Homolytic Base-Promoted Aromatic Alkylations by Alkylmercury Halides[1]

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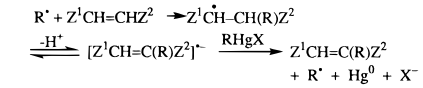
Abstract: Electron transfer chain reactions leading to substitution in electronegatively substituted benzene derivatives can be observed with alkylmercury halides in the presence of proton acceptors such as DABCO. Promotion by base involves the abstraction of a proton from the substituted cyclohexadienyl adduct radical to form a radical anion which readily transfers an electron to RHgX with the regeneration of R•. Aromatic substitutions involving *t*-Bu• are highly regioselective and yield products of only para attack for PhCHO, $PhCOCH_3$, $PhCOCMe_3$, PhCOPh, PhCN, phthalimides, or 1,2-dicyanobenzene. The ortho/para substitution products are observed for isophthaldehyde or 1,3-dicyanobenzene, while 1,4-dicyanobenzene yields the ortho substitution product. At 25−35 °C substitution by *t*-Bu• ortho to an ester group is not observed and *m*- or *p*-cyanobenzoate esters yield only products of substitution ortho to the cyano group. With the isopropyl radical substitution ortho to the ester function is observed with diethyl isophthalate. Intramolecular radical cyclizations of the radical adducts of 1-aryl-4-penten-1-ones leading to α-tetralones is also promoted by the presence of DABCO. When the aryl group contains a para ester function, spirocyclization occurs leading to a rearrangement acyl radical which can be oxidized by *t*-BuHgCl to the acyl cation and the carboxylic acid.

Introduction

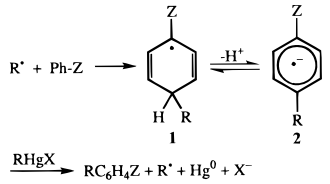
Bases, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), can promote the oxidative (substitutive) homolytic reactions of alkylmercury halides with unsaturated compounds when the adduct radicals possess acidic hydrogen atoms, Scheme 1.[2,3] Previously reported examples of alkylations occurring by Scheme 1 include coumarin,[4] maleimide,[5] acyclic 1,4-enediones,[6] 1,4-naphthoquinone,[4] furmaronitrile,[7] 2-substitution in benzothiazole and benzimidazole,[8] and intramolecular cyclizations leading to α-tetralones.[4,9]

It appeared to us that bimolecular aromatic homolytic substitutions should proceed by a similar mechanism involving

Scheme 1



Scheme 2



1 and **2** provided the substituent Z in Scheme 2 can stabilize the radical adduct **1** and the radical anion **2**.[10,12] Herein we describe such processes occurring in the photolysis of *t*-BuHgX with benzaldehyde, phenones, phthalimides and other disubstituted benzenes as well as further examples of homolytic cyclizations leading to α-tetralones.

⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) Electron Transfer Processes. Part 64.

(2) Promotion of electron transfer by deprotonation of a radical was originally described in the radical chain degradation of diazonium ions in CH_3OH ($CH_2{=}O^{\bullet-} + ArN_2^+ \rightarrow CH_2{=}O + ArN_2^{\bullet}$): Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1967**, *84*, 6712. Bunnett, J. F.; Takayama, H. *J. Am. Chem. Soc.* **1968**, *90*, 5173. Another early example was the formulation of the homolytic conversion of *p*-nitrobenzyl chloride to the stilbene: Russell, G. A.; Pecoraro, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3331. With R = *p*-$O_2NC_6H_4$ the reaction involves

$$RCH_2Cl^{\bullet-} \xrightarrow{-Cl^-} RCH_2^{\bullet} \xrightarrow{RCHCl:^-} RCH_2CH(Cl)R^{\bullet-} \xrightarrow{-Cl^-} RCH_2CHR^{\bullet} \xrightarrow{-H^+} RCH{=}CHR^{\bullet-} \xrightarrow{RCH_2Cl} RCH{=}CHR + RCH_2Cl^{\bullet-}$$

(3) Another example of promotion of electron transfer by loss of a proton is the $S_{RN}1$-type process in cyclizations of aryl radicals with an *o*-$(CH_2)_n$-NHC(S)R side chain (attack of Ar• upon S; *n* = 0, 1; R = Me, Ph) in the presence of AlBN and DABCO or Bu_3SnH. It is suggested that Bu_3SnH can also serve as a proton acceptor in these processes: Bowman, W. R.; Heaney, H.; Jordon, B. M. *Tetrahedron* **1991**, *47*, 10119.

(4) Russell, G. A.; Kim, B. H.; Kulkarni, S. V. *J. Org. Chem.* **1989**, *54*, 3768.

(5) Russell, G. A.; Kim, B. H. *Synlett* **1990**, 87.

(6) Russell, G. A., Kim, B. H. *Tetrahedron Lett.* **1990**, *31*, 6273.

(7) Russell, G. A.; Chen, P.; Yao, C.-F.; Kim, B. H. *J. Am. Chem. Soc.* **1995**, *117*, 5967.

(8) Russell, G. A.; Wang, L.; Rajaratnam, R. *J. Org. Chem.*, in press.

(9) Russell, G. A.; Kulkarni, S. V.; Khanna, R. *J. Org. Chem.* **1990**, *55*, 1080.

(10) Loss of a proton from a dihydropyridine radical cation is a key step in the oxidative homolytic alkylation of pyridinium ions in aqueous or Me_2SO solutions.[11] It has also been suggested that Bu_3SnH,[3] or I^-, can serve as a proton acceptor in homolytic cyclization reactions of *N*-(ω-iodoalkyl)pyridinium salts: Murphy, J. A.; Sherburn, M. S. *Tetrahedron Lett.* **1990**, *31*, 1625, 3495. Murphy, J. A.; Sherburn, M. S.; Dickinson, J. M.; Goodman, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1069.

(11) (a) Minisci, F.; Vismara, E.; Fontana, F.; Morini, G.; Serravalle, M.; Giordano, C. *J. Org. Chem.* **1987**, *52*, 730. (b) Russell, G. A.; Rajaratnam, R.; Wang, L.; Shi, B. Z.; Kim, B. H.; Yao, C. F. *J. Am. Chem. Soc.* **1993**, *115*, 10596.

(12) It has been suggested that at 160 °C, Bu_3SnH can remove a proton from the cyclohexadienyl radical formed by cyclization of PhN(Me)-$COCMe_2$•: Beckwith, A. L. J.; Storey, J. M. D. *J. Chem. Soc., Chem. Commun.* **1995**, 977. A more likely example is proton abstraction by Bu_3-SnH in refluxing toluene from the cyclohexadienyl radical formed by 1,6-cyclization of *o*-C_6H_4•N(Me)COAr and the sulfur analog.[3] One of the first examples of oxidative cyclization employing Bu_3SnH, and possibly involving proton abstraction, was the uninitiated 1,6-cyclization of *N*-(*p*-tosyl)-α-(halomethyl)piperidines at 22 °C: Koehler, J. J.; Speckamp, W. N. *Tetrahedron Lett.* **1977**, 631, 635.

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Scheme 3

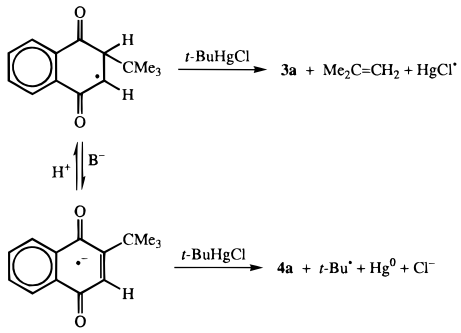


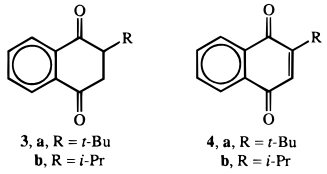
Table 1. Photolysis of *t*-BuHgX with Benzaldehyde in Me_2SO at 35−40 °C[a]

X	additive (equiv)	time, h	% **5a**[b]
Cl	none	24	3
I	none	24	0
I	KI (4), $K_2S_2O_8$ (2)	24	4
Cl	DABCO (4)	24	42
I	DABCO (4)	24	48
I	DABCO (4)	42	60

[a] 0.5 M PhCHO and 2 M *t*-BuHgX irradiated with a 275 W fluorescent sunlamp. [b] By GC with toluene as an internal standard. Unreacted benzaldehyde remained in all experiments.

Results and Discussion

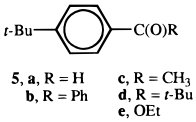
1,4-Naphthoquinone. Photolysis with *t*-BuHgCl in benzene at 35−40 °C produces the reductive and oxidative alkylation products **3a** and **4a**.[4] In the presence of acids such as HOAc



or NH_4^+, **3a** is the exclusive product, but in the presence of DABCO only **4a** is formed.[4] The results are consistent with Scheme 3.

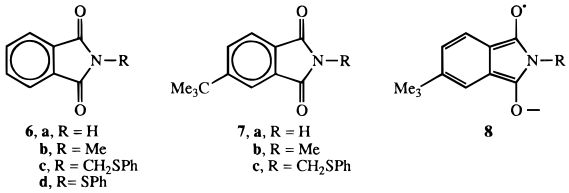
With *i*-PrHgCl, photolysis in Me_2SO produces only the mono- (**4b**) and diisopropylated quinones even in the presence of NH_4^+ or I^-. Apparently conversion of the adduct radical to the radical ion followed by electron transfer to RHgX occurs readily in Me_2SO. However, in benzene in the absence of any additive, **3b** and **4b** are formed (44 and 38%, respectively), while in the presence of 4 mol % of HOAc the yield of **3b** increases to 46% and **4b** decreases to 14%, and with 2 equiv of NH_4^+, **3b** and **4b** are formed in 58 and 24% yield. In the presence of 4 equiv of DABCO only **4b** is observed in 77% yield.

Benzaldehyde and Phenones. Photolysis of *t*-BuHgX (X = Cl, I) with PhCHO in Me_2SO in the presence of DABCO forms 4-*tert*-butylbenzaldehyde (**5a**) slowly but cleanly. In the absence of DABCO essentially no reaction is observed, Table 1.



With KI and $K_2S_2O_8$ as additives, *t*-Bu• formation is very rapid as evidenced by CIDNP for the $Me_2C{=}CH_2$ and Me_3CH formed by disproportionation.[13] However, **5a** is formed in only trace amounts in the presence of this high flux of *t*-Bu• and the oxidizing agent $S_2O_8^{2-}$. It is difficult to convert the adduct radical, probably formed reversibly, to **5a** in the absence of a basic reagent. Reaction of *t*-BuHgCl with *p*-chlorobenzaldehyde failed to yield alkylation products. If para attack by *t*-Bu• had occurred the resulting cyclohexadienyl radical would have readily eliminated Cl• with the formation of **5a**. There was also no indication of any product formation from benzaldehyde or *p*-chlorobenzaldehyde involving *t*-Bu• addition to the carbonyl group or abstraction of the aldehyde hydrogen atom. Photochemical reactions of *t*-BuHgI/DABCO with benzophenone, acetophenone, or *tert*-butyl phenyl ketone also yielded only the para substitution products: **5b** (50% yield in 35 h accompanied by 13% of 4,4′-di-*tert*-butylbenzophenone), **5c** (32% in 44 h), **5d** (19% in 47 h). Again, only traces of **5** are formed in the absence of DABCO. Ethyl benzoate was much less reactive than benzaldehyde and gave only 10% of ethyl 4-*tert*-butylbenzoate in 42 h, while benzonitrile gave 24% of the 4-*tert*-butyl derivative in 28 h. With $PhNO_2$ essentially no reaction was observed.[14]

Phthalimides. Phthalimides are surprisingly reactive upon photolysis with *t*-BuHgX in Me_2SO (Table 2). Photolysis of **6a** with *t*-BuHgCl or *t*-BuHgI produces only traces of **7a** in the absence of DABCO but excellent yields in its presence. Dark reactions of *t*-BuHgI in the presence of KI and DABCO also produce **7a**.[15] The formation of **7c** occurred in the absence of DABCO upon photolysis with *t*-BuHgCl/KI or in the dark with *t*-BuHgCl/KI/$K_2S_2O_8$. The yield of **7c** upon photolysis with *t*-BuHgCl/KI was drastically reduced by the presence of PTSA suggesting the intermediacy of **8**, even in the absence of DABCO. Although **6c** reacted to yield the aromatic substitution



product **7c**, **6d** reacted with *t*-Bu• to form *t*-BuSPh and the *N*-phthalimidyl radical which was converted to **6a** and alkylated to **7a**.

Benzothiazole and Benzimidazole.[8] The thiazole and imidazole undergo facile attack of *t*-Bu• at C-2. In the presence of PTSA or NH_4^+ the thiazole yields only the reductive alkylation product, while in the presence of DABCO only the oxidative alkylation product is formed. The reactions of benzothiazole thus parallel those of 1,4-naphthoquinone, see Scheme 3. 5-Methylbenzimidazole gives only the oxidative alkylation product possibly by the imidazole serving as the base in Scheme 2. The yield of alkylation product is drastically reduced by excess PTSA but without the formation of the reductive alkylation product.

(13) Russell, G. A.; Guo, D.; Baik, W.; Herron, W. J. *Heterocycles* **1989**, *28*, 143.

(14) With $PhNO_2$ and *t*-BuHgX in Me_2SO in the presence of I^- good yields of PhN(*t*-Bu)OBu-*t* are observed in the presence or absence of DABCO: Russell, G. A.; Yao, C.-F. *Heteroatom Chem.* **1993**, *4*, 433. Under forcing conditions (5 equiv of *t*-BuHgI, 10 equiv of KI, DMF, *hν* for 10 h) 65% of PhN(*t*-Bu)OBu-*t* and 30% of *p*-*t*-BuC_6H_4N(*t*-Bu)OBu-*t* are observed.

(15) The thermal or photochemical formation of *t*-Bu• from *t*-BuHgI is greatly increased by the presence of I^-, possibly from comproportionation to form $(t\text{-Bu})_2$Hg: Russell, G. A.; Hu, S.; Herron, S.; Baik, W.; Ngoviwatchai, P.; Jiang, W.; Nebgen, M.; Wu, Y.-W. *J. Phys. Org. Chem.* **1988**, *1*, 299.

Table 2. *tert*-Butylation of Phthalimides by *t*-BuHgX in Me_2SO at 35−40 °C[a]

substrate	X	additive (equiv)	time, h	product (%)
6a	Cl, I	none	20	**7a** (trace)[b]
6a	Cl	DABCO (4)	10	**7a** (59)[b]
6a	Cl	DABCO (4)	20	**7a** (93)[b]
6a	Cl (2 equiv)	DABCO (4)	20	**7a** (91)[b]
6a	I (2 equiv)	DABCO (4)	5	**7a** (63)[b]
6a	I	DABCO (4), KI (4)	35	**7a** (60)[b,c]
6b	Cl	KI (4)	20	**7b** (30)[d]
6b	Cl	DABCO (4)	20	**7b** (65)[d]
6c	Cl	none	14	**7c** (5)[d]
6c	Cl	KI (4)	14	**7c** (48)[d]
6c	Cl	$K_2S_2O_8$ (2), KI (4)	14	**7c** (76)[d,e]
6c	Cl	PTSA (4), KI (4)	14	**7c** (11)[d]

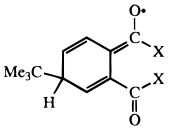
[a] Photolysis of 0.5 M substrate by a 275 W fluorescent sunlamp with 4 equiv of *t*-BuHgX. [b] Yield in Me_2SO-d_6 by ^1H NMR with toluene as an internal standard. [c] Dark reaction. [d] GC yield with toluene as an internal standard after workup with aqueous $Na_2S_2O_8$. [e] In a dark reaction **7c** was formed in 51% yield.

Table 3. *tert*-Butylation of 1,3-Dicyanobenzene in Me_2SO

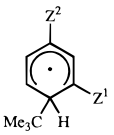
t-BuHgX (X, equiv)	DABCO, KI (equiv)	conditions	**11a**[a] (%)	**12a**[a] (%)
Cl, 1	4, 0	*hν*, 20 min, 35 °C	26	1
Cl, 1	4, 0	*hν*, 1.5 h, 35 °C	44	27
Cl, 4	4, 0	*hν*, 4.5 h, 35 °C		99
I, 2	4, 2	dark, 5.5 h, 25 °C	31	66
I, 4	4, 4	dark, 19 h, 25 °C		99
I, 4	0, 4	dark, 19 h, 25 °C	20	3

[a] By ^1H NMR with toluene as an internal standard in Me_2SO-d_6.

Other Ortho Disubstituted Benzenes. In sharp contrast to the phthalimides, the disubstituted benzene derivatives phthalic anhydride, phthaldehyde, or dimethyl phthalate failed to undergo reactions with *t*-BuHgCl/DABCO/*hν*. For the aldehyde and ester steric inhibition of resonance in the adduct radical **9** appears to be involved. Phthalic anhydride has a more negative



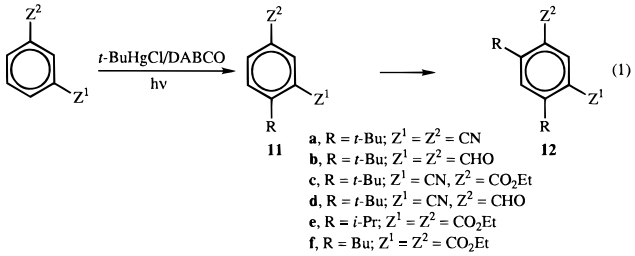
9, X = H or CO_2Me



10

reduction potential than phthalimide (−1.16 vs −0.70 V, SCE, in H_2O)[16] which may explain the reactivities observed since the transition state for attack of the nucleophilic *t*-Bu• upon an aromatic ring should be stabilized by $t\text{-Bu}^+$ $ArX^{\bullet -}$. 1,2-Dicyanobenzene was examined because of the low steric requirements of the cyano group as well as its favorable reduction potential. Indeed, sunlamp photolysis of the dinitrile with 4 equiv each of *t*-BuHgCl and DABCO in Me_2SO for 3 h produced 90% of 4-*tert*-butyl-1,2-dicyanobenzene and 10% of 1,5-di-*tert*-butyl-2,3-dicyanobenzene, while after 10 h of photolysis the yields were 84 and 16%, respectively.

1,3-Disubstituted Benzenes. For 1,3-disubstituted benzenes the adduct radicals **10** can be stabilized by both substituents. With *t*-Bu• the adduct radicals are readily formed only when Z^1 has a low steric requirement such as cyano or formyl. Thus, although no reaction was observed for diethyl isophthalate, 1,3-dicyanobenzene readily underwent base-promoted *tert*-butylation. Table 3 summarizes results for the formation of the mono- and di-*tert*-butylation products **11a** and **12a**, reaction 1. The initial kinetic chain length measured by the $(t\text{-Bu})_2NO^{\bullet}$ inhibition

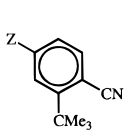


method[17] was 22 for 0.05 M 1,3-dicyanobenzene upon sunlamp photolysis with 4 equiv each of *t*-BuHgCl and DABCO at 35−40 °C. The alkylation also occurred slowly in the dark by use of *t*-BuHgI/KI.[15] This dark reaction occurred even in the absence of DABCO although it was greatly accelerated by its presence (Table 3). From the inhibition period observed with 2 mol % of $(t\text{-Bu})_2NO^{\bullet}$ (30 h) an initial kinetic chain length of 1000 was calculated for the iodide ion promoted dark reaction.

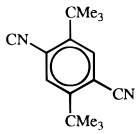
Isophthaldehyde was less reactive than 1,3-dicyanobenzene presumably because of steric strain in forming **10** with Z^1 = CHO. Photolysis with 2 equiv of *t*-BuHgCl and 4 equiv of DABCO for 4 h produced 46% of **11b** and 12% of **12b**. The 3-cyano derivatives of ethyl benzoate or benzaldehyde were more reactive. Thus, photolysis with 4 equiv each of *t*-BuHgCl and DABCO for 12 h produced **11c** in 99% yield without the formation of di-*tert*-butylated product. With 3-cyanobenzaldehyde, 3 h of photolysis yielded **11d** in 84% yield accompanied by 12% of **12d**. No reaction was observed with *m*-cyanoanisole or *m*-cyanonitrobenzene which appeared to act as a radical chain inhibitor.

With a radical having a lower steric requirement than *t*-Bu•, isophthalate esters are also reactive. Thus, photolysis of diethyl isophthalate for 11 h with 2 equiv of *i*-PrHgCl and 4 equiv of DABCO formed **11e** (67%) and **12e** (12%). Under the same conditions BuHgCl gave in 20 h 18% of **11f**.

1,4-Disubstituted Benzenes. The 1,4-disubstituted benzenes were much less reactive than the 1,3-derivatives. No reaction was observed for dimethyl terephthalate or terephthaldehyde. However, 1,4-dicyanobenzene formed a mixture of **13a** and **14** in 58 and 11% yields upon photolysis for 3 h which increased to 61% and 30% after 10 h. Ethyl *p*-cyanobenzoate reacted more slowly but cleanly formed **13b** in yields of 24, 46, 60, and 80% upon photolysis for 6, 18, 28, and 80 h, respectively.



13, **a**, Z = CN
b, Z = CO_2Et



14

Effect of DABCO on Intramolecular Cyclizations To Form α-Tetralones. Photolysis of *t*-BuHgX and $PhCOCH_2CH{=}CH_2$ leads to isomerization to give the α,β-unsaturated ketone. In the presence of I^- good yields of the adduct $PhCOCH(HgI)CH(CH_3)CMe_3$ are formed as evidenced by the isolation of $PhCOCH_2CH(CH_3)CMe_3$ after aqueous workup.[17] With 1-phenyl-4-penten-1-one (**15a**) modest yields of the α-tetralone **16a** are observed with a significant increase in yield in the presence of DABCO. The reaction seems to fit Scheme 2 where loss of a proton from the cyclized cyclohexadienyl

(16) Schwabe, K. *Polarographic and Chemische Konstitution Organische Verbindungen*; Academie-Verlag: Berlin, 1957.

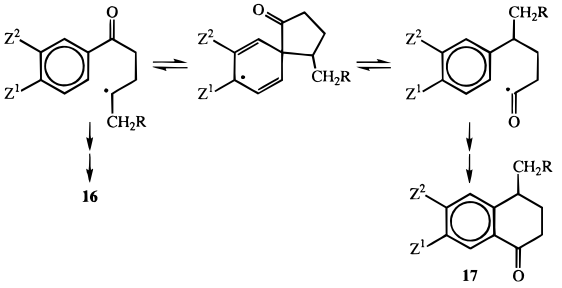
(17) Russell, G. A.; Li, C.; Chen, P. *J. Am. Chem. Soc.* **1995**, *117*, 3645; **1996**, *118*, 9831.

Table 4. Photolysis of RHgCl with 1-Phenyl-4-penten-1-one To Form **16a**[a]

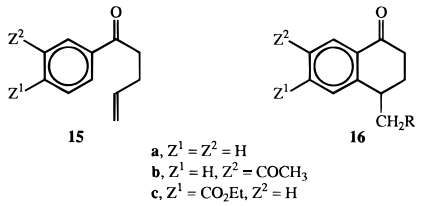
R	X	additive (equiv)	time, h	% **16a**
t-Bu	I	none	24	8
t-Bu	Cl	$K_2S_2O_8$ (2)	24	8
t-Bu	Cl	DABCO (4)	24	42
i-Pr	I	none	24	9
i-Pr	Cl	DABCO (4)	24	37

[a] Sunlamp irradiation of 0.02 M substrate with 0.08 M *t*-BuHgX in Me_2SO at 35−40 °C. [b] GC yield with toluene as an internal standard after workup with aqueous $Na_2S_2O_3$.

Scheme 4

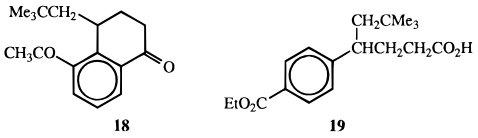


radical yields a radical anion which readily transfers an electron to *t*-BuHgX. Table 4 summarizes the observed yields of **16a**.



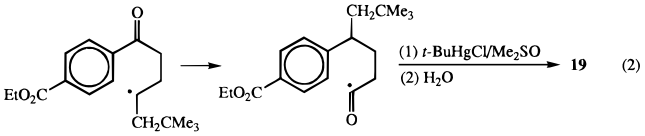
a, $Z^1 = Z^2 = H$
b, $Z^1 = H$, $Z^2 = COCH_3$
c, $Z^1 = CO_2Et$, $Z^2 = H$

Spirocyclization,[18,19] as shown in Scheme 4, would not be revealed in the reactions of **15a** ($Z^1 = Z^2 = H$) if the rearranged radical underwent cyclization. It was also not detected with $Z^1 = H$ and $Z^2 = CH_3CO$ since **15b** upon sunlamp photolysis in Me_2SO for 18 h with *t*-BuHgCl (3 equiv) and DABCO (4 equiv) formed a mixture of **16b** (R = *t*-Bu, 31%) and a second isomer assigned structure **18** (32%).



The formation of **18** was unexpected, but the ^1H NMR of the aromatic hydrogens requires a 1,3-diacyl substitution for **16b** (δ for the aromatic hydrogen between the two acyl groups ~8.5) and a vicinally trisubstituted benzene for **18**. Only the two isomers **16b** and **18** were detected in the crude reaction mixture as judged from ^1H NMR for *tert*-butyl groups.

With **15c** ($Z^1 = CO_2Et$, $Z^2 = H$) evidence for spirocyclization was obtained, but in a rather unexpected manner. Reaction according to the recipe used for **15b**, yielded only two *tert*-butylated products. Isolation and characterization showed the products to be **16c** (R = *t*-Bu, 40%) and the rearranged carboxylic acid **19** (33%). This product requires the rearrangement of the initial adduct radical, undoubtedly facilitated by the para carbonyl substituent, followed by oxidation of the acyl radical, reaction 2. The oxidation probably involves electron transfer from the acyl radical to *t*-BuHgCl followed by trapping

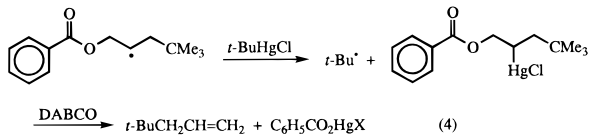


of the acyl cation by Me_2SO and hydrolysis, reaction 3. When Et_2NH was used as the base in PhH solution, photolysis of **15c** with *t*-BuHgCl yielded a mixture of **16c** and the *N*,*N*-diethylamide expected from the rearranged acyl cation. Rearranged cyclized product (such as **17**),[19] or decarbonylated products were

$$RCO^{\bullet} + t\text{-BuHgCl} \rightarrow RCO^{+} + t\text{-Bu}^{\bullet} + Hg^{0} + Cl^{-} \quad (3)$$

not detected indicating that the oxidation of the acyl radical must occur quite readily in either Me_2SO or PhH solution. In a similar manner, it has been previously observed that iminyl radicals (e.g., *t*-BuC═NR$^{\bullet}$) are oxidized by *t*-BuHgX in Me_2SO to form the amides or in benzene in the presence of aniline to form the amidines (*t*-BuC(NHPh)═NR).[20,21] The yields are excellent with R = Ph, and the amides and amidines can even be detected even with R = *t*-Bu or $PhCH_2$ where β-elimination from the imidyl radical occurs readily.[21]

Attempted cyclizations of allyl benzoate or diallyl isophthalate failed completely with *t*-BuHgCl/DABCO/$h\nu$. The reactions formed *t*-$BuCH_2CH{=}CH_2$ by β-elimination reaction 4. Numerous other allyl alcohol derivatives have been observed to yield



(4)

elimination products upon photolysis with *t*-BuHgX, and in some cases the intermediate adduct organomercury halides have been detected, e.g., *t*-$BuCH_2CH(HgCl)CH_2Y$ with Y = OH, OAc, OPh.[22] Similar addition-eliminations occur with derivatives of propargyl alcohol including the benzoate ester.[22] In the present case cyclization is slow because of the preferred s-trans conformation of the ester radical and formation of the 1:1 adduct by reaction with *t*-BuHgCl is the preferred reaction course.[17]

Reactivity of Substrates toward *t*-Bu$^{\bullet}$ in Competitive Oxidative Alkylations. Substrates should demonstrate a constant relative reactivity in oxidative and reductive alkylations (e.g., Scheme 3) provided that radical additions to the substrates are irreversible. This has been shown to be the case in competitive reductive (with I^- added) and oxidative (in the presence of DABCO) alkylations of *N*-methylmaleimide and fumaronitrile where the nitrile is 2.2−2.5 times as reactive as the imide under all conditions.[7] An extensive list of relative reactivities of substrates toward *t*-Bu$^{\bullet}$ in reductive alkylations has been reported using reaction 5 as a standard.[23] In Table 5 similar relative reactivities for oxidative alkylations are summarized based on product analysis of competitive *tert*-butylations.

$$t\text{-Bu}^{\bullet} + (E)\text{-ICH}{=}\text{CHPh} \xrightarrow[35\ ^{\circ}C]{k = 2.5 \times 10^4\ M^{-1}\ s^{-1}} (E)\text{-}t\text{-BuCH}{=}\text{CHPh} + I^{\bullet} \quad (5)$$

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Table 5. Reactivity of *t*-Bu• with Substrates Giving Substitutive (Oxidative) Alkylation at 35 °C in Me_2SO

substrate	standard	reactivity[a]
PhCHO	(*E*)-PhCH=CHI	0.015[b]
$PhCOCH_2CH_2CH=CH_2$	(*E*)-PhCH=CHI	0.047[b]
phthalimide	(*E*)-PhCH=CHI	0.12[b]
2,6-Me_2PyH^+	(*E*)-PhCH=CHI	0.86[c]
1,3-dicyanobenzene	(*E*)-PhCH=CHI	1.9[b]
PhNC	(*E*)-PhCH=CHI	6.5[d]
PyH^+	(*E*)-PhCH=CHI	15[c]
N-methylmaleimide	ethyl fumarate	2700[b,e,f]
fumaronitrile	ethyl fumarate	6400[b,e]
fumaronitrile	*N*-methylmaleimide	6000[b,f]

[a] Relative to (*E*)-PhCH=CHI. [b] In the presence of 1−4 equiv of DABCO. [c] Reference 11b. [d] To yield $PhN{\equiv}CCMe_3^+$ which is converted to $PhNHCOCMe_3$ in Me_2SO. [e] In reductive alkylation ethyl fumarate is 460 times as reactive as (*E*)-PhCH=CHI. In the presence of DABCO, ethyl fumarate gives only the reductive alkylation product while *N*-methylmaleimide or fumaronitrile give only oxidative alkylation.[f] In reductive alkylation (presence of I^-) *N*-methylmaleimide is 2300−2800 times as reactive as (*E*)-PhCH=CHI and fumaronitrile is 2.5 times as reactive as *N*-methylmaleimide.

The present results suggest that base-promoted homolytic aromatic substitutions may be a rather general process for electronegatively-substituted aromatics. By judicious use of basic reagents it may well be possible to promote other reactions such as the classical phenylation of aromatics by benzoyl peroxide.

Attempted Aromatic Alkylations with *tert*-Butyl Halides. The base-promoted *tert*-butylation reactions described in the previous sections, fail completely when *t*-BuBr or *t*-BuI are substituted for *t*-BuHgX. No reaction is observed in Me_2SO, DMF, or PhH upon photolysis of *t*-BuX and the dicyanobenzenes in the presence of Dabco, with AIBN at 70 °C in DMF or PhH, or upon photolysis of Bz_2O_2 in DMF or PhH at 35 °C. A chain reaction does not occur and unreacted *t*-BuX can be recovered in DMF or PhH. We find these observations to be perplexing because estimated $E°$-values for *t*-BuX reductions suggest that these molecules should participate in electron transfer with the dicyanobenzene radical anions. Some estimated $E°$-values (NHE) in Me_2SO and DMF are *t*-BuBr, −0.73, −0.92; *t*-BuI, −0.56, −0.77 V.[24a] Although the observed irreversible electrode reduction potentials are much more negative than the estimated values,[24] they are in the range of those reported for *t*-BuHgX, e.g., *t*-BuHgBr, $E^{1/2}(CH_3CN) = -1.08$ V (SCE);[25] *t*-BuI, $E^{1/2}$ (DMF) = −1.84 V (SCE),[24b] whereas the reduction potentials of the dicyanobenzenes are in the range of −1.5 to −1.6 V ($E°$, SCE). The lack of reactivity of *t*-BuBr in these reactions may reflect the slow rate of electron transfer from the radical anion to the alkyl halide. Thus, Lund has reported in DMF a correlation between the rate constant of electron transfer to *t*-BuBr from aromatic radical anions and the reduction potentials of the aromatics with the value for *k* being only 10 L/mol s at 25 °C for an aromatic with $E° = -1.5$ V (SCE).[26] A rate constant of only 10 L/mol s would be too slow for an efficient chain reaction and would lead to steady state radical anion concentrations where bimolecular termination reactions ($k > 10^6$ L/mol s) would become dominant. However, Savéant has reported in DMF that $\Delta G^‡$ is 9.7 kcal/mol [k(25 °C) = 4×10^5 L/mol s] for the reaction of *t*-BuI with terephthalonitrile radical anion ($E° = -1.51$ V), presumably a dissociative electron transfer process.[24b] Apparently the facile reaction of the dicyanobenzene radical anions with *t*-BuI does not generate a *free* tert-butyl radical that can continue a chain reaction. The formation of I• from reactions involving *t*-BuI may also be a complicating fact since I• would terminate an electron transfer chain reaction of *t*-BuI. For *t*-BuHgI chain reactions, I• does not terminate the reaction since reaction 6 occurs readily.[27] In fact, chain processes such as reaction 5 involve I• as a chain propagating species.[28]

$$I^• + t\text{-BuHgX} \rightarrow t\text{-Bu}^• + \text{IHgX} \qquad (6)$$

Experimental Section

General Procedures. The aromatic substrates (1−2 mmol) and reagents were dissolved in 4 mL of Me_2SO in a Pyrex test tube under a nitrogen atmosphere, often with continuous nitrogen bubbling, and irradiated with a 275 W Sylvania fluorescent sunlamp approximately 25 cm from the reaction tube. Workup involved treatment with 50 mL of aqueous $Na_2S_2O_3$ followed by CH_2Cl_2 extraction and washing of the CH_2Cl_2 extract with brine. After drying ($MgSO_4$) and evaporation of the solvent the reaction products were isolated on TLC plates using hexane−ethyl acetate as the eluent.

For reactions monitored by ^{1}H NMR integration, the substrate (0.05 mmol) and added reagents were dissolved in 0.6 mL of Me_2SO-d_6 in a 5 mm NMR tube with 0.1 mmol of toluene added as an internal standard.

^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ at 300 and 75.4 MHz with δ measured relative to internal Me_4Si or the central ^{13}C peak of $CDCl_3$, respectively. GCMS were obtained with a Finnegan 4000 spectrometer and HRMS with a Kratos MS-50 spectrometer. Analytical data were obtained with a Perkin Elmer Series II Analyzer 2400 or from Galbraith Laboratories. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected.

Dimethyl sulfoxide was distilled from CaH_2 and stored over 4A Molecular Sieves under nitrogen. *tert*-Butylmercury chloride was prepared from $HgCl_2$ and *t*-BuLi by a modification of a literature method:[29] mp 110−113 °C, ^{1}H NMR δ 1.51. *tert*-Butylmercury iodide was prepared by anion exchange with the chloride by treatment with 2 equiv of KI in Me_2SO followed by hydrolysis and ether extraction. The initially white crystals of *t*-BuHgI turned pale yellow when exposed to air and light. Material with ^{1}H NMR δ 1.53 was stored in a freezer in the dark.

For the known **4a**,[30] **4b**,[30] **5a**,[31] **5b**,[32] **5c**,[33] **5d**[34] 4-(1,1-dimethylethyl)-benzonitrile,[35] 4,4′-bis(1,1-dimethylethyl)benzophenone,[35,36] **7a**,[37] 4-(1,1-dimethylethyl)phthalonitrile,[38] 3,5-bis(1,1-dimethylethyl)phthalonitrile,[38] **12a**,[39] and **14**,[39] the observed mp and ^{1}H and ^{13}C NMR spectra were consistent with literature values, and the compounds all gave a HRMS consistent with their structures.

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2-(1,1-Dimethylethyl)-2,3-dihydro-1,4-naphthoquinone (3a). The compound was isolated by flash chromatography (silica gel) with hexane (95%)−ethyl acetate (5%) was a brown oil: FTIR (neat) 3072 (w), 2968 (m), 2910 (w), 1695 (vs), 1595 (m), 1291 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05−7.99 (m, 2H), 7.77−7.68 (m, 2H), 3.13 (d, J = 5.7 Hz, 2H), 2.89 (t, J = 5.7 Hz, 1H), 0.99 (s, 9H); ^1H NMR (Me_2-SO-d_6) δ 7.95−7.89 (m, 2H), 7.89−7.80 (m, 2H), 3.27 (dd, J = 16.8, 6.3 Hz, 1H), 3.05 (dd, J = 16.8, 5.7 Hz, 1H), 2.95 (t, J = 6.0 Hz, 1H), 0.92 (s, 9H); GC and HRMS *m/z* (rel intensity) 216 (0.02), 201.0912 (2, calcd for $C_{13}H_{13}O_2$ (M^+ − Me) 201.0916), 183 (2), 160 (100), 132 (12), 104 (8), 57 (26); CIMS (NH_3) 217.1230 (100, calcd for $C_{14}H_{17}O_2$ ($M+H^+$) 217.1229).

2-(1-Methylethyl)-2,3-dihydro-1,4-naphthoquinone (3b). The compound was isolated as a brown oil: FTIR (neat) 3070 (w), 2966 (m), 2910 (w), 1693 (vs), 1595 (m) cm^{-1}; ^1H NMR δ 8.07−7.95 (m, 2H), 7.75−7.68 (m, 2H), 3.13−2.95 (m, 2H), 2.90−2.83 (m, 1H), 2.28 (octet, J = 6.6 Hz, 1H), 0.98 (dd, J = 6.6, 1.2 Hz, 6H); GC and HRMS *m/z* (rel intensity) 202.0990 (5, calcd for $C_{13}H_{14}O_2$ 202.0994); 187 (16), 160 (100), 1313 (23), 104 (30), 76 (31).

4-(1,1-Dimethylethyl)isophthalonitrile (11a). The compound was isolated as a white solid, mp 56−57 °C: ^1H NMR δ 7.95 (d, J = 1.8 Hz, 1h), 7.80 (dd, J = 8.4, 1.8 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 1.55 (s, 9H); ^{13}C NMR δ 158.8, 138.5, 135.7, 127.6, 118.0, 116.7, 112.5, 111.0, 36.3, 29.8; HRMS *m/z* (rel intensity) 184.1005 (calcd for $C_{12}H_{12}N_2$ 184.1001). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 78.19; H, 6.78; N, 15.18.

4-(1,1-Dimethylethyl)-*N*-methylphthalimide (7b). The compound was isolated as a solid, mp 87−88 °C: ^1H NMR 7.88 (d, J = 1.2 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.71 (dd, J = 8.1, 1.5 Hz, 1H), 3.17 (s, 3H), 1.38 (s, 9H); GC and HRMS *m/z* (rel intensity) 217.1103 (25, calcd for $C_{13}H_{15}NO_2$ 217.1103), 203 (12), 202 (100), 174 (37), 117 (7), 115 (13), 77 (3), 57 (3).

4-(1,1-Dimethylethyl)-*N*-(phenylthiomethyl)phthalimide (7c). The compound was isolated as a liquid: FTIR ($CDCl_3$) 1774 (s), 1722 (s), 1620 (m) cm^{-1}; ^1H NMR δ 7.86−7.85 (m, 1H), 7.75−7.70 (m, 2H), 7.50 (dd, J = 7.5, 2.1 Hz, 2H), 7.29−7.26 (m, 3H), 5.04 (s, 2H), 1.36 (s, 9H); GC and HRMS *m/z* (rel intensity) 325.1133 (25, calcd for $C_{19}H_{19}NO_2S$ 325.1137), 216 (100), 201 (10), 186 (12), 155 (4), 109 (5), 91 (6), 57 (2).

4-(1,1-Dimethylethyl)isophthaldehyde (11b). The compound was isolated as a white solid, mp 42−44 °C: ^1H NMR δ 10.88 (s, 1H), 10.06 (s, 1H), 8.40 (d, J = 1.8 Hz, 1H), 8.02 (dd, J = 8.1, 1.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR δ 191.4, 191.0, 158.4, 136.1, 134.5, 132.49, 132.46, 127.4, 36.4, 32.7; GC and HRMS *m/z* (rel intensity) 190.0994 (11, calcd for $C_{12}H_{14}O_2$ 190.0994), 175 (100), 157 (24), 129 (39), 91 (16), 43 (40). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.75; H, 7.51.

Ethyl 3-Cyano-4-(1,1-dimethylethyl)benzoate (11c). The compound was isolated as a liquid: ^1H NMR δ 8.34 (d, J = 2.1 Hz, 1H), 8.15 (dd, J = 8.4, 2.1 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 4.40 (q, J = 7.2 Hz, 4H), 1.55 (s, 9H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 164.6, 158.2, 136.6, 133.4, 128.8, 126.6, 119.4, 111.1, 61.5, 36.0, 29.9, 14.2; GC and HRMS *m/z* (rel intensity) 231.1259 (21, calcd for $C_{14}H_{17}NO_2$ 231.1259), 216 (100), 188 (36), 115 (11), 43 (12). Anal. Calcd for $C_{14}H_{17}NO_2$: C,72.70; H, 7.41; N, 6.06. Found: C, 72.95; H, 7.51; N, 6.01.

3-Cyano-4-(1,1-dimethylethyl)benzaldehyde (11d). The compound was isolated as a solid, mp 112−115 °C: ^1H NMR δ 10.01 (s, 1H), 8.18 (d, J = 1.8 Hz, 1H), 8.02 (dd, J = 8.4, 1.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR 189.7, 160.0, 136.7, 134.3, 133.0, 127.3, 119.0, 112.0, 36.3, 29.9; GC and HRMS *m/z* (rel intensity) 187.0991 (16, calcd for $C_{12}H_{13}NO$ 187.0997), 172 (100), 144 (16), 57 (4). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.49; H, 7.22; N, 7.35.

Diethyl 4-(1-Methylethyl)isophthalate (11e). The compound was isolated as a liquid: ^1H NMR δ 8.38 (d, J = 2.1, 1H), 8.10 (dd, J = 8.4, 2.1 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 4.38 (q, J = 7.2 Hz, 3H), 3.76 (heptet, J = 6.9 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.28 (d, J = 6.9 Hz, 6H); ^{13}C NMR δ 167.6, 165.8, 154.4, 132.2, 130.8, 130.5, 127.8, 126.3, 61.1, 61.0, 29.7, 23.6, 14.2, 14.15; GC and HRMS *m/z* (rel intensity) 264.1361 (76, calcd for $C_{15}H_{20}O_4$ 264.1362), 236 (26), 219 (92), 218 (84), 217 (100), 203 (30), 115 (15). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.83; H, 7.77.

4,6-Bis(1,1-dimethylethyl)isophthaldehyde (12b). The compound was isolated as a solid, mp 130−132 °C: ^1H NMR δ 10.74 (s, 2H), 8.45 (s, 1H), 7.63 (s, 1H), 1.54 (s, 18H); ^{13}C NMR δ 191.5, 156.6, 134.4, 133.6, 125.2, 36.7, 32.4; GC and HRMS *m/z* (rel intensity) 246.1604 (3, calcd for $C_{16}H_{22}O_2$ 246.1620), 245 (8) 231 (100), 213 (16), 115 (12), 57 (20). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.34; H, 9.07.

5-Cyano-2,4-bis(1,1-dimethylethyl)benzaldehyde (12d). The compoound was isolated as a solid, mp 119−122 °C: ^1H NMR δ 10.75 (s, 1H), 8.22 (s, 1H), 7.62 (s, 1H), 1.542 (s, 9H); ^{13}C NMR δ 196.1, 158.1, 156.3, 137.5, 133.4, 124.8, 119.2, 109.2, 36.7, 36.4, 32.6, 29.9; GC and HRMS *m/z* (rel intensity) 243.1623 (11, calcd for $C_{16}H_{21}NO$ 243.1623), 228 (100), 210 (12), 186 (9), 154 (5), 57 (21). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.46; H, 9.09; N, 5.56.

Diethyl 4,6-Bis(1-methylethyl)isophthalate (12e). The compound was isolated as a liquid: ^1H NMR δ 8.16 (s, 1H), 7.44 (s, 1H), 43.7 (q, J = 7.2 Hz, 4H), 3.80 (heptet, J = 6.9 Hz, 2H), 1.39 (t, J = 7.2 Hz, 6H), 1.27 (d, J = 7.2 Hz, 12H); ^{13}C NMR δ 167.5, 153.2, 131.7, 127.4, 124.1, 60.9, 29.7, 23.7, 14.2; GC and HRMS *m/z* (rel intensity) 306.1827 (52, calcd for $C_{18}H_{26}O_4$ 306.1831), 277 (21), 261 (76), 260 (100), 259 (67), 245 (20). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 69.94; H, 8.71.

1,4-Dicyano-2-(1,1-dimethylethyl)benzene (13a). The compound was isolated as a solid, mp 150−151 °C: ^1H NMR δ 7.81−7.78 (m, 2H), 7.60 (dd, J = 7.8, 1.5 Hz, 1H), 1.55 (s, 9H); ^{13}C NMR δ 155.1, 136.0, 130.2, 129.5, 118.5, 117.5, 116.3, 115.1, 35.9, 29.8; GC and HRMS *m/z* (rel intensity) 184.1001 (17, calcd for $C_{12}H_{12}N_2$ 184.1001), 169 (100), 141 (30), 114 (8), 57 (5). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 78.29; H, 6.55; N, 14.94.

Ethyl 4-Cyano-3-(1,1-dimethylethyl)benzoate (13b). The compound was isolated as a liquid: ^1H NMR δ 8.16 (d, J = 1.5 Hz, 1H), 7.94 (dd, J = 7.8, 1.5 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 1.56 (s, 9H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 165.4, 154.1, 135.5, 133.8, 127.3, 126.9, 119.5, 114.6, 61.6, 35.7, 30.0, 14.2; GC and HRMS *m/z* (rel intensity) 231.1260 (14, calcd for $C_{14}H_{17}NO_2$ 231.1259), 216 (100), 188 (30), 144 (9). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.64; H, 7.40; N, 5.93.

4-(2,2-Dimethylpropyl)-3,4-dihydro-1(2*H*)-naphthalenone (16a, R = Me_3C). The compound was isolated as a liquid: FTIR ($CDCl_3$) 3063 (w), 2852 (s), 2865 (m), 1686 (vs) cm^{-1}; ^1H NMR δ 7.99 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.30−7.24 (m, 2H), 3.12−3.02 (m, 1H), 2.83 (ddd, J = 17.4, 12.3, 4.8 Hz, 1H), 2.57 (dt, J = 17.4, 4.8 Hz, 1H), 2.33−2.20 (m, 1H), 2.11 (dq, J = 18.0, 4.5 Hz, 1H), 1.75 (dt, J = 17.4, 4.8 Hz, 1H), 1.50 (dd, J = 14.4, 2.1 Hz, 1H), 1.04 (s, 9H); GC and HRMS *m/z* (rel intensity) 216.1517 (42, calcd for $C_{15}H_{20}O$ 216.1514), 160 (5), 145 (100), 131 (21), 117 (30), 103 (7), 91 (13), 57 (25).

4-(2-Methylpropyl)-3,4-dihydro-1(2*H*)-naphthalenone (16b, R = Me_2CH). The compound was isolated as a liquid: FTIR (neat) 2954 (m), 2924 (m), 2866 (w), 1684 (s) cm^{-1}; ^1H NMR δ 8.01 (d, J = 7.8 Hz, 1H), 7.48 (dd, J = 7.8, 1.2 Hz, 1H), 7.33−7.24 (m, 1H), 3.06−2.93 (m, 1H), 2.83−2.69 (m, 1H), 2.63−2.52 (m, 1H), 2.31−2.16 (m, 1H), 2.08−1.97 (m, 1H), 1.81−1.43 (m, 3H), 1.43 (m, 6H); GC and HRMS *m/z* (rel intensity) 202.1362 (29, calcd for $C_{14}H_{18}O$ 202.1358), 145 (100), 131 (19), 117 (34), 104 (27), 91 (12), 77 (9).

7-Acetyl-4-(2,2-dimethylpropyl)-3,4-dihydro-1(2*H*)-naphthalenone (16b, R = Me_3C). The compound was isolated as a solid, mp 39−41 °C: ^1H NMR δ 8.54 (d, J = 2.1 Hz, 1H), 8.11 (dd, J = 8.1, 2.1 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 3.12 (m, 1H), 2.86 (ddd, J = 17.7, 12.3, 5.1 Hz, 1H), 2.64 (s, 3H), 2.64 (dt, J = 18.0, 5.1 Hz, 1H), 2.29 (tt, J = 12.6, 4.5 Hz, 1H), 2.19−2.09 (m, 1H), 1.77 (dd, J = 14.4, 7.8 Hz, 1H), 1.48 (dd, J = 14.4, 2.7 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR δ 197.7, 197.3, 155.4, 135.4, 132.4, 131.6, 129.1, 127.7, 47.9, 34.8, 34.4, 31.5, 29.9, 28.0, 26.6; GC and HRMS *m/z* (rel intensity) 258.1622 (57, calcd for $C_{17}H_{22}O$ 258.1620), 243 (58), 188 (84), 187 (100), 115 (30).

4-(2,2-Dimethylethyl-6-(ethoxycarbonyl)-2,3-dihydro-1(2*H*)naphthalenone (16c, R = Me_3C). The α-tetralone was isolated as a liquid: ^1H NMR δ 8.04 (d, J = 8.1 Hz, 1H), 7.95 (s, 1H), 7.91 (dd, J

= 8.1, 1.8 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 3.13 (m, 1H), 2.85 (ddd, J = 17.4, 12.4, 5.1 Hz, 1H), 262 (dt, J = 17.7, 4.8 Hz, 1H), 2.27 (tt, J = 13.5, 4.5 Hz, 1H), 2.19−2.10 (m, 1H), 1.75 (dd, J = 14.7, 8.1 Hz, 1H), 1.53 (dd, J = 14.7, 3.0 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H), 1.06 (s, 9H); ^{13}C NMR δ 198.03, 165.9, 150.2, 145.1, 134.6, 129.9, 127.2, 127.0, 61.4, 48.1, 34.7, 34.5, 31.5, 29.9, 28.1, 14.1; GC and HRMS *m*/*z* (rel intensity) 288.1721 (35, calcd for $C_{18}H_{24}O_3$ 288.1725), 243 (14), 232 (14), 218 (74), 217 (100).

5-Acetyl-4-(2,2-dimethylpropyl)-2,3-dihydro-1(2*H*)-naphthalenone (18). The compound was isolated as a liquid: ^{1}H NMR δ 8.15 (dd, J = 7.8, 1.5 Hz, 1H), 7.76 (dd, J = 7.5, 1.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 3.93 (dq, J = 10.8, 3.0 Hz, 1H), 2.87 (ddd, J = 18.6, 14.4, 5.7 Hz, 1H), 2.60 (ddd, J = 18.6, 5.4, 2.1 Hz, 1H), 2.33 (m, 1H), 2.13 (tt, J = 14.4, 4.2 Hz, 1H), 1.61 (dd, J = 14.4, 11.4 Hz, 1H), 1.32 (dd, J = 14.7, 2.7 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR δ 202.0, 198.3, 149.8, 137.8, 133.4, 133.2, 130.5, 126.0, 46.3, 32.9, 31.2, 30.8, 30.6, 25.0, 30.3; GC and HRMS *m*/*z* (rel intensity) 258.1620 (39, calcd for $C_{17}H_{22}O_2$ 258.1620), 243 (6), 201 (100), 187 (21), 147 (14), 115 (16).

4-(4-Ethoxycarbonylphenyl)-6,6-dimethylheptanoic Acid (19). The compound was isolated as a liquid: ^{1}H NMR δ 10.5 (br s, 1H), 7.98−7.94 (m, 2H), 7.25−7.22 (m, 2H), 4.36 (q, J = 7.2 Hz, 1H), 2.78−2.69 (m, 1H), 2.18−1.72 (m, 1H), 1.56 (dd, J = 14.1, 3.3 Hz, 1H), 1.38 (q, J = 7.2 Hz, 3H), 0.76 (s, 9H); ^{13}C NMR δ 179.0, 166.6, 151.8, 129.8, 128.5 127.9, 60.8, 50.4, 42.0, 34.0, 31.9, 31.3, 30.0, 14.3; GC and HMRS *m*/*z* (rel intensity) 306.1827 (48, calcd for $C_{18}H_{26}O_4$ 306.1831), 261 (28), 249 (65), 203 (64), 189 (92), 177 (100).

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