggest that dialkylacetophenones in both cases (0 and 40°) result from an initial disproportionation of the monoalkylbenzene, a transfer which may be attributed to an essentially free alkyl cation generated from the protonated starting hydrocarbon. Furthermore, the rate of generation of the alkyl cation is slightly favored over direct acetylation of the monoalkylbenzene at the higher temperature as indicated by a corresponding increase in the yield of acetophenone.

The inverse acetylation of isopropylbenzene and *sec*-butylbenzene at 40° showed a drastic reduction in the formation of acetophenone (Table II) and a correspond-

TABLE II

ACETYLATION OF ALKYL BENZENES AT 40° INVERSE CONDITIONS

	Acetophenone, %	<i>p</i> -Alkylacetophenone, %
Isopropylbenzene	4.2	85.2
<i>sec</i> -Butylbenzene	3.4	93.4

ing increase in the yield of *p*-alkylacetophenone, indicating that a major portion of the acetylation reaction had occurred during the interval required for addition of the hydrocarbon (approximately 3–5 min). This was verified by repeating the reaction and quenching aliquots of the mixture at intervals of 5, 15, 30, 45, and 60 min after completion of addition of the hydrocarbon. Gas chromatographic analysis of these samples showed that essentially no quantitative change occurred after 15 min of refluxing.

The disparity between data of this investigation and those obtained by Nightingale and coworkers probably results from elimination of a possible delay between completion of addition of the hydrocarbon to aluminum chloride and subsequent rapid addition of the acetyl chloride, a delay which could result in a significant amount of disproportionation.

**Registry No.**—Ethylbenzene, 100-41-4; propylbenzene, 103-65-1; isopropylbenzene, 98-82-8; *sec*-butylbenzene, 135-98-8; *tert*-butylbenzene, 98-06-6.

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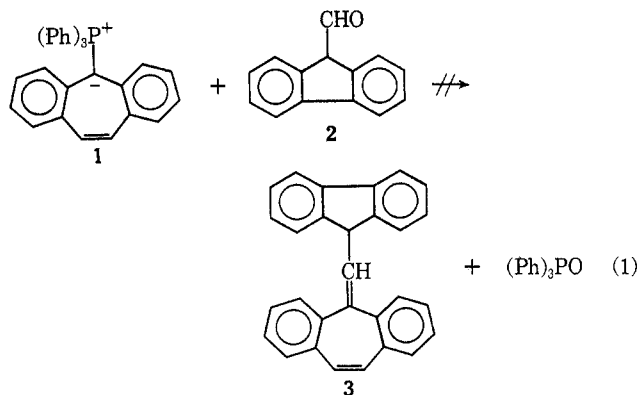
### A Divergent Reaction between a Phosphonium Ylide and an Aldehyde. $\alpha$ -Alkylation<sup>1</sup>

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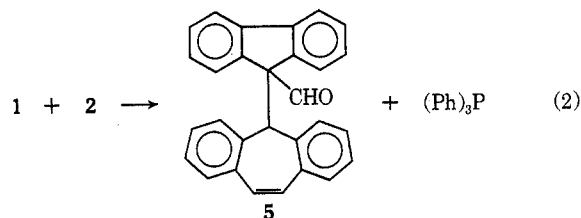
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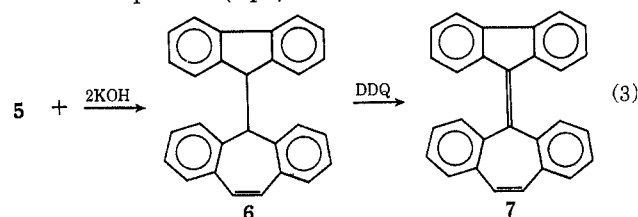
The Wittig reaction and its congeners have provided a highly useful alternative to the alcohol dehydration route to olefins. We attempted to use the Wittig reaction for the preparation of the fluorenylheptafulvene **3** (eq 1).



The interesting ylide **1** was generated by dehydrochlorination of the corresponding phosphonium chloride **4** with *n*-butyllithium. Treatment of the resulting brick red solution of the ylide with 9-fluorencarboxaldehyde (**2**) gave not the expected olefin **3** but a new aldehyde **5** and triphenylphosphine (eq 2).



The structure of **5** was proved by its elemental analysis, by nmr and ir spectra, and by conversion to **7**, a known compound<sup>3</sup> (eq 3).

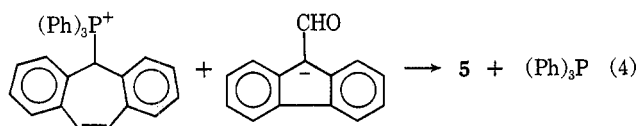


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(3) B. Pullman, A. Pullman, E. D. Bergman, H. Berthod, E. Fischer, Y. Hirshberg, D. Lavie, and M. Mayot, *Bull. Soc. Chim. Fr.*, 73 (1952).

The divergent reaction described by eq 2 is unprecedented. We suggest that alkylation took place at the  $\alpha$  position of the aldehyde because of the unusual acidity of the  $\alpha$  proton in 9-fluorencarboxaldehyde and eq 4 offers a plausible mechanism for this reaction.



If the proposed mechanism is correct, aldehydes and other carbonyl compounds containing  $\alpha$  protons of comparable acidity might be expected to undergo this  $\alpha$  alkylation reaction with phosphonium ylides.

#### Experimental Section<sup>4</sup>

**Preparation of 7-(1,2,4,5-Dibenzocycloheptatrienyl)triphenylphosphonium Chloride (4).**—7-Chloro-1,2,4,5-dibenzocycloheptatriene (680 mg, 3 mmol), prepared by the method of Berti,<sup>5</sup> was combined with triphenylphosphine (787 mg, 3 mmol) in 10 ml of dry benzene and the solution warmed at 50° for 12 hr. The mixture was cooled to room temperature and a white crystalline precipitate (1.138 g) was collected. This material showed the correct nmr spectrum.

*Anal.* Calcd for C<sub>28</sub>H<sub>20</sub>ClP: C, 81.07; H, 5.36. Found: C, 81.21; H, 5.24.

**Reaction of 9-Fluorencarboxaldehyde (2) with 7-(1,2,4,5-Dibenzocycloheptatrienylidene)triphenylphosphorane (1). Formation of the Aldehyde 5.**—The ylide 1 was generated *in situ* at 0° by treating 4 (8.8 g, 18 mmol) in 50 ml of dry ether with *n*-butyllithium (12 ml of a 1.5 mol hexane solution; Foote Chemical Co.) in a nitrogen atmosphere. The solution became brick red and was stirred for 40 min, after which time 9-fluorencarboxaldehyde (3.5 g, 18 mmol), prepared by the method of Wislicenus and Waldmuller,<sup>6</sup> in 25 ml of dry ether was introduced by means of a hypodermic syringe. A copious white precipitate formed immediately and the mixture was refluxed for 17 hr. The mixture was cooled to room temperature and the crystalline precipitate filtered. Evaporation of the filtrate provided a slightly yellow semisolid which was treated with warm pentane and filtered. The cooled filtrate deposited 2 g of a white solid which was shown to be triphenylphosphine by comparison with an authentic sample. The crystalline precipitate which was filtered from the original reaction mixture was treated with 300 ml of chloroform and 300 ml of water. The chloroform layer was separated, dried (MgSO<sub>4</sub>), and filtered. Evaporation of the filtrate gave a yellow oil which was shaken and refluxed with 50 ml of MeOH to give a crystalline colorless solid. The filtered dry solid (3.6 g) was homogeneous by tlc. The analytical sample was prepared by successive recrystallization from CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>-EtOH, and C<sub>6</sub>H<sub>6</sub>, to give colorless prisms, mp 183–186°. The product gave a positive test with Tollens reagent. The ir spectrum (KBr), in addition to a strong carbonyl band at 1709 cm<sup>-1</sup>, contained weak, sharp bands at 2817 and 2703 cm<sup>-1</sup>, characteristic of aldehydes.<sup>7</sup> The nmr spectrum (CDCl<sub>3</sub>) exhibited signals at  $\tau$  0.63 (s, 1, CHO), 2.5–3.2 (m, 14, Ar H), 3.43 (s, 2, ethylene), 3.78 (d, 2, *J* = 7 Hz, Ar H; the number 1 and 10 protons of the dibenzotropyliidene group are shifted upfield by shielding from the fluorenyl group), and 5.23 (s, 1, methine proton of the tropyliidene ring).

(4) Melting points are uncorrected. Nmr spectra were recorded on a Varian Associates A-60 spectrometer, ir spectra on a Perkin-Elmer Model 137 spectrometer, and uv spectra on a Cary Model 11 spectrometer. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and Schwarzkopf Laboratories, Woodside, N. Y.

(5) G. Berti, *Gazz. Chim. Ital.*, **87**, 293 (1957); *Chem. Abstr.*, **52**, 11803 (1958).

(6) W. Wislicenus and M. Waldmuller, *Chem. Ber.*, **42**, 786 (1909).

(7) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 48.

*Anal.* Calcd for C<sub>29</sub>H<sub>20</sub>O: C, 90.60; H, 5.24. Found: C, 90.63; H, 5.26.

**Decarbonylation of the Aldehyde 5 to Give 7-(9'-Fluorenyl)-1,2,4,5-dibenzocycloheptatriene (6).**—To a refluxing solution of 5 (192 mg, 0.5 mmol) in 50 ml of absolute EtOH was added 0.5 g of KOH pellets. A white precipitate formed immediately and the mixture was refluxed for 1 hr. The precipitate was filtered, washed with MeOH, and dried to give 174 mg of colorless solid, mp 293–294°. The melting point was unchanged on recrystallization from benzene: uv max (methylcyclohexane) 245 m $\mu$  ( $\epsilon$  19800), 269 (22500), 270 (18600), 290 (15030), and 302 (16100); ir max (Nujol) 12.31, 12.91, 13.10, 13.17, 13.33, 13.39, and 13.69  $\mu$ ; mass spectrum<sup>8</sup> *m/e* 356 (1, parent ion, C<sub>28</sub>H<sub>20</sub>), 191 (100, dibenzotropyliidene ion, C<sub>18</sub>H<sub>11</sub>), and 165 (79, fluorenyl ion, C<sub>13</sub>H<sub>9</sub>).

*Anal.* Calcd for C<sub>28</sub>H<sub>20</sub>: C, 94.36; H, 5.64. Found: C, 94.59; H, 5.51.

**Dehydrogenation of 6 to the Tetrabenzosquifulvalene 7.**—The hydrocarbon 6 (86 mg, 0.24 mmol) was combined with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DDQ (114 mg, 0.5 mmol) in 5 ml of bromobenzene and the mixture refluxed for 12 hr. The hydroquinone separated on cooling and was filtered. The filtrate was washed with saturated bicarbonate, dried (MgSO<sub>4</sub>), and filtered. Evaporation of the filtrate gave a pale yellow powder (83 mg), mp 298–300° (lit.<sup>3</sup> mp 303°). The melting point was unchanged on recrystallization from benzene. The uv spectrum contained a complex series of bands and was identical with that reported previously for this compound.<sup>3</sup>

**Registry No.**—4, 25992-35-2; 5, 25992-36-3; 6, 25966-99-8.

(8) We are grateful to Professor J. B. Westmore for kindly supplying the mass spectrum and its interpretation.

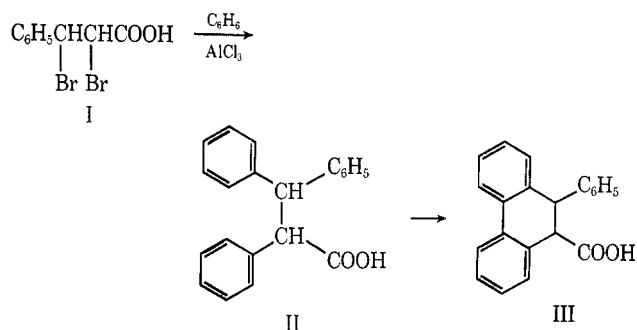
### The Friedel-Crafts Reaction with 2,3-Dibromo-3-phenylpropionic Acid

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The reaction of 2,3-dibromo-3-phenylpropionic acid (I) with benzene in the presence of aluminum bromide is a normal Friedel-Crafts synthesis, producing 2,3,3-triphenylpropionic acid (II).<sup>2</sup> However, Earl and



Wilson<sup>3</sup> have reported that when aluminum chloride was used in this reaction another substance, which they believed to be a phenanthrene derivative III, was

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(1) Abstracted from a thesis presented by A. Costa Neto to the Instituto de Química, Universidade Federal do Rio de Janeiro, for the M.S. degree, 1965.

(2) C. C. Price, *Org. Syn.*, **33**, 98 (1953).

(3) J. C. Earl and C. H. Wilson, *J. Proc. Roy. Soc., N. S. W.*, **65**, 178 (1932); *Chem. Abstr.*, **26**, 2976 (1932).