Solvent Effects on Isomer Distributions in Acylation of 1,2,3,4-Tetramethyldibenzofuran: Regiospecific Solvation of the Intermediate σ-Complex

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A large solvent effect is observed in Friedel–Crafts acylation of 1,2,3,4-tetramethyldibenzofuran (TMD). 8-Acyl-TMD is by far the major product in nitrohydrocarbons while 7-acyl-TMD is favoured in chlorohydrocarbons and is the major product in many cases. The influence of temperature, and the nature of the reaction medium, acylating agents, and added nitro-compounds on the isomer distribution, are examined in detail. It is demonstrated that neither rearrangement of the products, nor thermodynamic differences between the 7- and 8-position of TMD, nor reduction in electrophilicity of the acylium ion by solvation are responsible for the solvent effect. Specific association of a nitrohydrocarbon solvent with the intermediate σ-complex leading to 8-acyl-TMD is presented as the pathway of the reaction.

Solvents play a key role in aromatic substitution reactions in determining positional selectivity. For example, nitration of benzeneboronic acid with nitric acid occurs at the *ortho*-position in acetic anhydride and at the *meta*-position in sulphuric acid.[1] Chlorination of toluene with chlorine generally gives high *ortho*/*para* ratios in protic solvents compared with low ratios in aprotic solvents.[2] Friedel–Crafts acetylation of naphthalene takes place at the α-position in chloroform, whereas the reaction proceeds predominantly at the β-position in nitromethane.[3]

In the first example above, the nature of the substrate changes with a change in solvent whereas in the second case the solvent alters the nature of the electrophile. In the Friedel–Crafts acetylation of naphthalene, although some questions still remain to be answered,[4] it appears that steric interaction of the solvated electrophile with the *peri*-hydrogen is responsible for the positional selectivity.[5] As far as we know, there have been no reports of the solvation of the intermediate σ-complex significantly altering the positional selectivity.

In the course of our study on dibenzofuran chemistry, we have carried out Friedel–Crafts acylations of 1,2,3,4-tetramethyldibenzofuran (TMD) and observed that the isomer distributions at the 7- and 8-position in TMD change dramatically with a change in the nature of the solvent. We have attempted to interpret the solvent effects on the isomer distribution in terms of specific association of the solvent with the intermediate σ-complex during the course of the reaction.

Results and Discussion

Friedel–Crafts reaction of TMD with acyl chlorides gave acyl-TMDs (ATMDs) (1)—(20) (Scheme 1). The structure of the ATMDs was determined on a basis of their spectroscopic data (Table 6). The protons at the 1- or 9-position of dibenzofuran derivatives are very deshielded by the induced ring currents of the outer aromatic and furan rings.[6,7] In the u.v. spectra of dibenzofurans containing a strong electronic substituent such as an acyl group at the 3- or 7-position, the longest wavelength bands are, in general, shifted to longer wavelengths (at 310—330 nm) than in those of the corresponding derivatives substituted at other positions.[8] In addition, it is well known that the 1- (or 9-) and the 4- (or 6-) position of dibenzofuran are very low in reactivity towards electrophilic substitutions.[9]

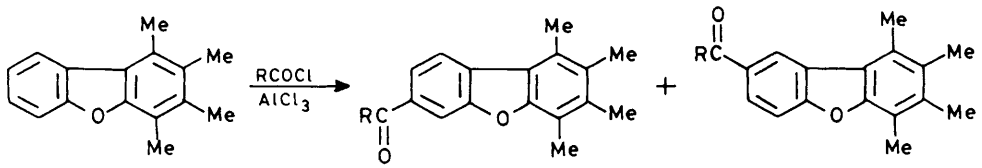
ATMDs (2), (4), (6), (8), (10), (12), (14), (16), (18), and (20) show proton resonances at δ 8.35—8.55 as singlets which are readily assigned to 9-H. The longest wavelength bands in the u.v. spectra for them are observed at 269—278 nm in ethanol. On the other hand, for ATMDs (1), (3), (5), (7), (9), (11), (13), (15), (17), and (19), 9-H signals are observed at δ 7.87—8.01 as doublets and the longest wavelength bands are observed in the region 314—328 nm. Consequently, it is concluded that the former are 8-acyl-TMDs (8-ATMDs), and the latter are 7-ATMDs.

The crude products were analysed by g.l.c. under various conditions. Little peaks showing the formation of other isomers, 6- or 9-ATMD, however, were detected in the vicinity of the retention times for 7- and 8-ATMD. Considering that the sum of the yields of 1- and 4-benzoyldibenozfurans in Friedel–Crafts benzoylation of dibenzofuran in nitrobenzene or tetrachloroethane was less than 1% of the total yield of monobenzoyldibenzofurans,[9d] products resulting from an attack at the 6- and 9-position of TMD by the acylating agents would be of little consequence. Therefore, we are concerned only with the formation of 7-and 8-ATMD. The distributions of 7- and 8-ATMD formed in the acetylation of TMD in various solvents were examined by g.l.c. in detail (Table 1).

The solvent effects on the isomer distribution can be divided into those of two solvent groups, *i.e.* nitrohydrocarbons giving a high ratio of the 8- to the 7-isomer and chlorohydrocarbons giving a low ratio. To examine whether a large difference in the isomer ratio exists between the two solvent groups, the reaction of TMD with a variety of acyl chlorides was carried out both in nitroethane and in 1,2-dichloroethane (Table 2). A similar large solvent effect on the isomer distribution was observed for all acylations.

Several possible mechanisms may account for the high ratio of 8-ATMD in nitrohydrocarbons. The results in Table 1 indicate no direct relationship between the isomer distribution and the dielectric constant of the solvent used. The proportion of 8-isomer formed changes little with a change in dielectric constant within the same group of solvents (for example, between nitroethane and nitrobenzene or between 1,2-dichloroethane and *m*-dichlorobenzene).

Acylation may occur first at the 7- and 8-position to yield both 7- and 8-ATMD but the resulting 7-ATMD may rearrange intramolecularly to 8-ATMD under the Friedel–Crafts reaction conditions to give a high proportion of 8-ATMD. However, 7-ATMD was recovered unchanged after being allowed to stand in nitroethane in the presence of aluminium chloride for 24 h at room temperature. 8-ATMD was recovered unchanged after similar treatment. Careful



TMD 7-ATMD 8-ATMD

R = Me	(1)	(2)
R = Et	(3)	(4)
R = Pr^i	(5)	(6)
R = Ph	(7)	(8)
R = p-MeC$_6$H$_4$	(9)	(10)
R = m-FC$_6$H$_4$	(11)	(12)
R = p-ClC$_6$H$_4$	(13)	(14)
R = p-FC$_6$H$_4$	(15)	(16)
R = p-Bu^{t}C$_6$H$_4$	(17)	(18)
R = p-MeOC$_6$H$_4$	(19)	(20)

Scheme 1.

Table 1. Solvent effect on the isomer distributions in the acetylation of TMD

Reaction solvent	Dielectric constant of solvent [a]	Conversion (%)	Isomer distribution (%) 7-Ac-TMD	8-Ac-TMD	8-isomer / 7-isomer
$MeNO_2$	35.87	85	15	85	5.7
$PhNO_2$	34.82	90	24	76	3.2
$EtNO_2$	28.06	81	16	84	5.3
Pr^nNO_2	23.24	80	16	84	5.3
CH_2ClCH_2Cl	10.36	96	58	42	0.7
$CHCl_2CH_3$	10.00	95	52	48	0.9
o-$Cl_2C_6H_4$	9.93	98	58	42	0.7
CH_2Cl_2	8.93	95	59	41	0.7
$CHCl_2CHCl_2$	8.20	95	54	46	0.9
CCl_3CH_2Cl	5.82	93	46	54	1.2
PhCl	5.62	95	46	54	1.2
m-$Cl_2C_6H_4$	5.04	96	44	56	1.3
CCl_3CHCl_2	2.41	93	34	66	1.9
CCl_4	2.24	92	35	65	1.9

[a] From F. A. Riddick and W. B. Bunger, ' Organic Solvents,' Wiley-Interscience, New York, 1970.

g.l.c. analyses of these recovered substances showed no evidence for the rearrangement of 7- to 8-ATMD, or the reverse.

Although not expected from the structure of the TMD molecule, there may be a significant thermodynamic difference between compounds with substituents of the 7- and 8-position of TMD as observed for the α- and β-position of naphthalene.[10] If such a difference exists, the isomer distributions of 7- and 8-ATMD should change with a change in reaction temperature. Competitive Friedel–Crafts acetylations between TMD and p-xylene or between naphthalene and p-xylene were examined in 1,2-dichloroethane solutions at various temperatures. As shown in Table 3, both the relative rates of TMD to p-xylene and of naphthalene to p-xylene decrease with an increase in the reaction temperature. The percentage of β-acetylnaphthalene, which is the thermodynamically controlled product, increases with an increase in the reaction temperature. In contrast, the isomer distributions of acetyl-TMD stayed constant over the temperature range 0—80 °C. Thus, it appears that there are essentially no thermodynamic differences between the 7- and 8-position of TMD.

It is well known from the selectivity rule [11] that isomer distributions in aromatic electrophilic substitution are affected by the electrophilicity of attacking agents. The electrophilicity of the acylating agents in nitrohydrocarbons may be decreased by solvation leading to high positional selectivity favouring 8-ATMD. In fact, the conversions in nitrohydrocarbons are lower than those obtained in chlorohydrocarbons. This shows that the reactivity of the acylating agents are indeed decreased by solvation.

The ^{1}H n.m.r. spectra of an equimolar complex of p-toluyl chloride and aluminium chloride were measured in various solvents at 23 °C, prior to addition to a solution of TMD dissolved in the same solvent. The chemical shifts for the ring protons at the 2- and 3-position and methyl protons at the 4-position in p-toluyl chloride–aluminium chloride complex are compiled together with the results of the isomer distributions for p-toluylation of TMD in Table 4.

Both the ring and methyl protons in the complex are gradually deshielded on going from nitrobenzene to tetrachloroethane. They are considerably shielded in nitrohydrocarbons, which preferentially yield 8-toluyl-TMD, relative to the protons in the same complex in chlorohydrocarbons. This indicates that the acylating agents are strongly solvated in the former media, thus decreasing their electrophilicity. However,

no simple relationships are observed between the degree of shielding effects and the isomer distribution. In addition, if the preferential formation of 8-ATMD in nitrohydrocarbon media is due to the decrease in the electrophilicity of acylating agents by solvation, the ratio of 8-ATMD in Friedel–Crafts aroylations of TMD in 1,2-dichloroethane solution would be related to the substituent constants with a negative slope because electron-donating groups generally reduce the electrophilicity of aroylating agents.[12] Contrary to this prediction, plots of the percentage of 8-ATMD in the product mixtures *versus* Brown's electrophilic substituent constant[13] gave a linear relationship with a positive slope (Figure 1). On the other hand, the same plots for the reactions in nitroethane solution gave an almost flat line which indicates that the ratio of 8-ATMD is independent of the nature of the aroylating agent.

Thus, the evidence presented so far demonstrates that neither intramolecular rearrangement, nor the thermodynamic difference between the 7- and 8-position of TMD, nor the

Table 2. Solvent effect on the isomer distributions in the acylation of TMD

Acylating agents	Conversion (%)	Isomer distribution (%) 8-ATMD in $EtNO_2$	7-ATMD (in CH_2ClCH_2Cl)
EtCOCl	80	85	15
	(98	37	63)
Pr^iCOCl	80	84	16
	(97	47	53)
PhCOCl	90	81	19
	(96	47	53)
p-MeC_6H_4COCl	86	80	20
	(95	41	59)
p-ClC_6H_4COCl	80	80	20
	(98	48	52)
m-FC_6H_4COCl	84	84	16
	(97	55	45)
p-FC_6H_4COCl	80	80	20
	(98	47	53)
p-$Bu^tC_6H_4COCl$	78	79	21
	(96	41	59)
p-$MeOC_6H_4COCl$	25 [a]	65 [a]	35 [a]
	(90	33	67)

[a] Results for the reaction in nitrobenzene. The conversion of the reaction in $EtNO_2$ was too low to measure the isomer distribution.

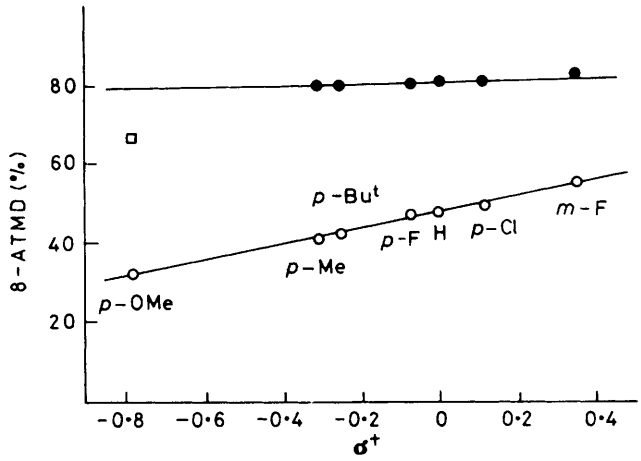


Figure 1. Plot of percentage of 8-ATMD in the products of the aroylations of TMD *versus* electrophilic substituent constant for the substituents in the aroylating agents: ● in $EtNO_2$, □ in $PhNO_2$, ○ in CH_2ClCH_2Cl

Table 3. Temperature effect on the isomer distributions and the relative rates for the competitive acetylations of TMD or naphthalene (NA) with *p*-xylene (X) [a]

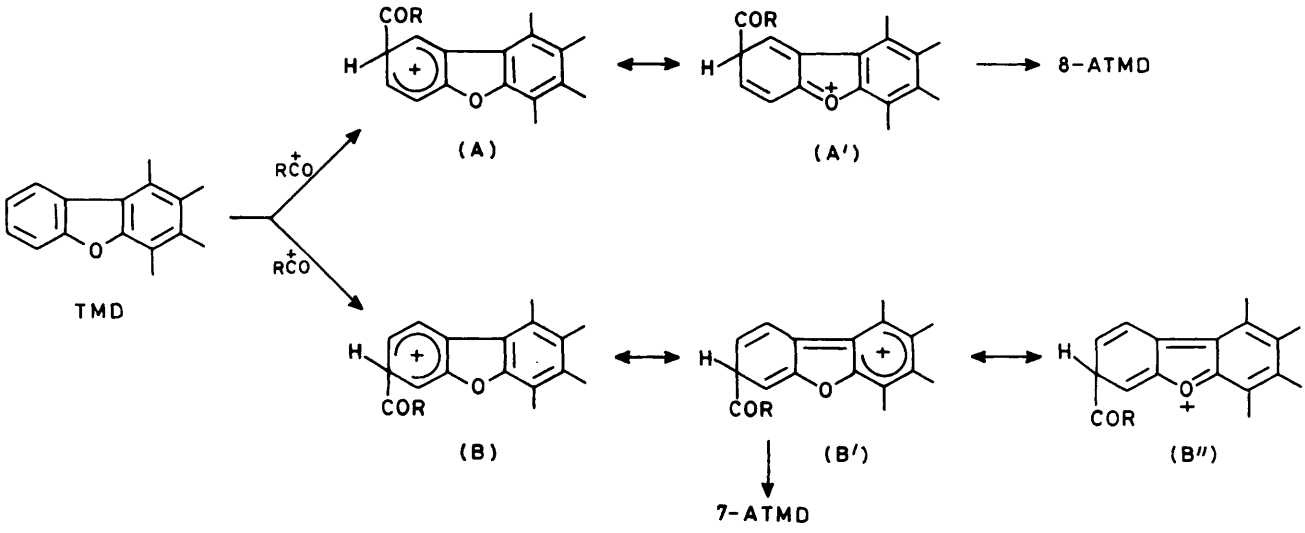
Reaction temperature (°C)	For TMD–X Relative rate	7-Ac-TMD	8-Ac-TMD	For NA–X Relative rate	α-Ac-NA	β-Ac-NA
0	378	52	48	6.47	23	77
15	231	53	47	5.38	15	85
30	135	52	48	3.76	11	89
50	107	53	47	3.38	11	89
80	55	51	49	2.33	10	90

[a] The reactions were carried out in CH_2ClCH_2Cl.

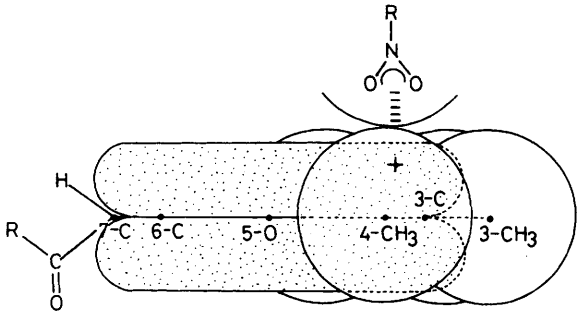
Table 4. Solvent effects on the ^1H n.m.r. chemical shifts of *p*-toluyl chloride–aluminium chloride complex and on the isomer distributions in the *p*-toluylation of TMD

Solvent	^1H Chemical shift δ of the complex [a] 2-H	3-H	4-Me	Isomer distribution (%) 7-isomer	8-isomer
$PhNO_2$	*b*	*b*	2.13	18	72
$MeNO_2$	7.82	7.20	2.23	21	79
$EtNO_2$	7.94	7.32	2.38	20	80
Pr^nNO_2	8.02	7.40	2.43	16	84
o-$Cl_2C_6H_4$	8.04	*b*	2.60	76	24
m-$Cl_2C_6H_4$	8.14	*b*	2.63	62	38
$CHCl_2CH_3$	8.69	7.94	3.00	64	36
CH_2Cl_2	8.83	8.07	3.12	66	34
CH_2ClCH_2Cl	8.89	8.12	3.17	59	41
$CHCl_2CH_2Cl$	8.94	8.18	3.25	51	49
CCl_3CHCl_2	9.01	8.25	3.35	50	50
$CHCl_2CHCl_2$	9.01	8.28	3.35	61	39

[a] From external $SiMe_4$ in capillary. [b] Overlapped with solvent peaks.



Scheme 2.



Scheme 3.

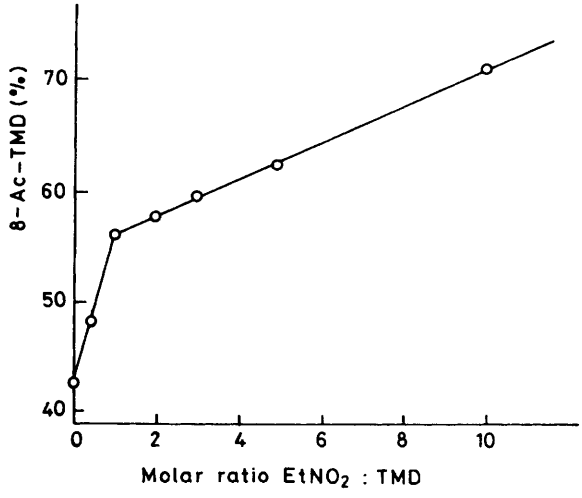


Figure 2. Plot of percentage of 8-acetyl-TMD in the products of the acetylation of TMD in CH_2ClCH_2Cl *versus* molar ratio of the added $EtNO_2$

reduction in electrophilicity of the acylating agent by solvation are responsible for the preferential formation of 8-ATMD in Friedel–Crafts acylation of TMD in nitrohydrocarbon media.

Finally, we have come to the conclusion that the mode of solvation of the intermediates yielding the different ATMDs is different in nitrohydrocarbons and chlorohydrocarbons. The positive charge in the σ-complex (A), (A′) formed by acylation at the 8-position is delocalized within the acyl-substituted ring system involving the oxygen atom. On the other hand, three structures (B), (B′), and (B″) are possible for the σ-complex of acylation at the 7-position, of which (B″) contributes little to the stabilization of the complex because the structure bears a large strain in the furan ring. Therefore, the positive charge in the σ-complex formed by acylation at the 7-position is delocalized in both the ring systems. In fact, the positive charge is more stabilized in the ring substituted with four methyl groups (B′) because of the electron-donating effects of methyl groups.

Van der Waals radii of a 2*p* orbital and a methyl group are 1.70 and 2.00 Å, respectively.[14] A nucleophilic solvent such as nitroethane can approach efficiently and thus stabilize carbonium ion (A) or the oxonium ion (A′) but such an approach is not possible in carbonium ion (B′) because the positive charge is delocalized into the adjacent ring flanked by the sterically bulky methyl groups. This situation can be seen more clearly in the picture drawn with a side-view of the TMD molecule (Scheme 3).

Consequently, this intermolecular stabilization of the σ-complex (A) or (A′) by the solvent molecule would be very significant in reactions carried out in nitrohydrocarbons. Thus, in those reaction media predominant substitution at the 8-position occurs. In contrast, in the reactions in lower nucleophilic solvents such as 1,2-dichloroethane, intramolecular stabilization by conjugation as illustrated by structure (B′) would be preferred, and substitution at the 7-position would be favourable.

If this mechanism is correct, an increase in nucleophilicity of nitrohydrocarbons should affect the isomer distributions in Friedel–Crafts acylation of TMD. To test this hypothesis, Friedel–Crafts acetylation of TMD was carried out in the presence of nitro-compounds in 1,2-dichloroethane solution at 15 °C. The percentage of 8-acetyl-TMD in the products is plotted *versus* the molar ratio of the added nitroethane (Figure 2). As predicted, the percentage of 8-acetyl-TMD increases with an increase in molar ratio of nitroethane. A break in the line is seen when the molar ratio is unity, which perhaps indicates some 1 : 1 complex formation of the reaction intermediate with nitroethane.

Friedel–Crafts acetylation in the presence of a five-fold molar excess of substituted nitrobenzenes demonstrates that the nature of the added nitro-compound also significantly influences the isomer distribution. A plot of the percentage

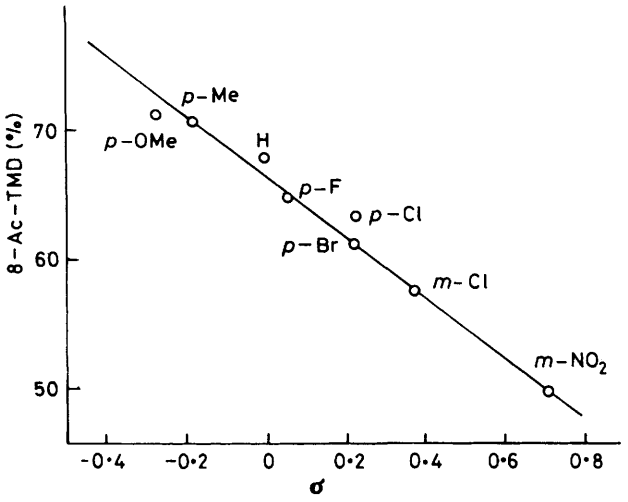


Figure 3. Plot of percentage of 8-acetyl-TMD in the products of the acetylation of TMD in the presence of nitrobenzenes *versus* the Hammett substituent constant for substituents in nitrobenzenes (r 0.993)

of 8-acetyl-TMD against the Hammett substituent constant for the substituents in the nitrobenzenes gave a linear correlation (Figure 3).

Addition of nitrobenzenes possessing electron-donating groups which would enhance the nucleophilicity of the nitro-group increases the ratio of 8-acetyl-TMD in the acetylated TMD.

On the other hand, in chlorohydrocarbons which lack such specific solvation ability, intramolecular stabilization as shown in structure (B′) would be more significant in the transition state. This carbonium ion should be more stable in solvents providing a larger reaction field. In fact, the percentage of 7-acetyl-TMD in the product in the acetylation of TMD increases linearly with an increase in the dielectric constant of the chlorohydrocarbon (Table 1). In addition, the percentage of 7-ATMD in the aroylation of TMD in 1,2-dichloroethane solution increases from 45 to 67% with an increase in the electron-donating ability of the substituents in the aroylating agent (Table 2). This suggests that a decrease in electrophilicity of the attacking agent results in an increase in the positional selectivity at the 7-position.

To confirm such solvent effects on the electronic polarization as described above, the u.v. spectra of TMD were measured in a few solvents (Table 5). According to our previous studies,[8] the ^1L_b band at 312 nm in ethanol is for the transition moment along the short axis of the TMD molecule, which corresponds to polarization involving the oxygen atom in the phenyl ether system. On the other hand, the ^1L_a band at 287.5 nm in ethanol is for the transition moment along the long axis, which corresponds to polarization within the diphenyl system. The ^1L_b band in ethanol or tetrahydrofuran is observed at longer wavelengths relative to that in chlorohydrocarbons. In contrast, the ^1L_a band in dichloromethane or 1,2-dichloroethane is observed at longer wavelengths than that in ethanol. This may suggest that nucleophilic solvents augment polarizations such as in the intermediate (A′) assumed for Friedel–Crafts acylation of TMD, whereas chlorohydrocarbons induce polarization involving the intermediate (B′).

In conclusion, the dramatic solvent effect on the isomer distribution observed in Friedel–Crafts acylation of TMD can be explained by regiospecific solvation by nitrohydrocarbon of the σ-complex leading to the 8-isomer.

Table 5. Solvent effects on the u.v. spectra of TMD

Solvent	^1L_a Band $\lambda_{max.}$/nm (log ε)	^1L_b Band $\lambda_{max.}$/nm (log ε)
EtOH	287.5 (4.28)	312.0 (3.51)
THF	287.5 (4.30)	312.0 (3.51)
$(Pr^i)_2O$	287.5 (4.29)	312.5 (3.55)
$CHCl_3$	289.0 (4.30)	310.0sh (3.30)
CH_2Cl_2	289.0 (4.30)	310sh (3.30)
CH_2ClCH_2Cl	290.0 (4.24)	310sh (3.53)

Experimental

1,2,3,4-Tetramethyldibenzofuran (TMD), m.p. 111 °C, was prepared according to the procedure described in our previous paper.[7] All solvents used for reactions were of spectroscopic grade. All chemicals used are commercially available. I.r. spectra were recorded on a Hitachi model EPI-S2 spectrophotometer for KBr pellets. U.v. spectra were recorded on a Beckman model DB-GT spectrophotometer for ethanol solutions. ^{1}H N.m.r. spectra were recorded on a JEOL-4H model 100 spectrometer in tetrachloromethane solution with $SiMe_4$ internal standard. G.l.c. analyses were carried out on a Hitachi model GC 163 gas chromatograph equipped with a hydrogen flame ionization detector and a stainless steel column (3 m × 3 mm) packed with 3% Dexil 300 GC on Chromosorb W. Isomer distributions were calculated from peak areas obtained by a Takeda model TR 2220A integrator after calibrating for each authentic compound.

Isolation of Acyl-TMD (ATMD).—To a solution of TMD (2.00 g, 9 mmol) in nitromethane (10 cm^3), a solution of acetyl chloride (0.84, g 11 mmol) and aluminium chloride (1.42 g, 11 mmol) in nitromethane (10 cm^3) was added with stirring at 0 °C over 10 min. After the reaction mixture was stirred for 2 h at 15 °C, 0.1M-hydrochloric acid (30 cm^3) was added and then the solvent and unchanged TMD were distilled off with steam to give a crude product (2.00 g, 85%), m.p. 115—119 °C as the residue. The crude product was chromatographed on alumina with benzene to give 8-acetyl-1,2,3,4-tetramethyldibenzofuran (2) (0.56 g, 24%), m.p. 140—143 °C. Recrystallization from ethanol gave (2), m.p. 145—146 °C. In a similar manner, Friedel–Crafts reactions of TMD with acyl chlorides were carried out in nitromethane to give the 8-ATMDs (4), (6), (8), (10), (12), (14), (16), (18), and (20).

Friedel–Crafts acetylation in 1,2-dichloroethane under the same conditions as described above gave a crude product (2.35 g, 99%), m.p. 139—149 °C. The product was heated with ethanol (*ca.* 10 cm^3) under reflux for *ca.* 10 min and then filtered immediately to give 7-acetyl-1,2,3,4-tetramethyldibenzofuran (1) as a residue of the filtration (1.02 g, 43%), m.p. 161—163 °C. Recrystallization from ethanol gave (1), m.p. 165—166 °C. In a similar manner, Friedel–Crafts reactions of TMD with acyl chlorides were carried out in 1,2-dichloroethane to give the 7-ATMDs (3), (5), (7), (9), (11), (13), (15), (17), and (19). The analytical and spectroscopic data are summarized in Table 6.

Solvent Effects on the Isomer Distributions.—To a solution of TMD (1.00 g, 4 mmol) in a given solvent (20 cm^3), a

Table 6. Analytical data for ATMDs (1)—(20)

Compound (Formula)	Yield (%)	M.p. [a] (°C)	Found (%) (Required) C	H	$\nu_{C=O}$(KBr)/cm^{-1}	$\lambda_{max.}$(log ε)/nm (in EtOH)	δ (9-H) [b] (CCl_4)
(1)	43	165—166	81.1	6.7	1 680	314(4.42)	7.90
($C_{18}H_{16}O_2$)			(81.2	6.8)			
(2)	24	145—146	81.0	6.9	1 682	248(4.39)	8.37
($C_{18}H_{18}O_2$)			(81.2	6.8)		270(4.51)	
(3)	30	146—147	81.5	7.3	1 685	314(4.50)	7.87
($C_{19}H_{20}O_2$)			(81.4	7.2)			
(4)	45	147—148	81.4	7.3	1 685	248(4.41)	8.40
($C_{19}H_{20}O_2$)			(81.4	7.2)		269(4.52)	
(5)	46	156—157	81.7	7.6	1 665	315(4.44)	7.94
($C_{20}H_{22}O_2$)			(81.6	7.5)			
(6)	26	127—128	81.5	7.5	1 672	248(4.46)	8.55
($C_{20}H_{22}O_2$)			(81.6	7.5)		270(4.56)	
(7)	38	147—148	84.1	6.1	1 654	322(4.42)	7.95
($C_{23}H_{20}O_2$)			(84.1	6.1)			
(8)	32	156—157	84.1	5.9	1 654	254(4.14)	8.44
($C_{23}H_{20}O_2$)			(84.1	6.1)		275(4.54)	
(9)	22	165—166	84.1	6.6	1 653	260(4.17)	7.97
($C_{24}H_{22}O_2$)			(84.2	6.5)		323(4.36)	
(10)	23	154—155	84.2	6.3	1 647	258sh(4.43)	8.43
($C_{24}H_{22}O_2$)			(84.2	6.5)		275(4.57)	
(11)	4	136—137	79.9	5.6	1 652	328(4.36)	7.98
($C_{23}H_{19}FO_2$)			(79.7	5.5)			
(12)	11	149—150	79.7	5.7	1 650	256(4.37)	8.48
($C_{23}H_{19}FO_2$)			(79.7	5.5)		278(4.48)	
(13)	6	151—152	76.1	5.3	1 656	260(4.27)	8.01
($C_{23}H_{19}ClO_2$)			(76.1	5.3)		327(4.37)	
(14)	34	159—160	76.1	5.3	1 660	263(4.49)	8.38
($C_{23}H_{19}ClO_2$)			(76.1	5.3)		278(4.57)	
(15)	29	158—159	79.7	5.7	1 655	324(4.49)	8.01
($C_{23}H_{19}FO_2$)			(79.7	5.5)			
(16)	45	167—168	79.7	5.4	1 645	254(4.35)	8.50
($C_{23}H_{19}FO_2$)			(79.7	5.5)		275(4.45)	
(17)	29	140—141	84.4	7.4	1 650	261(4.26)	7.95
($C_{27}H_{28}O_2$)			(84.3	7.3)		324(4.43)	
(18)	41	160—161	84.4	7.5	1 645	256sh(4.45)	8.45
($C_{27}H_{28}O_2$)			(84.3	7.3)		275(4.59)	
(19)	55	161—162	80.4	6.1	1 655	256sh(4.03)	7.98
($C_{24}H_{22}O_3$)			(80.4	6.2)		322(4.44)	
(20)	6	157—158	80.5	6.2	1 655	254(4.29)	8.35
($C_{24}H_{22}O_3$)			(80.4	6.2)		275(4.50)	

[a] From ethanol. [b] Other signals are not given, but ^{1}H n.m.r. spectra of all compounds were consistent with their assigned structures.

solution of aluminium chloride (0.72 g, 5 mmol) and acyl chloride (5 mmol) in the same solvent (10 cm^3) was added at 15 °C over 20 min, and the homogeneous solution was then stirred at the same temperature for 2 h. After addition of 0.1M-hydrochloric acid (20 cm^3), the solvent and unchanged TMD were distilled off with steam to give a crude ATMD which was analysed by g.l.c. to determine the isomer distribution.

Influence of the Reaction Temperature.—To a solution of naphthalene (0.282 g, 2.2 mmol) or TMD (0.493 g, 2.2 mmol) and *p*-xylene (0.234 g, 2.2 mmol) in 1,2-dichloroethane (5 cm^3), a solution of acetyl chloride (0.032 g, 0.4 mmol) and aluminium chloride (0.053 g, 0.4 mmol) in the same solvent (2.5 cm^3) was added over 20 min at a given temperature, and then the reaction mixture was stirred for 2 h at the same temperature. After work-up as described above, the crude products were analysed by g.l.c.

Preparations and ^{1}H *N.m.r. Measurements of* p-*Toluyl Chloride–Aluminium Chloride Complex.*—*p*-Toluyl chloride (0.278 g, 1.8 mmol) and aluminium chloride (0.240 g, 1.8 mmol) were dissolved in a given solvent (5 cm^3) with stirring under nitrogen at room temperature. Part of the homogeneous solution was placed in a n.m.r. tube and the ^{1}H n.m.r. spectrum was measured on a 100 MHz ^{1}H n.m.r. spectrometer with external (capillary) $SiMe_4$ as the standard at 23 °C.

The rest of the solution was added to a solution of TMD (0.400 g, 1.8 mmol) in the corresponding solvent (15 cm^3) with stirring at 15 °C over 20 min and then the mixture was stirred for 3 h at the same temperature. After work-up as described above, the crude products were analysed by g.l.c.

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