

**Cyclopentanone-2,2,5,5- $d_4$ .**—Ten grams (0.119 mol) of freshly distilled, dry cyclopentanone was added to 40 ml of heavy water. Stirring was begun and 0.05 ml of 40% sodium deuterioxide in deuterium oxide was added. After 5 min, the solution was extracted with three 20-ml portions of methylene chloride. The combined methylene chloride layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The process was repeated with a fresh 40-ml portion of heavy water and the product (6.80 g, 65%) distilled, that portion boiling from 126–129° being retained. Analysis by nmr indicated greater than 98 at. % D on the  $\alpha$  positions.

**Methylene- $d_2$ -cyclopentane-2,2,5,5- $d_4$ .**—To 2.439 g (0.0546 mol) of sodium hydride (53.6%) dispersed in mineral oil and 20.0 g (0.0555 mol) of methyl- $d_3$ -triphenylphosphonium bromide, was added approximately 250 ml of freshly distilled bis(2-ethoxyethyl) ether while the system was swept with dry nitrogen. The nitrogen sweep was passed through three traps, the first cooled with ice and the remaining two cooled with Dry Ice. After addition of the solvent, the temperature of the mixture was raised, over the period of 1 hr, to 60–70° and maintained at this level for 3 hr. The formation of the intermediate methylene- $d_2$ -triphenylphosphorane was evidenced by the appearance of a yellow color shortly after stirring was begun. The mixture was then cooled to 30° and 4.81 g (0.0545 mol) of cyclopentanone-2,2,5,5- $d_4$  was added dropwise. The mixture was then heated to 85–90° over the period of 1 hr and maintained at this temperature overnight while the system was swept slowly with nitrogen. The crude product was recovered from the first Dry Ice trap. The nmr spectrum showed that ~10–15% benzene had been produced. The isotopic purity, determined from the integrated nmr spectrum was ~98 at. % D on the exocyclic methylene group. The product was purified by gas chromatography, using a 6 ft  $\times$  0.25 in. o.d. column of 15% di(2-ethylhexyl) sebacate on diatomaceous earth at room temperature. Although 2–3% of the mixture consisted of impurities other than benzene, no attempt was made to isolate or identify these components. Benzene was identified by its nmr signal and its retention time on the chromatographic column compared to the retention time of an authentic sample. This procedure yielded 3.05 g (64%) of product.

**Methylenecyclopentane-2,2,5,5- $d_4$ .**—The methylenetriphenylphosphorane was formed by adding 12.8 ml of a 2.96 *N* solution of butyllithium in benzene to a slurry of 12.5 g (0.0352 mol) of methyltriphenylphosphonium bromide in approximately 150 ml of bis(2-methoxyethyl) ether. The procedure above was then followed. A yield of 1.18 g (39%) was obtained from 3.05 g of cyclopentanone-2,2,5,5- $d_4$ . Analysis of the product by nmr showed greater than 98 at. % D on the 2,5 positions and less than 1 at. % D on the exocyclic methylene.

**Registry No.**—Methyl- $d_3$ -triphenylphosphonium bromide, 1787-44-6; cyclopentanone-2,2,5,5- $d_4$ , 3997-89-5; methylene- $d_2$ -cyclopentane-2,2,5,5- $d_4$ , 25966-75-0; methylenecyclopentane-2,2,5,5- $d_4$ , 25966-76-1.

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### Friedel-Crafts Acetylation of Monoalkylbenzenes in Refluxing Carbon Disulfide

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Nightingale, Hucker, and Wright<sup>1</sup> reported that Friedel-Crafts acetylation of primary and secondary

monoalkylbenzenes in refluxing carbon disulfide (40°) gave acetophenone and a dialkylacetophenone along with the corresponding *p*-alkylacetophenone. This abnormal behavior was attributed to an initial disproportionation of the primary or secondary monoalkylbenzene, competitive with the acetylation reaction. Tertiary monoalkylbenzenes however gave low yields of the normal product with an apparent absence of the corresponding dialkylacetophenone and acetophenone, a result which appears incongruous in terms of the mechanism suggested by Nightingale, *et al.*, for the disproportionation of the primary and secondary alkylbenzenes.

Disproportionations associated with the acetylation of secondary and tertiary alkylbenzenes at 0° have been accounted for in terms of an intermolecular transfer of an alkyl group as an essentially free cation generated from the  $\alpha$  complexed hydrocarbon,<sup>2,3</sup> whereas disproportionation of primary alkylbenzenes with essentially no rearrangement of the alkyl group has been attributed to a different mechanism.<sup>4</sup>

Barring the operation of an alternate mechanism, it is difficult to reconcile the products and mechanism suggested for acetylations carried out at 40° in carbon disulfide with those established for the same reaction at 0°. In order to account for these anomalies and to correlate the acetylations at 40° with those run at 0° a re-examination of the reaction has been undertaken.

#### Experimental Section

The acetylations in refluxing carbon disulfide were carried out as directed by Nightingale, Hucker, and Wright,<sup>1</sup> with particular attention being paid to the sequence and mode of addition of reagents. Thus the monoalkylbenzene was quickly added to the stirred mixture of aluminum chloride in carbon disulfide and immediately followed by addition of the acetyl chloride. The latter was added as rapidly as permitted by the exothermic reaction. Following a 3-hr reflux and subsequent work-up, the ether was removed by means of a spinning-band column. Samples (1  $\mu$ l) of the residual liquid were fractionated on a Model 817 Packard dual column gas chromatograph fitted with a thermal detector. Quantitative analysis was accomplished on a 6 ft  $\times$  0.25 in. column of 10% Apiezon L on 70–80 mesh Anakron A programmed at 5°/min from 100 to 250°, using *p*-methylacetophenone as an internal standard. Samples of the individual components of the reaction mixture were isolated by means of a Wilkens Autoprep gas chromatograph equipped with a 20 ft  $\times$  3/8 in. silicone gum rubber column. These samples were utilized for elemental analysis, ir examination, and preparation of phenylhydrazone derivatives.

These reactions were rerun under identical conditions with the exception that the reaction mixture was maintained at 0° throughout. Acetylations were also carried out at 40° by employing the inverse addition of the hydrocarbon to the acetyl chloride-aluminum chloride complex.

#### Results and Discussion

The identity of the products following gas chromatographic separation was checked by means of carbon and hydrogen analysis, ir spectra, and the preparation of 2,4-dinitrophenylhydrazones. Agreement to  $\pm 0.1\%$  for carbon and hydrogen analysis and 1° in melting point was observed. Quantitative gas chromatographic analysis of the product mixture showed the presence of trace amounts of aromatic hydrocarbons. The yields of the major components are listed in Table I.

(2) R. L. Burwell, Jr., and A. D. Shields, *J. Amer. Chem. Soc.*, **77**, 2766 (1955).

(3) D. A. McCauley and A. P. Lien, *ibid.*, **75**, 2411 (1953).

(4) A. Streitwieser, Jr., and L. Reif, *ibid.*, **86**, 1988 (1964).

(1) D. V. Nightingale, H. B. Hucker, and O. L. Wright, *J. Org. Chem.*, **18**, 244 (1953).

TABLE I  
ACETYLTION 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

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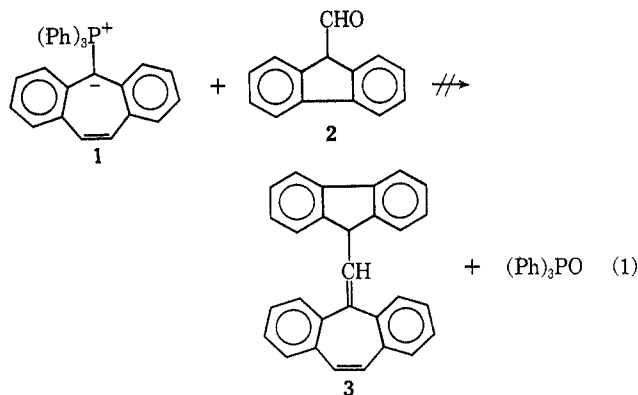
### A Divergent Reaction between a Phosphonium Ylide and an Aldehyde. $\alpha$ -Alkylation<sup>1</sup>

L. SALISBURY<sup>2</sup>

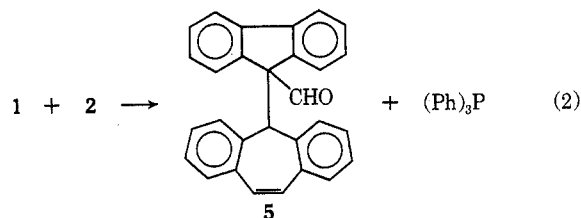
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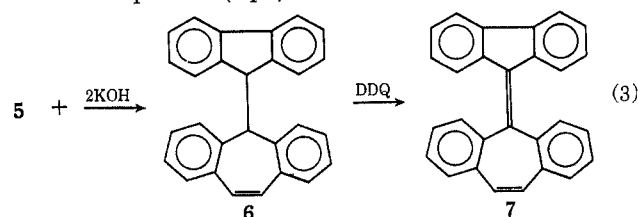
The Wittig reaction and its congeners have provided a highly useful alternative to the alcohol dehydration route to olefins. We attempted to use the Wittig reaction for the preparation of the fluorenylheptafulvene **3** (eq 1).



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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(2) Department of Chemistry, Newark State College, Union, N. J.

(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).