the C9-C*H*$(CH_3)_2$ multiplet is centered at δ 2.81 in **12c**. The C7-OCH_3 resonances appear at δ 3.54 and C7-CH_3 at 2.15 in **12e** and **12f**, respectively. Peaks at δ 1.81-1.86 (C3-CH_3), 2.18-2.27 (C2-CH_3), 4.70-4.95 (NH), 5.28-5.42 (C7-H_2), and 6.35-7.90 (Ar H) characterize the ^1H NMR parameters for pyrazoles **13**. In **13b**, C7-CH_3 (1.63); in **13c** the C7-CH_3's are at 1.69 and 1.78, whereas in **13d** C3-CH_2CH_3 (1.10) and C3-CH_2CH_3 (2.41, J = 7.6). The aromatic OCH_3 in **13e** and CH_3 in **13f** appear at δ 3.68 and 2.24, respectively.

Tables IV and V (supplementary material) list the ^{13}C NMR parameters for compounds **12** and **13**, respectively. The ranges for the ^{13}C NMR parameters for **12** (Table IV) are as follows: C3-CH_3 at δ 6.4-6.7, C2-CH_3 at δ 11.8-12.2, C9-CHRR^1 at δ 26.6-27.3 (**12b** and **12c** at 30.8 and 36.9, respectively), C9 at δ 62.7-63.6 (**12b**, **12c**, and **12i** at 67.0, 69.9, and 70.5, respectively), C3 at δ 90.1-92.6 (**12d** at 98.5), C2 at δ 143.5-146.5, C3a at δ 145.0-148.0. The ranges for the ^{13}C NMR parameters for **13** (Table V) are as follows: C3-CH_3 at δ 7.5-7.9, C2-CH_3 at δ 12.1-12.7, C3 at δ 107.7-110.0 (**13d** at 114.9), C7 δ 109.5-110.2 (**13b** and **13c** at 119.0 and 122.6, respectively).

Precise mass spectra were recorded using a Du Pont 21-492B instrument with a resolution of 3300 or 5000. Table VI (supplementary material) lists the mass spectral data for compounds **12** and **13**. All precise mass found were within 0.003 mass units of the calculated values. The major fragment ions and in many cases the base peaks for compounds **12** were $M^+ - 77$ (Ph) and M^+ - (C9-CHRR^1). Pyrazoles **13** had peaks for $M^+ - 1$ and (Ph - CRR^1)$^+$ in their mass spectra.

Reactions of Phosphoranes 7 with Isocyanates 8: Preparations of 4,9-Dihydropyrazolo[5,1-*b*]quinazolines 12 and *N*-α-Styryl-5-(phenylamino)pyrazoles 13. General Method. A solution of the freshly distilled isocyanate **14** (2.5 mmol) in 10 mL of dry toluene was added dropwise with stirring at room temperature to a solution of the phosphorane **7**[11] (2.0 mmol) in 35 mL of dry toluene. After all of the isocyanate was added, the mixture was heated under reflux for 16 h. The solvent was removed in vacuo, and the mixture were chromatographed, eluting with petroleum ether/ethyl acetate (increasing polarity from 90/10 to 80/20). This procedure cleanly separated the following in order of elution:

(a) *N*-α-Styryl-5-(phenylamino)pyrazoles **13** were obtained as orange oils, which resisted recrystallization; the samples were determined to be pure by TLC and NMR (>97%) analyses. Precise mass analyses were shown to be within 0.002 of that calculated (see Table VI in supplementary material).

(b) 4,9-Dihydropyrazolo[5,1-*b*]quinazolines **12** were obtained as off-white solids, which were recrystallized to a constant melting point from diethyl ether; the samples were determined to be pure by TLC and NMR (>97%) analyses. Precise mass analyses were shown to be within 0.002 of that calculated (see Table VI in supplementary material).

(c) Triphenylphosphine oxide.

Supplementary Material Available: ^1H NMR, ^{13}C NMR, and mass spectral data for 4,9-dihydropyrazolo[5,1-*b*]quinazolines **12** and *N*-α-styryl-5-(phenylamino)pyrazoles **13** (Tables II-VI) (5 pages). Ordering information is given on any current masthead page.

Synthesis of 1,3,5-Tri-*n*-alkylbenzene Compounds

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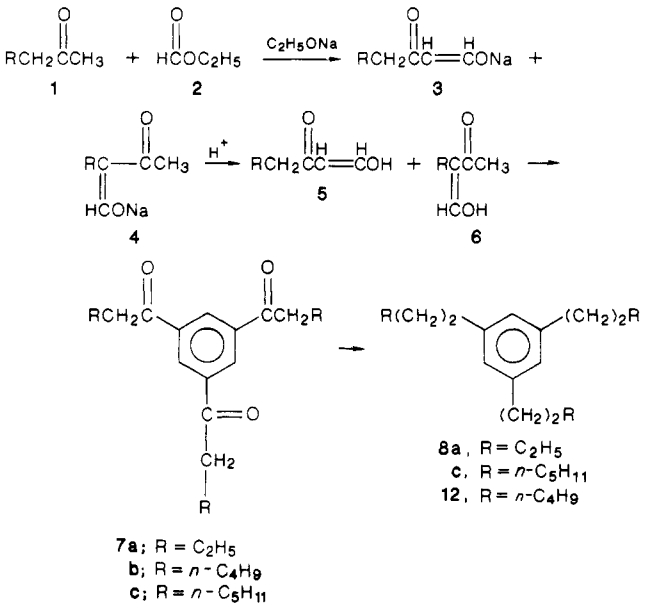
Our previous study[2] was concerned with the formation of carbon-carbon σ bonds by $NiCl_2$(dppe)[3]-catalyzed cross-coupling of Grignard reagents and polychlorobenzenes. By this method we were able to prepare pure tri- and tetraalkylated benzene compounds, which were required for related studies concerned with chemical structure versus physical property correlation of high temperature stable fluids.[4] In our continuing studies we have examined an alternate synthesis of 1,3,5-trialkylbenzenes by reduction of 1,3,5-triacylbenzenes. We have also extended our original study of synthesizing pure 1,3,5-trialkylated benzenes to the synthesis of mixtures of trialkylated benzenes. Such mixtures should provide improved rheologic properties to the resulting fluid materials for wide liquid range fluid applications.

Chart I



Reduction of Triacylbenzene Compounds. We have synthesized 1,3,5-trialkylbenzene compounds by the reduction of 1,3,5-triacylbenzenes. The triacylbenzenes were synthesized by a method previously reported for the preparation of hydroxymethylene ketones,[5-8] where the former were byproducts. For the present study, experimental conditions were chosen to facilitate the cyclization reaction leading to triacylbenzenes. The method involves base-catalyzed condensation of methyl ketones with ethyl formate, which provides a mixture of sodium salts of hydroxymethylene ketones (**3** and **4**) (see Chart I). Decomposition of these salts with acid leads to self-condensation of one of the components to a symmetrical triacylbenzene as shown in Chart I.

The hydrolysis product of **3** yielded **5**, which spontaneously cyclized to **7**; however, the hydrolysis product of **4** yielded **6**, which is not capable of trimerization. The ratio of **3** to **4** may depend on the type of methyl ketone and the base used. In our studies with sodium ethoxide and longer chain methyl ketones (**1**, R = C_2H_5, *n*-C_4H_9, and *n*-C_5H_{11}), the **3** isomer predominated since yields of ~ 60-70% of **7** were obtained. With the methyl ketones we

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(2) Eapen, K. C.; Tamborski, C. *J. Org. Chem.* **1984**, *49*, 478.
(3) The ligand dppe refers to $Ph_2P(CH_2)_2PPh_2$.
(4) Eapen, K. C.; Snyder, C. E., Jr.; Gschwender, L.; Tamborski, C. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* **1984**, *29*(4), 1053.
(5) Mariella, R. P.; Godar, E. *J. Org. Chem.* **1957**, *22*, 566.
(6) Benary, E.; et al. *Ber.* **1926**, *59*, 2198.
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0022-3263/88/1953-5564$01.50/0

Table I. Mixed 1,3,5-Trialkylbenzenes

RMgX, R	mol RMgX/$C_6H_3Cl_3$	bp range, °C	GC area, %	yield,[a]%	MS analyses (EI) (m/e)[b]
n-C_6H_{13} (**10**)	2.0	153–184	**12** 30.0	79	330 $(M)^+$, 260 $(M - C_5H_{10})^+$
n-C_8H_{17} (**11**)	1.0	at 0.1 mm	**13** 47.8		358 $(M)^+$, 288 $(M - C_5H_{10})^+$, 260 $(M - C_7H_{14})^+$
			14 19.4		386 (M)+, 316 $(M - C_5H_{10})^+$, 288 $(M - C_7H_{14})^+$
			15 2.8		414 $(M)^+$, 316 $(M - C_7H_{14})^+$
n-C_8H_{17} (**11**)	2.0	195–230	**15** 31.8	77	414 $(M)^+$, 316 $(M - C_7H_{14})^+$
n-$C_{10}H_{21}$ (**16**)	1.0	at 0.005 mm	**20** 47.1		442 $(M)^+$, 344 $(M - C_7H_{14})^+$, 316 $(M - C_9H_{18})^+$
			21 20.0		470 $(M)^+$, 372 $(M - C_7H_{14})^+$, 344 $(M - C_9H_{18})^+$
			22 1.1		not determined
n-C_6H_{13} (**10**)	3.0	[c]	**12** 19.9	76	330 $(M)^+$, 260 $(M - C_5H_{10})^+$
n-$C_{10}H_{21}$ (**16**)	2.0		**17** 44.1		386 $(M)^+$, 316 $(M - C_5H_{10})^+$, 260 $(M - C_9H_{18})^+$
			19 30.5		442 $(M)^+$, 372 $(M - C_5H_{10})^+$, 316 $(M - C_9H_{18})^+$
			22 5.5		498 $(M)^+$, 372 $(M - C_9H_{18})^+$
n-C_6H_{13} (**10**)	3.0	[c]	**12** 11.7	78	330 $(M)^+$, 260 $(M - C_5H_{10})^+$
n-C_8H_{17} (**11**)	2.0		**13** 25.6		358 $(M)^+$, 288 $(M - C_5H_{10})^+$, 260 $(M - C_7H_{14})^+$
n-$C_{10}H_{21}$ (**16**)	1.0		**14**, **17** 30.2		386 $(M)^+$, 316 $(M - C_5H_{10})^+$, 288 $(M - C_7H_{14}$ 260 $(M - C_9H_{18})^+$
			15, **18** 20.4		414 $(M)^+$, 344 $(M - C_5H_{1,0})^+$, 316 $(M - C_7H_{14})^+$ 288 $(M - C_9H_{18})^+$
			19 9.4		442 $(M)^+$, 372 $(M - C_5H_{10})^+$, 344 $(M - C_7H_{14})^+$
			20		316 $(M - C_9H_{18})^+$
			21 2.5		470 $(M)^+$, 372 $(M - C_7H_{14})^+$, 344 $(M - C_9H_{18})^+$
			22 0.25		not determined

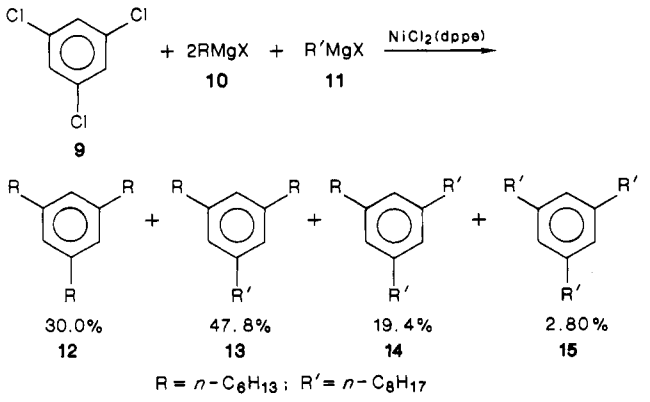
[a] Yield based on $C_6H_3Cl_3$ and average molecular weight of the product expected from ratio of Grignards used. [b] Only pertinent data given. [c] Isolated and purified by column chromatography on alumina.

investigated, the reaction of ethyl formate was mainly at the methyl group yielding **5** preferentially. Small amounts of the hydroxy ketone **6** were, however, observed in the reaction mixture.

Reduction of the three carbonyl functions to methylene groups proved to be somewhat difficult. Various reduction methods such as Clemmensen reduction, Wolff–Kishner reduction in dimethyl sulfoxide,[9] reductions using trialkylsilanes (R_3SiH) in trifluoroacetic acid,[10] and catalytic methods were tried. The most promising method we used was a catalytic reduction at atmospheric pressure by hydrogen using 5% palladium on carbon in glacial acetic acid containing concentrated H_2SO_4.[11] Even this method required 7 to 10 days for reduction. In addition to the trialkylbenzenes, intermediates such as mono- and diketones as well as acetic acid esters of the keto alcohols were invariably present. The reduction rate could be increased to some extent by the continuous addition of hydrogen into the reaction mixture and periodic addition of ketone and fresh catalyst. It was noted that by this reduction process, small amounts, 3–5%, of lower homologues of the alkylbenzene differing in one to four methylene groups were formed as byproducts. The amount of these lower homologues increased when the reduction process was performed at elevated hydrogen pressures. The trialkylsilane–trifluoroacetic acid reduction process also gave considerable amounts of these lower homologues. The formation of these lower homologues is not understood at this time. Their separation from the expected trialkylbenzenes was difficult due to their close boiling points.

Catalyzed Cross-Coupling Reactions. The mixed 1,3,5-trialkylbenzenes were prepared following our previously described procedure,[2] which was based on the original studies reported by Kumada et al.[12] using $NiCl_2$(dppe)-catalyzed reactions between chlorobenzene and aliphatic Grignard reagents. Our cross-coupling reactions were carried out by adding mixtures of aliphatic Grignards in

Chart II



diethyl ether to 1,3,5-trichlorobenzene and $NiCl_2$(dppe) in diethyl ether at 0 °C. The reactions were allowed to warm to room temperature over a period of ca. 18 h. The course of the reaction was followed by periodically removing aliquot samples and analysis by gas chromatography. In certain instances where the rate of reaction was slow, the reaction mixture was further refluxed until the gas chromatographic analysis showed no further change in composition.

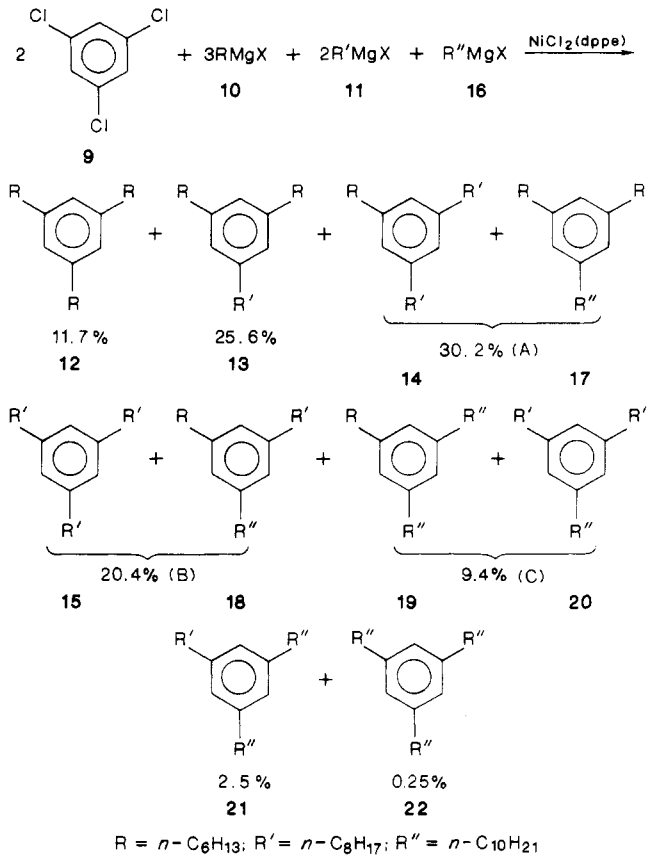
As an example the reactions between two different Grignards n-$C_6H_{13}MgBr$ (**10**), n-$C_8H_{17}MgBr$ (**11**), and 1,3,5-trichlorobenzene (**9**) gave four different mixed alkylbenzenes (**12–15**) as shown in Chart II.

The ratio of the various products can be changed by varying the ratio of the Grignards. In addition the complexity of the reaction products may be altered by using more than two Grignard mixtures. As an example, the use of three different Grignard reagents can produce up to 10 different polyalkylated products as shown in Chart III.

It was interesting to note that certain pairs of compounds (A, B, C) had identical gas chromatographic retention times. Each pair had the same number of carbon atoms, e.g., in pair A, **14** and **17** had a total of 22 carbon atoms in the alkyl substituents on each benzene ring. The same held true in identical carbon content in pairs B and C. Even though the pairs of compounds were not separable by gas chromatographic analysis using a 30-m SP2100

(9) Cram, D. J.; Sahyun, M. R. V. *J. Am. Chem. Soc.* **1962**, *84*, 1734.
(10) West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. P. *J. Org. Chem.* **1973**, *38*, 2675.
(11) Burnham, J. W.; Eisenbraum, E. J. *J. Org. Chem.* **1971**, *36*, 737.
(12) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.

Chart III



capillary column, the cracking pattern from GC/MS analysis of the various peaks clearly showed the presence of both components (see Table I).

The advantage of synthesizing a mixture of trialkylated benzene compounds over the monomolecular, pure trialkylated benzene compounds[4] is that a melting point depression of the product can be realized as one would expect. Thus liquid materials may be prepared from such mixtures as opposed to the higher melting point monomolecular, pure 1,3,5-trialkylbenzene.

Experimental Section

Commercial anhydrous diethyl ether was used without further purification. The *n*-alkyl bromides and methyl ketones were commercial products. *n*-Alkylmagnesium bromides were made from the bromides and Grignard grade magnesium by standard procedures. Commercial (1,2-bis(diphenylphosphino)ethane)-nickel(II) chloride [$NiCl_2$(dppe)] from Strem Chemical Co., Newburyport, MA, was used without further purification. The reactions were followed by GC with either a Perkin-Elmer Sigma 1 or Sigma 2B instrument using a 6 ft × 0.25 in. stainless steel column packed with 10% SE30 on Chromosorb W. A 30-m SP2100 capillary column was used in separation of the mixed trialkylbenzene compounds. Mass spectra were determined by chemical ionization or electron impact on a DuPont Type 21-491B instrument.

1,3,5-Tri-*n*-hexanoylbenzene (7b). Under a nitrogen atmosphere, sodium ethoxide (12.1 g, 0.18 mol) was suspended in dry diethyl ether (150 mL) at about 10 °C. A mixture of 2-heptanone (17.1 g, 0.15 mol) and ethyl formate (11.1 g, 0.15 mol) in dry diethyl ether (50 mL) was slowly added while maintaining the temperature below 20 °C. The addition took about 90 min. The sodium ethoxide appeared to dissolve and a bulky precipitate was formed, most of which dissolved on stirring at room temperature overnight. The reaction mixture was poured into ice water, forming a yellow aqueous layer and an ether layer. The aqueous layer was extracted twice with diethyl ether to remove unreacted ketone and ester. The aqueous layer, which contained the dissolved sodium salts of the formylated ketone, was carefully acidified (pH 6.0) with dilute H_2SO_4 (1 N) to generate the free keto aldehyde, which was immediately extracted with diethyl ether. Removal of the diethyl ether under vacuum produced 14.9 g of the crude product as a light red liquid. During gas chromatographic analysis of this product, self-condensation to the 1,3,5-tri-*n*-hexanoylbenzene was taking place probably due to the high temperature used in the chromatographic columns.

The product from above was dissolved in toluene (50 mL), and the contents were refluxed overnight, using a Dean–Stark receiver to remove the water formed during self-condensation. The toluene was removed under vacuum, yielding the cyclized product 1,3,5-tri-*n*-hexanoylbenzene as a red viscous liquid. This was distilled to collect 12.7 g of a yellow viscous liquid boiling at 204–6 °C/0.03 mm: yield 61%; IR (neat) showed a strong absorption at 1690 cm^{-1} due to carbonyl group; MS (CI), *m/e* 372 $(M)^+$, 357 $(M - CH_3)^+$, 316 $(M - C_4H_8)^+$, 301 $(M - C_5H_{11})^+$. Anal. Calcd for $C_{24}H_{36}O_3$: C, 77.42; H, 9.68. Found: C, 77.41; H, 9.56.

The lower molecular weight tri-*n*-ketobenzene compounds could be distilled under reduced pressure. The tri-*n*-heptanoylbenzene, however, on distillation began to decompose. It and higher members must be purified by alumina column chromatography using hexane and toluene as eluents.

1,3,5-Tri-*n*-hexylbenzene (12). A 5% Pd/C (0.5 g) and acetic acid (25 mL) solution was placed into a 500 mL, three-necked flask. A stream of hydrogen was bubbled through the vigorously stirred solution. The 1,3,5-trihexanoylbenzene (8.5 g, 0.023 mol) dissolved in a mixture of glacial acetic acid (100 mL) and concentrated sulfuric acid (4.0 mL) was slowly added from a droppng funnel over a period of 3 days. Periodically small amounts of fresh catalyst (total 0.8 g) in glacial acetic acid were added to the reaction mixture. After the addition of all the triketone, the reaction was stirred at room temperature for two additional days with continuing hydrogen addition. A GC/MS analysis of the reaction mixture showed the expected 1,3,5-tri-*n*-hexylbenzene in addition to various intermediates such as mono- and diketones, acetic acid esters of alcohols, and keto alcohols. The reaction mixture was poured into water and extracted with petroleum ether (bp 40–60 °C). On removal of the solvent, 6.8 g of the crude product was obtained as a yellow liquid. [A gas chromatographic analysis indicated a 75% (area percent) yield of product.] The crude product was distilled under reduced pressure on a Vigreaux column. The best fraction of 1,3,5-tri-*n*-hexylbenzene (4.05 g) distilled at 138–40 °C/0.03 mm: yield 54%; IR (neat) did not show any absorption at the carbonyl region; MS (EI), *m/e* 330 $(M)^+$, 301 $(M - C_2H_5)^+$, 287 $(M - C_3H_7)^+$, 273 $(M - C_4H_9)^+$, 260 $(M - C_5H_{10})^+$, 245 $(M - C_6H_{13})^+$. Anal. Calcd for $C_{24}H_{42}$: C, 87.27; H, 12.73. Found: C, 87.19; H, 12.82.

A GC/MS analysis of the compound showed two impurities in less than 3% (GC area percent). They had molecular weights of 316 and 302, indicating that they are lower homologues of the main product.

1,3,5-Tri-*n*-butylbenzene (8a). This compound was prepared by the reduction of 1,3,5-tributyroyl benzene (**7a**) as described above. The overall yield of the hydrocarbon from 2-pentanone was 34%: bp 100–102 °C/0.03 mm; MS (EI), *m/e* 246 $(M)^+$, 231 $(M - CH_3)^+$, 217 $(M - C_2H_5)^+$, 203 $(M - C_3H_7)^+$, 189 $(M - C_4H_9)^+$. Anal. Calcd for $C_{18}H_{30}$: C, 87.8; H, 12.2. Found: C, 87.85; H, 12.26.

Two lower homologues of molecular weights 218 and 190 were detected in trace amounts.

1,3,5-Tri-*n*-heptylbenzene (8c). This compound was prepared from 2-octanone as described previously. The triketone, 1,3,5-triheptanoylbenzene (**7c**), obtained could not be purified by distillation as it started to decompose at about 200 °C at 0.01 mm while distillation was attempted. Hence it was purified by chromatography on alumina using hexane and toluene as eluents. The triketone was isolated in approximately 70% yield. Reduction as described before gave 1,3,5-tri-*n*-heptylbenzene in 42% yield: bp 152–4 °C/0.02 mm; MS (EI), *m/e* 372 $(M)^+$, 329 $(M - C_3H_7)^+$, 301 $(M - C_5H_{11})^+$, 288 $(M - C_6H_{12})^+$, 273 $(M - C_7H_{15})^+$. Anal. Calcd for $C_{27}H_{48}$: C, 87.10; H, 12.90. Found: C, 87.35; H, 12.56. Two lower homologues of molecular weights 358 and 344 were present in approximately 3%.

Mixture of Tri-*n*-(hexyl–octyl)benzenes 12–15. A mixture of 1,3,5-trichlorobenzene (60 g, 0.33 mol) and $NiCl_2$(dppe) (0.30

g, 5.68×10^{-4} mol) in anhydrous diethyl ether (200 mL) was stirred and cooled in an ice bath. A 2 M diethyl ether solution of a mixture of n-$C_6H_{13}MgBr$ (126.2 g, 0.667 mol) and n-$C_8H_{17}MgBr$ (72.3 g, 0.333 mol) was added and the mixture was allowed to warm to ambient temperature overnight. The contents, which now contained a considerable amount of white solids, were refluxed for another 4 h. The reaction mixture was hydrolyzed by the slow addition to a diluted HCl–ice mixture and phase separated, and the diethyl ether layer was dried and subjected to a rotary vacuum evaporator. The residual pale yellow liquid was dissolved in pentane and passed through an alumina column in order to remove the color. The colorless liquid was subjected to distillation to yield 112.1 g of a liquid: bp 153–84 °C (0.1 mm). A gas chromatographic analysis showed four components with the following GC area percent: **12**, 30%; **13**, 47.8%; **14**, 19.4%; and **15**, 2.8%. The components had the same GC retention time as known standard compounds prepared and fully characterized previously.[2] The mass spectral analysis is shown in Table I.

The other mixtures of trialkylbenzenes shown in Table I were prepared by the same general procedure as described above. The compounds were characterized by comparing the GC retention times with those of known compounds[2] and GC/MS analysis. In experiment 4 (see Table I) only seven of the ten possible components were seen by GC analysis on a 30-m SP2100 capillary column. On mass spectral analysis, three of the GC peaks were found to contain two compounds each (see Table I).

Registry No. 1 (R = n-C_5H_{11}), 111-13-7; **2**, 109-94-4; **7a**, 116785-83-2; **7b**, 14269-14-8; **7c**, 116785-84-3; **8a**, 841-07-6; **8c**, 29536-29-6; **9**, 108-70-3; **10**, 3761-92-0; **11**, 17049-49-9; **12**, 29536-28-5; **13**, 87969-87-7; **14**, 87969-85-5; **15**, 7694-77-1; **16**, 17049-50-2; **17**, 87969-89-9; **18**, 116785-85-4; **19**, 87969-86-6; **20**, 87969-90-2; **21**, 87969-88-8; **22**, 87969-78-6; $NiCl_2$, 7718-54-9; 2-heptanone, 110-43-0; 3-ketooctanal, 3223-40-3.

Photochemical Synthesis of 1-Hydroxyfluorenes: A Correction[1]

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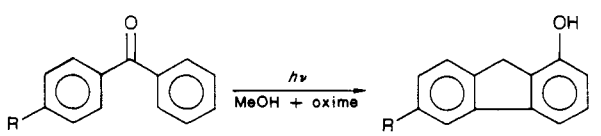
In recent years three publications have appeared,[3] emanating from the same laboratories, in which it is asserted that irradiation of a methanolic solution of benzophenone oxime (quartz) or a mixture of benzophenone and its oxime (Pyrex) gives, in respectiable yield, 1-hydroxyfluorene. The latter was identified by its melting point and that of its acetate[4] and by the mass spectrum, which gave a strong M + 1 peak at m/e 183. An analysis, though referred to,[3c] was not recorded. A variety of data were provided concerning the effect of solvents—the yield in 2-propanol was low and, in acetonitrile, negligible.[3b] Further, the reaction was extended to 4-methyl- and 4-methoxybenzophenone,[3b,c] giving the corresponding, previously unknown 1-hydroxyfluorene derivatives. These



R = H, Me, OMe 1: R = H, Me, OMe

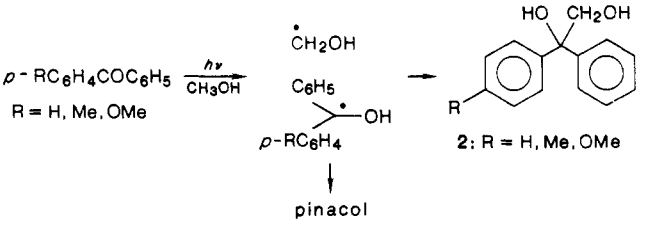
Table I. Melting Points (°C) of 1 and 2

	1[a]	"1"[b]	2[c]	2 (lit.)
R = H	119–120.5 (acetate: 90–91.5)	120 (acetate: 91)	120–121 (benzene)	120–121[d] (monoacetate: 85–86[d])
R = Me		81–82 (74–75)	85 (hexane)	84.5–85.5[e]
R = Me		100–101	105–106 (hexane–benzene)	101–102[f]

[a] Reference 4 [b] Reference 3. [c] This work; recrystallization solvents are given in brackets. [d] Reference 5. [e] Reference 6a. [f] Reference 6b.

were identified by analogy with the unsubstituted derivative and by analysis.[3c] For further information the original papers should be consulted, but it should be noted from the study of mixed ketone–oxime irradiations that the fluorene moiety was derived from the ketone only and that acetone oxime could be substituted for benzophenone oxime.

We were struck by the substantial yield (~65%) from what, if correctly interpreted, must be a lengthy sequence of steps and by the bizarre mechanism indicated. Despite the assertion[3b] that the fluorene was not obtained by irradiation in MeOH in the absence of the oxime, we obtained a substance having the properties described for 1 (R = H), together with benzpinacol and unchanged ketone. The same substance was also obtained when benzophenone and acetone oxime mixture were irradiated in methanol. In the latter experiment, acetone oxime was not consumed (monitored by VPC). Indeed, the reaction of benzophenone in methanol was already described in the literature[5] as giving **2** (R = H). Its melting point and that of its acetate are those recorded[5] for **2** (R = H) (Table I) (and, *by coincidence are also those of 1 (R = H) and its acetate*). The formation of **2** is unexceptional, being a consequence of H abstraction from the solvent followed by cage combination of the resultant ketyl and hydroxymethyl radicals. The diol **2** (R = H) gave a very strong M – 31 peak (at m/e 183) in the 70 eV mass spectrum: the parent ion was only detected at 30 eV.



In a similar way irradiation of 4-methylbenzophenone and 4-methoxybenzophenone gave **2** (R = Me) and **2** (R = OMe) with the melting points and other properties ascribed[3b] to **1** (R = Me) and **1** (R = OMe). These derivatives of **2** are known substances[6] (see Table I). We conclude, therefore, that despite minor anomalies remaining (see Experimental Section) the claim of photochemical formation of 1-hydroxyfluorene is in error.

Experimental Section

Chemicals. Acetone oxime was crystallized from hexane; the benzophenones were available in the laboratory; 80-200 mesh silica

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(2) Holder of NSERC Summer Scholarship.
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