acetate of **24**: mp 269–272 °C; IR ($CHCl_3$) 1770, 1680, 1620, 1580 cm^{-1}.

7-Methoxy-6-hydroxynaphthacene-5,12-dione (25). This was prepared from **1b** (48 mg, 0.25 mmol) and **5** (40 mg, 0.25 mmol) by method A. Recrystallization from chloroform gave pure **25**: mp 260.5–261.5 °C (lit.[1] 260.5–261.5 °C); IR ($CHCl_3$) 1665, 1615, 1580 cm^{-1}.

Dimethyl 8-Methoxy-1-hydroxynaphthalene-2,3-dicarboxylate (26). This was prepared from **1b** (50 mg, 0.26 mmol) and **8** (37 mg, 0.26 mmol) by method B. Recrystallization from ethanol gave pure **26**: mp 144–145 °C (lit.[4] 145.5 °C); IR ($CHCl_3$) 3330, 1725, 1705 cm^{-1}.

3-(Phenylsulfonyl)-2-cyclohexen-1-one (31). This was prepared from 3-chloro-2-cyclohexen-1-one (**30**) by the modification of the reported method.[22] Purification of the crude oil by column chromatography on silica gel using benzene–ethyl acetate (15:1) as eluting solvent gave pure **31**: IR ($CHCl_3$) 1680, 1570, 1510, 1420, 1310, 1200 cm^{-1}.

3-*endo*-Carboxynorborn-5-en-2-*endo*-ylacetic Anhydride (34). This was obtained according to the reported method.[12]

Dimethyl 3-Methoxyhomophthalate (35). This was obtained from the known[23] dimethyl 3-hydroxyhomophthalate by methylation with diazomethane. To a stirred solution of dimethyl 3-hydroxyhomophthalate (500 mg, 2.23 mmol) in ether (3 mL) was added an ethereal solution of diazomethane at 0 °C. The mixture was stirred at room temperature overnight and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using benzene and benzene–ethyl acetate (15:1) as eluting solvent to give **35**: 61% yield; bp 110 °C (0.2 torr) (lit.[24] bp 116 °C (0.4 torr)); IR ($CHCl_3$) 1730, 1595, 1470, 1435 cm^{-1}; NMR ($CDCl_3$) δ 3.62 (s, 2 H), 3.64 (s, 3 H), 3.80 (s, 3 H), 3.87 (s, 3 H), 6.81 (br d, 2 H, J = 8 Hz), 7.24 (t, 1 H, J = 8 Hz).

Reaction of the Lithium Salt of Dimethyl 3-Methoxyhomophthalate (35) with 2-Chloro-6-oxo-5,6,7,8-tetrahydro-1,4-naphthoquinone 1,2-Ethanediyl Acetal (2). The lithium salt obtained from the homophthalate **35** (119 mg, 0.50 mmol) and LDA (0.50 mmol) in anhydrous THF was treated with **2** (127 mg, 0.50 mmol) in anhydrous THF was treated with **2** (127 mg, 0.50 mmol) at −78 °C for 1 h. Workup of the reaction mixture as described for the general procedures for the cycloaddition of **1a,b** gave the [2 + 2] cycloadduct **36**: 160 mg (69%). Recrystallization from benzene–ether gave pure sample: mp 195.5–196.5 °C; IR ($CHCl_3$) 1805, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (t, 2 H, J = 6.5 Hz), 2.85–3.1 (m, 4 H), 5.10 (s, 1 H), 5.49 (br s, 1 H), 6.66 (d, 1 H, J = 8 Hz), 6.87 (d, 1 H, J = 8 Hz), 7.29 (t, 1 H, J = 8 Hz); exact mass calcd for $C_{23}H_{21}O_8Cl$, 460.0923; found, 460.0918.

Acknowledgment. We thank Hatsuo Maeda and Fumio Fukata for technical assistance.

Registry No. **1a**, 703-59-3; **1b**, 74794-52-8; **2**, 83043-87-2; **5**, 130-15-4; **6**, 922-67-8; **7**, 623-47-2; **8**, 762-42-5; **9**, 762-21-0; **10**, 23055-10-9; **11**, 4070-75-1; **12**, 69833-10-9; **13**, 69833-09-6; **14**, 475-38-7; **15**, 6336-86-3; **15** acetate, 88036-06-0; **16**, 948-03-8; **17**, 33950-71-9; **18**, 36112-45-5; **19**, 68376-15-8; **20**, 88036-07-1; **21**, 88036-08-2; **22**, 19938-28-4; **23**, 88036-09-3; **24**, 3677-09-6; **24** triacetate, 73682-92-5; **25**, 88036-10-6; **26**, 88036-11-7; **30**, 5682-75-7; **31**, 88036-12-8; **34**, 77411-77-9; **35**, 1214-87-5; **36**, 88036-13-9; dimethyl 3-hydroxyhomophthalate, 43071-26-7.

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Regiospecific Synthesis of Aromatic Compounds via Organometallic Intermediates. 3. *n*-Alkyl-Substituted Benzene[1]

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High molecular weight tri- and tetra-*n*-alkylbenzenes have been synthesized by the cross-coupling of the appropriate chlorinated benzenes with long-chain *n*-alkylmagnesium bromides using (1,2-bis(diphenylphosphino)ethane)nickel(II) chloride [$NiCl_2$(dppe)] as catalyst. The reactions proceeded without any positional scrambling or alkyl group isomerization. A new method is described for the preferential substitution of one chlorine atom by an *n*-alkyl group in 1,3,5-trichlorobenzene. The reaction between an *n*-alkylmagnesium bromide and 1,3,5-trichlorobenzene catalyzed by nickel acetylacetonate [$Ni(acac)_2$] at low temperature and in tetrahydrofuran solvent favors monosubstitution. The cross-coupling reactions of these *n*-alkyldichlorobenzenes with other *n*-alkylmagnesium bromides, in the presence of $NiCl_2$(dppe), proceeded at a much slower rate than those of 1,3,5-trichlorobenzene to yield the asymmetric 1,3,5-tri-*n*-alkylbenzenes.

Introduction

The formation of a carbon–carbon σ bond by the nickel–phosphine complex catalyzed cross-coupling of Grignard reagents with organic halides has received considerable attention since its discovery in 1972.[3,4] The reaction has been successfully extended to a variety of Grignard reagents and organic halides using different nickel–phosphine complexes. Besides Grignard reagents, other organometallic reagents have been employed for cross-coupling reactions, using in many cases, $Pd[PPh_3]_4$ as a suitable catalyst precursor. Such organometallic reagents include those of lithium, zinc, boron, aluminum, and zirconium.[5,6]

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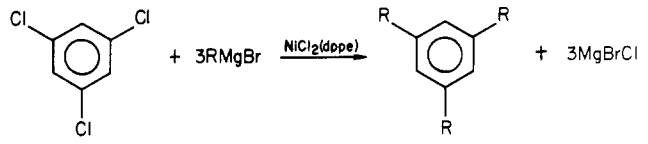
0022-3263/84/1949-0478$01.50/0

Chart I



1

a, R = n-C_6H_{13}; b, R = n-C_7H_{15}; c, R = n-C_8H_{17}; d, R = n-C_9H_{19}; e, R = n-$C_{10}H_{21}$

In spite of the large number of the organic halides studied, most of these substrates contained only one or two halogen atoms. Studies with halides containing more than two halogen atoms appear to have been limited to the cross-coupling of CH_2=$C(CH_3)MgBr$ with 1,3,5-trichloro- and 1,2,4,5-tetrachlorobenzenes and in these instances only partial substitutions have been realized.[5] This report describes the application of this useful cross-coupling reaction to 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes, 1,2,4,5-tetrachlorobenzene, and 3,5-dichloroalkylbenzenes and long chain n-alkylmagnesium bromides. The products obtained are high molecular weight liquids some of which have potential application as high-temperature fluids.

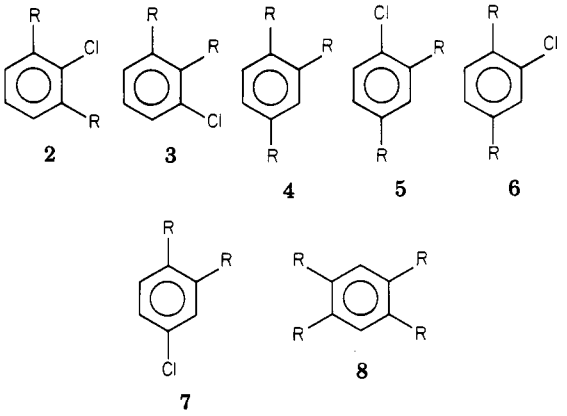
Results and Discussion

The tri- and tetraalkylbenzenes (**1a–e**, **4**, and **8**) were made by the same experimental procedure described earlier,[3] with minor modifications. As the catalyst, we selected $NiCl_2$(dppe)[7] since it was not substantially different in activity than (1,3-bis(diphenylphosphino)-propane)nickel(II) chloride [$NiCl_2$(dppp)]. The cross-coupling reactions were carried out by adding the Grignard reagent in diethyl ether to a mixture of the chlorinated substrate and catalyst in dry diethyl ether at 0 °C and allowing the resultant mixture to slowly warm to room temperature overnight. In cases where the reactions were incomplete, they were refluxed to complete the reactions. The isolated yields obtained for **1a–e** varied from 75% to 90% (Chart I).

In all these reactions small amounts of partial substitution products, homocoupling products both from the Grignard reagent and the organic halide, and dehalogenation products could be detected in the final hydrolyzed reaction mixture. As an example, during the preparation of **1b**, the minor products identified by GC/MS analysis include tetradecane, trichlorobiphenyl, dichloroheptylbenzene, chlorodiheptylbenzene, as well as diheptylbenzene.

The trialkylbenzenes formed were essentially pure and were not contaminated with any isomers. NMR data showed that the cross-coupling reaction proceeded without any positional isomerization or alkyl group isomerization, in conformity with earlier observations[5] with shorter n-alkyl groups. It should be pointed out however, that the cross-coupling reaction between secondary alkyl Grignard reagents such as i-PrMgCl and chlorobenzene is reported to be accompanied by alkyl group isomerization from secondary to primary. Reduction of the halide, the extent of which is strongly dependent on the electronic nature of the phosphine ligand, has also been noted.[8,9] An example of isomerization from primary to secondary has been

Chart II[a]



[a] **2–7**, R = n-C_8H_{17}; **8**, R = n-C_6H_{13}.

reported in the reaction of 3-butenyl bromide with PhMgBr using $NiCl_2$(dppp) as catalyst.[10]

The cross-coupling reactions were also studied with 1,2,3- and 1,2,4-trichlorobenzenes for comparison and were also extended to 1,2,4,5-tetrachlorobenzene. With n-octylmagnesium bromide, 1,2,3-trichlorobenzene gave less than 1% of a trialkylbenzene, detected by GC/MS, even after 3 days in refluxing diethyl ether. The major product (71% yield) was a dioctylchlorobenzene which was a pure isomer as indicated by capillary GC. Of the two possible positional isomers **2** and **3** (Chart II), NMR data clearly indicate that the isomer formed is the symmetrical isomer **2** which would also be expected on steric considerations. With 1,2,4-trichlorobenzene, the trioctylbenzene **4** was obtained in only 44% yield. However, a dioctylchlorobenzene was also isolated in 22% yield. GC analysis on capillary column as well as proton NMR spectrum indicated that it was a mixture of two isomers in the ratio of 90:10, although three positional isomers **5–7** are possible. The nature of the individual isomers was not established, but they may be **5** and **6** rather than **7**. 1,2,4,5-Tetrachlorobenzene and n-hexylmagnesium bromide, after two days in refluxing diethyl ether, gave 55% yield of the fully substituted product 1,2,4,5-tetra-n-hexylbenzene (**8**). One of the byproducts identified was 1,2,4-trihexylbenzene in about 5% yield.

Attempts to substitute one chlorine atom in 1,3,5-trichlorobenzene using $NiCl_2$(dppe) and 1 molar equivalent of alkylmagnesium bromide in diethyl ether led to trialkylbenzene as the major product, unreacted trichlorobenzene, and small amounts of alkyldichloro- and dialkylchlorobenzenes. Therefore, other catalysts, as for example nickel acetylacetonate [$Ni(acac)_2$] were studied under different conditions. With this catalyst, no substitution was observed in refluxing diethyl ether. However, the reaction proceeded in tetrahydrofuran (THF) giving alkyldichlorobenzene and small amounts of dialkylchlorobenzenes in addition to a host of byproducts. It was found that conducting the reaction in THF above 0 °C or for long periods of time led to substantial dehalogenation. The most promising conditions for providing a monosubstituted product involved treatment of 1,3,5-trichlorobenzene with 2.5–3.0 molar equivalent of n-alkylmagnesium bromide in the presence of $Ni(acac)_2$ in THF at −20 °C for 6 h. Yields of only 40–50% were obtained due to the large number of minor side products. For instance, in reactions using n-octylmagnesium bromide, some

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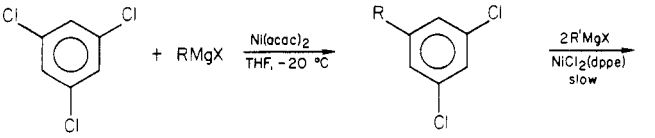
Table I. Cross-Coupling of Chlorobenzenes with *n*-Alkylmagnesium Bromides

chloride (mol)	Grignard reagent (mol)	time,[a] h	major product	bp, °C (mm)	yield,[b] %
$1,3,5\text{-}Cl_3C_6H_3$ (0.06)	$n\text{-}C_6H_{13}MgBr$ (0.198)	20[c]	**1a**	142/0.02	82
$1,3,5\text{-}Cl_3C_6H_3$ (0.11)	$n\text{-}C_7H_{15}MgBr$ (0.37)	20[c]	**1b**	179-80/0.04	87
$1,3,5\text{-}Cl_3C_6H_3$ (0.07)	$n\text{-}C_8H_{17}MgBr$ (0.23)	20[c]	**1c**	208-10/0.01	76
$1,3,5\text{-}Cl_3C_6H_3$ (0.25)	$n\text{-}C_9H_{19}MgBr$ (0.83)	20[c]	**1d**	248-50/0.1	75
$1,3,5\text{-}Cl_3C_6H_3$ (0.15)	$n\text{-}C_{10}H_{21}MgBr$ (0.47)	20[c]	**1e**	255-7/0.01	93
$1,2,3\text{-}Cl_3C_6H_3$ (0.25)	$n\text{-}C_8H_{17}MgBr$ (0.80)	72	**2**	155/0.05	71
$1,2,4\text{-}Cl_3C_6H_3$ (0.2)	$n\text{-}C_8H_{17}MgBr$ (0.66)	20	**4**	205/0.02	44
$1,2,4,5\text{-}Cl_4C_6H_2$ (0.05)	$n\text{-}C_6H_{13}MgBr$ (0.25)	48	**8**	195-6/0.2	55
$1,3,5\text{-}Cl_3C_6H_3$ (0.5)	$n\text{-}C_6H_{13}MgBr$ (1.25)	6[d]	**9a**	87/0.25	50
$1,3,5\text{-}Cl_3C_6H_3$ (0.2)	$n\text{-}C_8H_{17}MgBr$ (0.5)	6[d]	**9b**	107/0.05	52
$1,3,5\text{-}Cl_3C_6H_3$ (0.1)	$n\text{-}C_{10}H_{21}MgBr$ (0.25)	5[d]	**9c**	135/0.25	42
$1,3\text{-}Cl_2\text{-}5\text{-}(n\text{-}C_6H_{13})C_6H_3$, **9a** (0.095)	$n\text{-}C_8H_{17}MgBr$ (0.19)	240	**10a**	178-9/0.1	56
$1,3\text{-}Cl_2\text{-}5\text{-}(n\text{-}C_6H_{13})C_6H_3$, **9a** (0.065)	$n\text{-}C_{10}H_{21}MgBr$ (0.13)	168	**10b**	215-7/0.01	58
$1,3\text{-}Cl_2\text{-}5\text{-}(n\text{-}C_8H_{17})C_6H_3$, **9b** (0.062)	$n\text{-}C_6H_{13}MgBr$ (0.136)	240	**10c**	161-3/0.01	54
$1,3\text{-}Cl_2\text{-}5\text{-}(n\text{-}C_8H_{17})C_6H_3$, **9b** (0.05)	$n\text{-}C_{10}H_{21}MgBr$ (0.11)	240	**10d**	230-1/0.01	73
$1,3\text{-}Cl_2\text{-}5\text{-}(n\text{-}C_{10}H_{21})C_6H_3$, **9c** (0.1)	$n\text{-}C_6H_{13}MgBr$ (0.22)	216	**10e**	192/0.05	44
$1,3\text{-}Cl_2\text{-}5\text{-}(n\text{-}C_{10}H_{21})C_6H_3$, **9c** (0.1)	$n\text{-}C_8H_{17}MgBr$ (0.22)	240	**10f**	202/0.01	15[e]

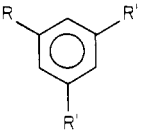
[a] Refers to time of reaction in refluxing diethyl ether unless otherwise stated. [b] Isolated yields. [c] 18 h from 0 °C to ambient temperature followed by refluxing the diethyl ether solution for 2 h. [d] Reactions in THF at −20 °C. [e] The unusually low yield obtained is attributed to the catalyst sample used which has apparently lost most of its activity.

of these products, identified by GC/MS and/or comparison of GC retention times with authentic samples, were *n*-octane, octene, *n*-octyl chloride, hexadecane, mono-, di-, and trichlorobiphenyls, *m*-dichlorobenzene, chlorobenzene, and octyl tetrahydrofuran. These observations clearly point to a free radical pathway for these partial substitution reactions. Even though a number of byproducts were obtained by this reaction, the desired 3,5-dichloro-*n*-alkylbenzenes could be isolated by careful fractional distillation. By this process compounds **9a–c** were synthesized (Chart III).

Chart III



9a, R = $n\text{-}C_6H_{13}$
b, R = $n\text{-}C_8H_{17}$
c, R = $n\text{-}C_{10}H_{21}$



10a, R = $n\text{-}C_6H_{13}$; R′ = $n\text{-}C_8H_{17}$
b, R = $n\text{-}C_6H_{13}$; R′ = $n\text{-}C_{10}H_{21}$
c, R = $n\text{-}C_8H_{17}$; R′ = $n\text{-}C_6H_{13}$
d, R = $n\text{-}C_8H_{17}$; R′ = $n\text{-}C_{10}H_{21}$
e, R = $n\text{-}C_{10}H_{21}$; R′ = $n\text{-}C_6H_{13}$
f, R = $n\text{-}C_{10}H_{21}$; R′ = $n\text{-}C_8H_{17}$

Asymmetric 1,3,5-tri-*n*-alkylbenzenes with two different *n*-alkyl groups (**10a–f**) were made from the monoalkyldichlorobenzene (**9a–c**) by treatment with the appropriate *n*-alkylmagnesium bromide in diethyl ether using $NiCl_2$(dppe) as catalyst. All these reactions with alkyldichlorobenzenes proceeded at such slow rates that the reaction mixtures had to be refluxed in diethyl ether for periods of 7–10 days and often with periodic addition of fresh catalyst, to obtain reasonable yields of the trialkylbenzenes (**10a–f**). Compared to this is the smooth and rapid formation of trialkylbenzenes from trichlorobenzene even when a 3-fold excess of trichlorobenzene over the *n*-alkylmagnesium bromide is used.

It is interesting to note that in both alkylation of 1,3,5-trichlorobenzene and 1-alkyl-3,5-dichlorobenzene small amounts of intermediate alkylation products such as alkyldichloro- and dialkylchlorobenzenes were observed when the reactions were followed by GC/MS. However, we were unable to detect at any stage of the reaction a higher concentration of the intermediates compared to the final fully alkylated product. This might appear surprising in view of the reduced reactivity observed by the introduction of an alkyl substituent and might indicate that the substitution of the halogen atoms does not occur in stepwise fashion. A similar trend of reduced reactivity by an alkyl group was noted[5] when the reactivities of various chlorotoluenes and dichlorobenzenes were compared.

Table I lists the compound synthesized.

Experimental Section

Reaction flasks were dried thoroughly in an oven before use. Commercial anhydrous diethyl ether was used without further purification. Tetrahydrofuran was freshly distilled from metallic sodium before use. The *n*-alkyl bromides were commercial products. *n*-Alkylmagnesium bromides were made from the bromides and Grignard reagent grade magnesium by standard procedures. Commercial (1,2-bis(diphenylphosphino)ethane)-nickel(II) chloride [$NiCl_2$(dppe)] from Strem Chemical Co., Newburyport, MA, nickel acetylacetonate [$Ni(acac)_2$] from Aldrich Chemical Co., Milwaukee, WI, and the chlorobenzenes were used without further purification.

The reactions were followed by GC with either a Perkin-Elmer Sigma-1 or Sigma 2B instrument using 6 ft × 0.25 in. stainless steel columns packed with 10% SE-30 on Chromosorb W. A 12-m glass capillary column containing methyl silicone as stationary phase was used for separation of isomers wherever necessary. IR spectra were recorded on a Beckman Microlab 600 or Perkin-Elmer Model 257 spectrophotometer. Mass spectra were determined by chemical ionization, unless indicated otherwise, on a DuPont Type 21-491B instrument. A Varian A-56/60A spectrophotometer was used for recording ^1H NMR (60 MHz) spectra.

All reactions were carried out under an atmosphere of dry nitrogen. The amounts of $NiCl_2$(dppe) used were 0.1–0.3 mol% and $Ni(acac)_2$ 0.5–1.0 mol% with respect to the aryl chloride. In slow reactions like substitution of alkyldichlorobenzenes, where periodic addition of $NiCl_2$(dppe) was helpful, the total amount of catalyst added was about five times the normal quantity. Only typical experimental procedures are given and the compounds prepared similarly are described immediately thereafter. All the pure products were colorless liquids.

1,3,5-Tri-*n*-decylbenzene (1e). A mixture of 1,3,5-trichlorobenzene (27.2 g, 0.15 mol) and $NiCl_2$(dppe) (0.20 g, 3.86×10^{-4} mol) in dry diethyl ether (250 mL) was cooled in an ice bath with stirring. A 2 M solution of *n*-decylmagnesium bromide in

diethyl ether (114 g, 0.465 mol) was added, and the reaction mixture was warmed to 25 °C overnight, diluted with dry diethyl ether (100 mL), and refluxed for another 2 h. After hydrolysis, by slow addition to dilute HCl–ice, the diethyl ether layer was separated, and the solvent removed in a rotary vacuum evaporator. The pale yellow liquid obtained was dissolved in pentane and passed through a short alumina column, eluting with pentane. The colorless liquid obtained after removal of solvent was subjected to fractional distillation under reduced pressure using a 1-ft Vigreaux column to yield 69.3 g (93%) of pure 1,3,5-tri-*n*-decylbenzene: IR (neat) 3010 (w), 2955 (s), 2920 (s), 1595 (m), 1455 (m), 1370 (w), 855 (w), 715 (w), 705 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 CH_3), 0.9–1.7 (m, 24 CH_2), 2.53 (br t, 3 CH_2 next to ring), 6.8 (s, 3 Ar H); mass spectrum, *m/e* 498 (M^+). Anal. Calcd for $C_{36}H_{66}$: C, 86.75; H, 13.25. Found: C, 86.80; H, 13.16.

1,3,5-Tri-*n*-hexylbenzene (1a): IR (neat) 3010 (w), 2955 (s), 2920 (s), 2850 (s), 1592 (m), 1450 (m), 1368 (w), 860 (w), 715 (w), 700 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 CH_3), 0.92–1.68 (m, 12 CH_2), 2.54 (br t, 3 CH_2 next to ring), 6.80 (s, 3 Ar H); mass spectrum, *m/e* 330 (M^+). Anal. Calcd for $C_{24}H_{42}$: C, 87.27; H, 12.72. Found: C, 87.31; H, 12.86.

1,3,5-Tri-*n*-heptylbenzene (1b): IR (neat) 3015 (w), 2960 (s), 2925 (s), 2855 (s), 1600 (m), 1460 (m), 1375 (w), 860 (w), 720 (w), 710 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 CH_3), 0.9–1.7 (m, 15 CH_2), 2.54 (br t, 3 CH_2 next to ring), 6.8 (s, 3 Ar H); mass spectrum (EI), *m/e* 372 (M^+) (base), 329, 289, 288, 204, 203, 190, 189. Anal. Calcd for $C_{27}H_{48}$: C, 87.10; H, 12.90. Found: C, 87.14; H, 12.86.

1,3,5-Tri-*n*-octylbenzene (1c): IR (neat) 3010 (w) 2950 (s), 2920 (s), 2850 (s), 1585 (m), 1450 (m), 1365 (w), 860 (w), 715 (w), 700 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 CH_3), 0.93–1.61 (m, 18 CH_2), 2.54 (br t, 3 CH_2 next to ring), 6.80 (s, 3 Ar H); mass spectrum, *m/e* 414 (M^+). Anal. Calcd for $C_{30}H_{54}$: C, 86.96; H, 13.04. Found: C, 86.73; H, 13.86.

1,3,5-Tri-*n*-nonylbenzene (1d): IR (neat) 3010 (w), 2955 (s), 2925 (s), 2855 (s), 1600 (m), 1460 (m), 1380 (w), 860 (w), 805 (w), 735 (w), 725 (w), 715 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 CH_3), 0.9–1.7 (m, 21 CH_2), 2.55 (br t, 3 CH_2 next to ring), 6.8 (s, 3 Ar H); mass spectrum, *m/e* 456 (M^+). Anal. Calcd for $C_{33}H_{60}$: C, 86.84; H, 13.16. Found: C, 87.05; H, 13.38.

1,2,4-Tri-*n*-octylbenzene (4) was obtained in 44% yield along with 22% of two isomers (ratio ~ 9:1) of chlorodi-*n*-octylbenzenes. Compound **4** and the chlorodi-*n*-octylbenzenes could be separated by fractional distillation using a 1-ft Vigreaux column. Compound **4** was collected at 205 °C (0.02 mm): IR (neat) 3045 (w), 3005 (w), 2955 (s), 2860 (s), 1615 (w), 1500 (w), 1465 (m), 1380 (w), 890 (w), 830 (w), 755 (w), 725 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 CH_3), 1.55 (m) and 1.29 (br s) (18 CH_2), 2.53 (t, 3 CH_2 next to ring), 6.91 (d, 1 Ar H), 6.93 (s, 1 Ar H), 7.03 (d, 1 Ar H); mass spectrum, *m/e* 414 (M^+). Anal. Calcd for $C_{30}H_{54}$: C, 86.88; H, 13.12. Found: C, 86.72; H, 13.08. The isomeric mixture of chlorodioctylbenzenes distilled in the range 165–172 °C (0.01 mm).

2-Chloro-1,3-di-*n*-octylbenzene (2):[11] IR (neat) 3075 (w), 2975 (s), 2942 (s), 2875 (s), 1600 (w), 1470 (s), 1440 (m), 1380 (w), 1300 (w), 1052 (m), 790 (w), 778 (m), 740 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 0.87 (t, 2 CH_3), 1.0–1.9 (m, 12 CH_2), 2.75 (br t, 2 CH_2 next to ring), 7.14 (s, 3 Ar H); mass spectrum, *m/e* 336, 338 (1 Cl, M^+). Anal. Calcd for $C_{22}H_{37}Cl$: C, 78.41; H, 11.07; Cl, 10.52. Found: C, 78.31; H, 10.93; Cl, 10.07.

1,2,4,5-Tetra-*n*-hexylbenzene (8): IR (neat) 3005 (w), 2955 (s), 2925 (s), 2860 (s), 1508 (w), 1470 (m), 1385 (w), 1120 (w), 900 (w), 760 (w), 735 (w), 730 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 4 CH_3), 0.95–1.75 (m, 16 CH_2), 2.58 (br t, 4 CH_2 next to ring), 6.92 (s, 2 Ar H); mass spectrum, *m/e* 414 (M^+). Anal. Calcd for $C_{30}H_{54}$: C, 86.96; H, 13.04. Found: C, 86.75; H, 13.17.

1,3-Dichloro-5-*n*-octylbenzene (9b). A mixture of 1,3,5-trichlorobenzene (90.7 g, 0.5 mol) and Ni(acac)$_2$ (1.0 g, 3.64×10^{-3} mol) dissolved in dry tetrahydrofuran (350 mL) was cooled to −25 °C. *n*-Octylmagnesium bromide (271.5 g, 1.25 mol) in tetrahydrofuran (1250 mL) was slowly added to the stirred reaction mixture at such a rate as to maintain the temperature below −20 °C. The green reaction mixture changed to grey and finally brown. The contents were stirred for a total of 6 h at −20 °C and hydrolyzed by addition to 2.5 L of cold dilute HCl. The mixture was then extracted three time with diethyl ether and the solvent was removed to obtain a dark brown liquid. GC/MS showed the major product to be **9b**, but there were a number of minor side products, some of which could be identified (see Results and Discussion). The product was dissolved in pentane and passed through an alumina column, eluting with pentane. Removal of the solvent gave a pale yellow liquid which was subjected to fractional distillation under reduced pressure using a 1-ft Vigreaux column. Pure **9b** distilled at 107 °C (0.05 mm) as a colorless mobile liquid: yield 50%; IR (neat) 3080 (w), 2950 (s), 2925 (s), 2855 (s), 1585 (m), 1560 (m), 1460 (w), 1425 (m), 1375 (w), 1110 (w), 850 (m), 792 (m), 680 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 1 CH_3), 1.2–1.6 (m, 6 CH_2), 2.7 (br t, 1 CH_2 next to ring), 7.1 (m, 3 Ar H); mass spectrum, *m/e* 258, 260, 262 (2 Cl, M^+). Anal. Calcd for $C_{14}H_{20}Cl_2$: C, 64,86; H, 7.72; Cl, 27.41. Found: C, 64.79; H, 7.69; Cl, 27.50.

1,3-Dichloro-5-*n*-hexylbenzene (9a): IR (neat) 3080 (w), 2950 (s), 2925 (s), 2855 (s), 1585 (m), 1560 (s), 1460 (w), 1425 (m), 1375 (w), 1110 (w), 842 (m), 790 (m), 678 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 1 CH_3), 1.2–1.6 (m, 4 CH_2), 2.6 (br t, 1 CH_2 next to ring), 7.08 (d, 2 Ar H), 7.18 (t, 1 ar H); mass spectrum, *m/e* 230, 232, 234 (2 Cl, M^+). Anal. Calcd for $C_{12}H_{16}Cl_2$: C, 62.34, H, 6.93. Found: C, 62.47, H, 6.98.

1,3-Dichloro-5-*n*-decylbenzene (9c): IR (neat) 3080 (w), 2950 (s), 2920 (s), 2850 (s), 1585 (m), 1570 (s), 1465 (m), 1435 (m), 1380 (w), 1120 (w), 1100 (w), 855 (m), 800 (m), 790 (w), 735 (w), 725 (w), 690 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 1 CH_3), 1.26 (s, 7 CH_2), 1.60 (m, 1 CH_2), 2.53 (br t, 1 CH_2 next to ring), 7.03 (d, 2 Ar H), 7.15 (t, 1 Ar H); mass spectrum, *m/e* 286, 288, 290 (2 Cl, M^+). Anal. Calcd for $C_{16}H_{24}Cl_2$): C, 66.90, H, 8.42; Cl, 24.68. Found: C, 67.64; H, 8.82; Cl, 24.50.

1-*n*-Hexyl-3,5-di-*n*-octylbenzene (10a). To a mixture of **9a** (22.0 g, 0.095 mol) and $NiCl_2$(dppe) (0.05 g, 9.6×10^{-5} mol) in dry diethyl ether (100 mL) stirred at room temperature was added *n*-octylmagnesium bromide (41.23 g, 0.19 mol) in diethyl ether. The contents were then refluxed for a total of 10 days, during which time additional catalyst (4 × 0.05 g) was added periodically. The reaction mixture was then hydrolyzed by adding to cold dilute HCl and extracted with diethyl ether, and the solvent was removed to yield a pale yellow liquid. This was passed through a short alumina column, eluting with pentane, and the colorless liquid obtained was purified by fractional distillation. Compound **10a** (yield 56%) distilled at 178–9 °C (0.1 mm): IR (neat) 3010 (w), 2950 (s), 2920 (s), 2850 (s), 1595 (m), 1455 (m), 1375 (w), 860 (w), 715 (w), 705 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 CH_3), 0.95–1.7 (m, 16 CH_2), 2.58 (br t, 3 CH_2 next to ring), 6.82 (s, 3 Ar H); mass spectrum, *m/e* 386 (M^+). Anal. Calcd for $C_{28}H_{50}$: C, 87.05; H, 12.95. Found: C, 86.95; H, 12.55.

1-*n*-Hexyl-3,5-di-*n*-decylbenzene (10b): IR (neat) 3015 (w), 2960 (s), 2925 (s), 2855 (s), 1600 (m), 1460 (m), 1375 (w), 860 (w), 718 (w), cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 CH_3), 0.95–1.7 (m, 20 CH_2), 2.58 (br t, 3 CH_2 next to ring), 6.82 (s, 3 Ar H); mass spectrum, *m/e* 442 (M^+). Anal. Calcd for $C_{32}H_{58}$: C, 86.88; H, 13.12. Found: C, 86.97; H, 13.35.

1-*n*-Octyl-3,5-di-*n*-hexylbenzene (10c): IR (neat) 3010 (w), 2955 (s), 2920 (s), 2850 (s), 1595 (m), 1455 (m), 1372 (w), 855 (w), 715 (w), 703 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 CH_3), 0.95–1.7 (m, 14 CH_2), 2.58 (br t, 3 CH_2 next to ring), 6.83 (s, 3 Ar H); mass spectrum, *m/e* 358 (M^+). Anal. Calcd for $C_{26}H_{46}$: C, 87.15; H, 12.85. Found: C, 87.29; H, 12.93.

1-*n*-Octyl-3,5-di-*n*-decylbenzene (10d): IR (neat) 3015 (w), 2960 (s), 2930 (s), 2860 (s), 1600 (m), 1460 (m), 1378 (w), 865 (w), 718 (w), 708 (w), cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 CH_3), 0.95–1.7 (m, 22 CH_2), 2.58 (br t, 3 CH_2 next to ring), 6.82 (s, 3 Ar H); mass spectrum, *m/e* 470 (M^+). Anal. Calcd for $C_{34}H_{62}$: C, 86.81; H, 13.19. Found: C, 86.52; H, 13.54.

1-*n*-Decyl-3,5-di-*n*-hexylbenzene (10e): IR (neat) 3010 (w), 2955 (s), 2920 (s) 2850 (w), 1600 (m), 1460 (m), 1380 (w), 865 (w), 805 (w), 735 (w), 725 (w), 710 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 CH_3), 0.95–1.7 (m, 16 CH_2), 2.58 (br t, 3 CH_2 next to ring), 6.83 (s, 3 Ar H); mass spectrum, *m/e* 386 (M^+). Anal. Calcd for $C_{28}H_{50}$: C, 87.05; H, 12.95. Found: C, 87.06; H, 13.30.

1-*n*-Decyl-3,5-di-*n*-octylbenzene (10f): IR (neat) 3018 (w), 2960 (s), 2925 (s), 2855 (s), 1605 (m), 1460 (m), 1380 (w), 870 (w), 805 (w), 735 (w), 725 (w), 710 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88

(11) The ^{13}C NMR data also favor the structure assigned because they show four aromatic carbon types, as expected for structure **2**.

(t, 3 CH_3), 0.9–1.7 (m, 20 CH_2), 2.55 (br t, 3 CH_2 next to ring), 6.83 (s, 3 Ar H); mass spectrum, m/e 442 (M^+). Anal. Calcd for $C_{32}H_{58}$: C, 86.88; H, 13.12. Found: C, 87.08; H, 13.42.

Registry No. **1a**, 29536-28-5; **1b**, 29536-29-6; **1c**, 7694-77-1; **1d**, 29536-30-9; **1e**, 87969-78-6; **2**, 87969-79-7; **4**, 87969-80-0; **8**, 87969-81-1; **9a**, 87969-82-2; **9b**, 87969-83-3; **9c**, 87969-84-4; **10a**, 87969-85-5; **10b**, 87969-86-6; **10c**, 87969-87-7; **10d**, 87969-88-8; **10e**, 87969-89-9; **10f**, 87969-90-2; 1,3,5-$Cl_3C_6H_3$, 108-70-3; 1,2,3-$Cl_3C_6H_3$, 87-61-6; 1,2,4-$Cl_3C_6H_3$, 120-82-1; 1,2,4,5-$Cl_4C_6H_2$, 95-94-3; n-$C_6H_{13}MgBr$, 3761-92-0; n-$C_7H_{15}MgBr$, 13125-66-1; n-$C_8H_{17}MgBr$, 17049-49-9; n-$C_9H_{19}MgBr$, 39691-62-8; n-$C_{10}H_{21}MgBr$, 17049-50-2; $NiCl_2$(dppe), 38754-20-0; $Ni(acac)_2$, 3264-82-2; (n-$C_8H_{17})_2ClC_6H_3$, 87969-91-3.

Nucleophilic Addition to Olefins. 9.[1] Kinetics of the Reaction of Benzylidenemalononitrile with Malononitrile Anion

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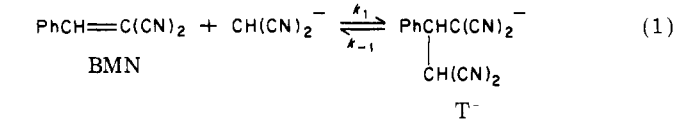
The rates of the reversible addition of $CH(CN)_2^-$ to benzylidenemalononitrile, to form $PhCH(CH(CN)_2)C(CN)_2^-$, have been measured in water and in 50% Me_2SO–50% water. In water at 20 °C, $k_1 = 2.30 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 5.95$ s^{-1}, and $K_1 = 3.86 \times 10^4$ M^{-1}. In 50% Me_2SO–50% water at 20 °C, $k_1 = 9.50 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 6.52$ s^{-1}, and $K_1 = 1.45 \times 10^5$ M^{-1}. The pK_a of the adduct is about 5 pK units lower than that of malononitrile. K_1 for the addition of $CH(CN)_2^-$ is much higher than K_1 for piperidine addition, despite the slightly lower proton basicity of $CH(CN)_2^-$. This reflects the common observation that the carbon basicity of carbanions is higher than that of amines. The intrinsic rate constant for nucleophilic attack by $CH(CN)_2^-$ appears to be somewhat smaller than for amine attack, just as the intrinsic rate constant for protonation of $RC(CN)_2^-$ is lower than for the protonation of amines. This is not unexpected, since structural factors should affect the coordination of bases with Lewis acids in a similar way as coordination with the proton. The change from water to 50% Me_2SO–50% water has the effect of increasing k_1 by a slightly larger factor (4.13) than K_1 (3.75). This implies that the intrinsic rate constant is higher in the less aqueous solvent, which is consistent with the notion that solvent reorganization contributes to the intrinsic barrier of the reaction.

We report a kinetic study of the Michael addition of malononitrile anion to benzylidenemalononitrile (BMN; eq 1). Reaction 1 and similar additions of malononitrile



(1)

anion to ylidenemalononitriles represent the first step in many synthetically useful reactions[2,3] and thus are of considerable interest to organic chemists. Our own main interest in studying reaction 1 is aimed at expanding our systematic investigations of structure–reactivity relationships in nucleophilic additions to activated double bonds[1,4] by including carbanionic nucleophiles.

On a more practical level, kinetic information on reaction 1 is also needed in order to carry out a full analysis of the hydrolysis of BMN (eq 2). This is because reaction 1

$$PhCH{=}C(CN)_2 + OH^- \rightarrow PhCH{=}O + CH(CN)_2^- \quad (2)$$

occurs in competition with reaction 2; i.e., the malononitrile anion produced during the hydrolysis of BMN can attack unreacted BMN under certain reaction conditions.[5]

Results

Upon mixing of an aqueous solution of BMN with a solution of malononitrile anion, the adduct T^- is rapidly formed. This manifests itself by the disappearance of the absorption of BMN (λ_{max} 309 nm) and the appearance of a new species whose spectrum is similar to that of malononitrile anion, as shown in Figure 1. Due to the rapid hydrolysis of BMN at a pH greater than $pK_a^{CH_2(CN)_2}$, the spectrum of T^- was obtained in a borate buffer at pH ~8.5. Even at this pH, hydrolysis is not negligible, and absorbance values had to be obtained by extrapolation to zero time. Further complications arose owing to the nonquantitative conversion of BMN into T^-, and because $CH(CH)_2^-$ contributes to the observed spectrum. This necessitated appropriate corrections, as detailed in the Experimental Section, and affected the accuracy of the spectrum of T^-, for which we estimate a ±10 to ±15% uncertainty in ϵ.

Table I. Reaction of BMN with $CH(CN)_2^-$ at pH 12.52 in Water at 25 °C, μ = 0.5 M[a]

$[CH(CN)_2^-]$[b] × 10^4, M	τ^{-1}, s^{-1}	k_{hyd}, s^{-1}
0		8.0
0.11	~17.0	~7.0
0.22	~22.0	~5.0
1.07	40.8	~2.6
1.60	54.4	~1.7
1.91	75.0	
2.13	74.3	
2.86	110	
3.82	136	
4.05	132	~0.36
5.72	211	
7.63	265	

[a] $[BMN]_0 = 6.6 - 22.8 \times 10^{-6}$ M. [b] Calculated from $[CH_2(CN)_2]_0$ based on $pK_a^{CH_2(CN)_2} = 11.19$.

The kinetics of reaction 1 were measured in aqueous solution at 25 and 20 °C and also in 50% Me_2SO–50%

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