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Electrochemical *t*-Butylation of Some Aromatic Ketones

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Anion radicals or dianions of aryl ketones react with *t*-butyl halides; a reductive *t*-butylation takes place predominantly in the *para* position of the aromatic nucleus and at the carbonyl group. Minor amounts of di- or tributylated products are found in some cases. Cyano substituents may be displaced by a *t*-butyl group.

Electrochemical reduction of a number of substrates in the presence of alkyl halides leads to alkylated products;[1] thus aromatic hydrocarbons,[2] heteroaromatic compounds [3] and activated olefins [4,5] have been alkylated using this method.

t-Butylation of ketones at the carbonyl group is generally possible using organometallic reagents, and it has been reported recently [6] that *t*-butylmagnesium chloride reacts with benzophenone and derivatives thereof not only at the carbonyl group, but also at the aromatic ring in a reaction involving initial transfer of one electron from the Grignard reagent to the ketone.

This paper reports on the electrochemical *t*-butylation of some aromatic ketones: 2,2-dimethyl-1-phenylpropan-1-one (*1*, pivalophenone), 4-*t*-butylpivalophenone (*2*), 4-methylpivalophenone (*3*), cyclopropyl phenyl ketone (*4*), benzophenone (*5*), 4-*t*-butylbenzophenone (*6*), 2-(*7*), 3-(*8*), 4-cyanobenzophenone (*9*), and 4,4′-dimethoxybenzophenone (*10*).

RESULTS AND DISCUSSION

Some of the ketones have previously [7–9] been investigated by cyclic voltammetry (CV) in *N*,*N*-dimethylformamide (DMF) and they exhibit two one-electron waves (Table 1), the first one being reversible, the second one reversible only in media of very low proton activity.[10,11]

Addition of *t*-butyl bromide (*11*) to *1*–*6* and *10* during a CV-experiment causes the first

Table 1. Peak potentials of compounds *1* to *10* at a hanging mercury electrode in DMF/0.1 M TBAI *vs.* Ag/AgI,0.1 M I^- and products from preparative electrolysis in the presence of *t*-butyl halide; yields (%) in parantheses.

Compound	Ep_1	Ep_2	$R^1R^2C(OH)(t\text{-Bu})$	$R^1COC_6H_4C_4H_9$	Other products
1	−1.80		*12* (16)	*2*(37)	*13* (16), *14* (5) *15* (16), *16* (1)
2	−1.87		*13* (57)	*14* (38)	
3	−1.88		*17* (46)		*3*(24), *18* (5)
4	−1.62		*21* (30)	*20* (50)	
5	−1.30	−1.95	*22* (60)	*6* (8)	*23* (25), *24* (7)
6	−1.32	−2.05	*23* (53)	*24* (33)	*25* (7)
7	−1.14		*27* (25)	*28* (32)	*26* (42)
8	−1.07	−1.70	*30* (34)	*31* (53)	
9	−0.85	−1.54	*32* (33)	*6* (50)	
10	−1.52	−2.25	*33* (72)		*34* (5), *35* (7)

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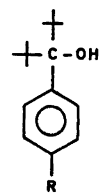
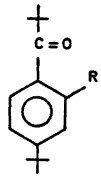
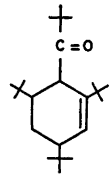
wave to grow and become irreversible. The cyanobenzophenones are, however, reduced at less negative potentials than the other ketones and the influence of *11* on the first peak of *7 – 9* is negligible; the reversible second peak of *9*, formation of the dianion, becomes irreversible on addition of *t*-butyl bromide. The behaviour of the ketones in CV is consistent with a reductive coupling of *t*-butyl radicals with the ketones or their reduction products.

Preparative experiments show that *t*-butylation takes place in good yield; the attack generally occurs at the carbonyl group or at the *para* position, but minor amounts of further reduced and alkylated compounds are found. Table 1 gives the main products and yields of these compounds.

1 gave a number of products on *t*-butylation. Besides the carbonyl-butylated compound, 2,2,4,4-tetramethylpentan-3-phenyl-3-ol (*12*) (16 % yield) and the *para* butylated product, 1-(4-*t*-butylphenyl)-2,2-dimethylpropan-1-one (*2*, 37 % yield) higher butylated derivatives were isolated, such as 3-(4-*t*-butylphenyl)-2,2,4,4-tetramethylpentan-3-ol (*13*, 16 %), 1-(2,4-di-*t*-butylphenyl)-2,2-dimethylpropan-1-one (*14*, 5 %), 1-(2,4,6-tri-*t*-butylcyclohex-2-enyl)-2,2-dimethylpropan-1-one (*15*, 16 %) together with a small amount (1 %) of the corresponding pinacol, 2,2,5,5-tetramethyl-3,4-diphenylhexan-3,4-diol (*16*).







12 R=H
13 R=*t*-Butyl
17 R=CH_3

2 R=H
14 R=*t*-Butyl

15

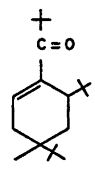
The coupling takes place [1–5] on reaction between *t*-butyl radicals and either the substrate or its anion radical; the *t*-butyl radical is formed on electron transfer from the substrate anion radical followed by a fast cleavage of the carbon-halogen bond.

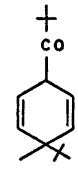
12 is a simple, reductive coupling product, whereas the formation of *2* requires an oxidation after the coupling either in the catholyte or during work-up. If the coupling is a radical-substrate coupling, the oxidation is just a loss of one electron and a proton (or a hydrogen atom); the radical-radical ion coupling produces the anion of a dihydro compound, which, however, also is easily oxidizable.

The formation of *13* and *14* seems to require that *2* is present in the catholyte. *13* is a simple reductive coupling product from *2* analogous to *12* from *1*; *14* is formed from *2* just as *2* is formed from *1*.

15 may be formed by reductive alkylation of a dihydro-di-*t*-butylated substrate (dihydro-*14*) after base-induced rearrangement of the double bonds to an α,β-unsaturated ketone. The reason why the double bond in *15* is not conjugated with the carbonyl group might be steric; in a conjugated system the pivaloyl group and the *t*-butyl group would be in the same plane. The reductive alkylation of *2* gives mainly *13* and *14* which might indicate that *15* is formed through an initial attack at the 2-position of the phenyl ring. The absence of a product only *t*-butylated in the *ortho* position might be due to a relatively easy loss of such a group on oxidation of the dihydro compound.[6]

Reductive coupling of *p*-methylpivalophenone gave 2,2,4,4-tetramethyl-3-(4-methylphenyl)pentan-3-ol (*17*, 46 %), *3* (24 %), and 1-(4,6-di-*t*-butyl-4-methylcyclohex-1-enyl)-2,2-dimethylpropan-1-one (*18*, 5 %). *3* was not present in the catholyte immediately after the reduction and must be formed during work-up from an unstable product; such a product might be a compound butylated in the *p*-position and thus having a geminal methyl and *t*-butyl group (*19*), and it could regenerate the aromatic system by losing the elements of isobutane or methane. In the HPLC a small peak is found with the same retention time as *2*, but the compound was not isolated and positively identified as *2*.



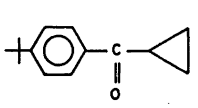


18 *19*

An unusual five-bond coupling is found in the ^1H NMR-spectrum of *18*; this is possible in a rigid system [12,13] and indicates that the cyclohexene ring to a large degree is frozen in a single conformer with the five bonds forming a W in a plane.

18 might be formed through *19*, which could isomerize by base to a reducible α-β-unsaturated ketone; this is then reductively alkylated in the β-position.

4 is reductively *t*-butylated to 4-*t*-butylphenyl cyclopropyl ketone (*20*, 50 %) and 1-cyclopropyl-2,2-dimethyl-1-phenylpropan-1-ol (*21*, 30 %). No ring-opened products or compounds *t*-butylated in the cyclopropyl ring were found.



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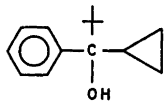
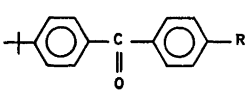
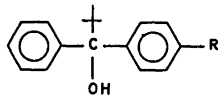


21

Benzophenone is reductively *t*-butylated mainly to 2,2-dimethyl-1,1-diphenylpropan-1-ol (*22*, 60 %) and 1-(4-*t*-butylphenyl)-2,2-dimethyl-1-phenylpropan-1-ol (*23*, 25 %) together with *6* (8 %) and 4,4′-di-*t*-butylbenzophenone (*24*, 7 %)



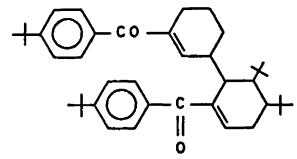


6 R=H
24 R=*t*-Bu

22 R=H
23 R=*t*-Bu

The yields given are average yields and differ up to 20 % (relative) between otherwise identical reductions. The reason might be that the products alkylated in the benzene ring are dihydro compounds which may lose the alkyl group during the oxidative rearomatization. The relatively high yield of *22* may thus be partly caused by the easy loss of a *t*-butyl group; another reason might be that the carbonyl group in *5* is sterically less hindered towards an attack perpendicular to the carbonyl group than in derivatives of pivalophenone.

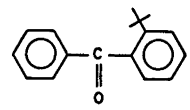
4-*t*-Butylbenzophenone *6* yields on reduction in the presence of *t*-butyl bromide the expected products *24* (33 %) and *23* (53 %) together with a minor amount (7 %) of a dimer (*25*) which precipitates during the reduction. The compound has been assigned the structure 5,6-di-*t*-butyl-2,3′-di-(4-*t*-butylbenzoyl)-1,4,5,6,1′,4′,5′,6′-octahydrobiphenyl on the basis of the NMR spectrum.



25

Cyano groups may, on reductive coupling, be replaced by the attacking reagent; thus 4-cyanopyridine forms 4-*t*-butylpyridine on reductive *t*-butylation and derivatives of 4-acetylpyridine on reductive acetylation.[14] The three cyanobenzophenones *7*, *8*, and *9* were therefore investigated.

Reductive *t*-butylation of 2-cyanobenzophenone gives 2-*t*-butylbenzophenone (*26*, 42 %), 3-*t*-butyl-3-phenyl-phthalide (*27*, 25 %) and 6-*t*-butyl-3-phenylphthalide (*28*, 32 %).



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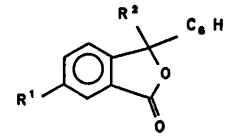
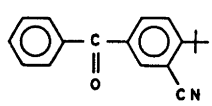


27 R^1=H, R^2=*t*-butyl
28 R^1=*t*-butyl, R^2=H

26 is probably formed through an intermediate anion of 2-*t*-butyl-2-cyano-1,2-dihydrobenzophenone (*29*) which loses cyanide ion with formation of *26*. The rather high yield of *26* indicates that attack at the *ortho* position by *t*-butyl radicals is not sterically hindered and it raises the question whether such an attack is more common than suggested by the isolated products and that the low yield of such products is due to loss of the *t*-butyl group from the initially formed dihydro compound. In the case of *29* the cyano group is a good leaving group which is lost in preference to the *t*-butyl group.

Other substituents could possibly be replaced by alkyl groups on reductive alkylation, but the substituent must not be lost too easily. If the cleavage of the anion radical is too fast, the parent compound is formed before attack by



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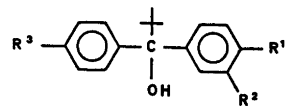
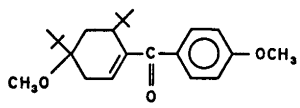


30 $R^1=R^3=H$, $R^2=CN$
32 $R^1=CN$, $R^2=R^3=H$
33 $R^1=R^3=OCH_3$, $R^2=H$



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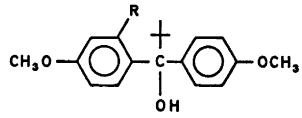

33 R=H
35 R=*t*-butyl

the alkyl radical. Bromo and chloro substituents are thus not suited for directing an alkyl into a desired position in a benzophenone.

27 is formed by coupling at the carbonyl group followed by attack of the alcohol anion on the cyano group; the azomethine group of the ring-closed compound is hydrolyzed with formation of *27*. *28* is formed similarly after coupling in the *para* position which leaves the negative charge on oxygen; ring closure and hydrolysis lead to *28*.

3-Cyanobenzophenone (*8*) behaves as benzophenone, *t*-butylation takes place at the carbonyl group (*30*, 34 %) and at the 4-position (*31*, 53 %). The structure of *31* is based on the ^{13}C NMR spectrum. No products were isolated in which the coupling was *para* to the cyano group and *ortho* to the benzoyl group, or in which the cyano group was lost.

4-Cyanobenzophenone (*9*) behaves as *7*, the cyano group is lost during the formation of *6* (50 %) and retained when the carbonyl group is attacked (*32*, 33 %).

The main product from 4,4'-dimethoxybenzophenone (*10*) is the tertiary alcohol (*33*, 72 %); besides *33* minor amounts of *34* (5 %) and *35* (7 %) were isolated, which tentatively were assigned the structures shown.

In conclusion, the electrochemical *t*-butylation of aromatic ketones occur at the carbonyl group or in the aromatic ring, mainly in the *para* position. An electron-withdrawing substituent in a ring promotes attack in that ring, whereas an electron-donating group favours an attack at the carbonyl group.

EXPERIMENTAL

Apparatus. High pressure liquid chromatography (HPLC): The pump was a Milton Roy reciprocating pump (max. flow 2.3 ml/min), and the detector a Cecil UV-detector with variable wavelength (210 – 420 nm). The packing material was delivered by Merck, and the columns were packed by a slurry technique using either 1,2-dibromoethane or a 1:1 mixture of dioxane – methanol for preparing the slurry. The 270 MHz NMR spectra were recorded on a Bruker WH-270 spectrometer, all others on a A60 Varian instrument.

Chemicals. Pivalophenone *1*,[15] 4-*t*-butylpivalophenone *2*,[16] 4-methylpivalophenone *3*,[16] 4-*t*-butylbenzophenone *6*,[17] 2-cyanobenzophenone *7*,[18] 3-cyanobenzophenone *8*[19] and 4-cyanobenzophenone [19] were prepared according to the references given.

General procedure for electrolysis. All the electrolyses were performed in DMF containing 0.1 M tetrabutylammonium iodide (TBAI) as supporting electrolyte. The working electrode was a mercury pool and as reference electrode the Ag/AgI electrode was used in the same solvent – electrolyte system. After completion of the electrolysis the catholyte was diluted with water and acidified with 4 M aqueous HCl (to remove a variable amount of tributylamine formed during electrolysis) and extracted three times with diethyl ether. The extracts were washed with water and dried over $MgSO_4$.

Reduction of pivalophenone 1 *in the presence of* t*-butylchloride* 36. *1* (2 g) and *36* (10 ml) were reduced at $E=-1.75$ V, $n=2.8$ F Mol^{-1}. The crude product was separated by preparative HPLC and the yields were determined by quantitative HPLC on a 5 μ m RP-18 column, eluent $CH_3CN-H_2O=4:1$. Isolated were:

2,2,4,4-Tetramethyl-3-phenylpentan-3-ol 12 (16 % yield) liquid. The NMR data were consistent with the data in the literature.[20]

1-(4-t-Butylphenyl)-2,2-dimethylpropan-1-one 2 (38 %) m.p. 45.3–45.5 °C (liquid),[21] oxime m.p. 205 °C (205–206 °C).[21]

3-(4-t-Butylphenyl)-2,2,4 4-tetramethylpentan-3-ol 13 (16 %), liquid. ^{1}H NMR spectrum ($CDCl_3$): δ 1.10 (18 H, s), 1.30 (9 H, s), 7.2–7.8 (4 H, arom.). MS [*m/e* (%)]: 275 (4), 239 (5), 211 (2), 169 (6), 123 (7), 109 (8), 85 (48), 57 (100).

1-(2,4-Di-t-butylphenyl)-2,2-dimethylpropan-1-one 14 (4 %). It was not possible to separate this compound from *13* so the assignment of the structure from the NMR and MS spectra of the mixture is only tentative.

1-(2,4,6-Tri-t-butylcyclohex-2-enyl)-2,2-dimethylpropan-1-one 15 (13 %), m.p. 83.2–83.4 °C. ^{1}H NMR ($CDCl_3$): δ 0.87 (9 H, s), 0.90 (9 H, s), 1.05 (9 H, s), 1.25 (9 H, s), 1.2–2.4 (4 H, m), 3.18 (1 H, dd, J 7.7 and 2.5 Hz), 5.50 (1 H, dd, J 7.0 and 2.5 Hz). MS [*m/e* (%)]: 334 (0.5), 277 (5), 249 (5), 221 (3), 193 (3), 179 (7), 163 (6), 123 (9), 85 (23), 57 (100).

The structure of *15* is based on the ^{1}H NMR spectrum. Besides signals from 4 *t*-butyl groups at δ 0.87, 0.90, 1.05, and 1.25 and an unresolved multiplet (4 H) there is a double doublet (J = 7.7 and 2.5 Hz) at 3.2 and one at 5.5 (J = 7.0 and 2.5 Hz). The signal at δ 3.2 is interpreted as the proton α to the carbonyl group which couples with one neighbouring hydrogen and one allylic hydrogen (2.5 Hz); the signal at 5.5 is the olefinic proton which couples with one neighbouring hydrogen and the proton α to the carbonyl group.

2,2,5,5-Tetramethyl-3,4-diphenylhexan-3,4-diol 16[22] (1 %) m.p. 140–142 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (18 H, s), 1.35 (2 H, s), 7.0–7.6 (10 H, arom.). MS [*m/e* (%)]: 326 (1), 270 (4), 243 (9), 191 (14), 179 (35), 137 (17), 81 (29), 69 (61), 57 (100). IR ($CHCl_3$) cm^{-1} (intensity): 3600 (s).

Reduction of 4-t-butylpivalophenone 2. *2* (2 g) and *36* (10 ml) were reduced at E = −1.90 V, n = 2.1 F mol^{-1}. Quantitative HPLC was performed directly on the catholyte and compounds *13* and *14* were identified in 57 % and 38 % yields, respectively.

Reduction of 4-methylpivalophenone 3. *3* (2 g) and *36* (10 ml) were reduced at E = −1.90 V, n = 2.8 F mol^{-1}. The crude product was separated by preparative HPLC on a 5 μm RP-18 column, eluent CH_3CN:H_2O = 4:1 and the yields were determined by quantitative HPLC under the same conditions. Isolated were:

2,2,4,4-Tetramethyl-3-(4-methylphenyl)pentan-3-ol 17 (46 %), liquid, ^{1}H NMR ($CDCl_3$): δ 1.05 (18 H, s), 1.90 (1 H, s), 2.30 (3 H, s), 7.2–7.8 (4 H, arom.).

1-(4,6-Di-t-butyl-4-methylcyclohex-1-enyl)-2,2-dimethylpropan-1-one 18 (4 %), m.p. 83 °C. ^{1}H NMR (270 MHz) ($CDCl_3$): δ 0.80 (9 H, s), 0.83 (9 H, s), 0.98 (3 H, s), 1.30 (9 H, s), 1.78 (1 H, dt, J 17.4 and 2.6 Hz), 1.97 (1 H, ddd, J 15.3, 8.5 and 3.0 Hz), 2.27 (1 H, ddd, J 17.3, 7.2 and 2.8 Hz), 2.86 (1 H, ddt, J 8.3, 2.2 and 0.8 Hz), 6.45 (1 H, ddd, J 7.3, 2.5 and 0.8 Hz). The integration of the region δ 0.8–1.5 revealed the presence of at least one proton. MS [*m/e* (%)]: 292 (1), 277 (2), 233 (60), 193 (3), 179 (100), 138 (80), 121 (56), 109 (23), 93 (31), 57 (98).

The structure of *18* was deduced from the ^{1}H NMR spectrum. Besides three singlets at δ 0.80, 0.83, and 1.30 (*t*-Bu) and one at 0.98 (Me) 6 one-proton signals were found: A double triplet (H3-a) at 1.78 (J = 17.4, 2.6 and 2.6 Hz) and one (H6) signal with twelve lines at 2.86 (J = 8.25, 8.25, 2.2 and 0.8 Hz), an 8-line signal (H5-a) at 1.97 (J = 15.3, 8.5 and 3.0 Hz) another one (H3-b) at 2.27 (J = 17.3, 7.2 and 2.8 Hz), and a third one (H2) at 6.45 (J = 7.3, 2.5 and 0.8 Hz); besides that an ill-defined signal (H5-b) from one proton is found among the 4 singlets.

Decoupling experiments show that the ethylenic proton (at C-2) is neighbour to the methylene group (at C-3) which has the geminal coupling 17.3 Hz. An unusual coupling (~2.8 Hz) through 5 single bonds is found between H3-b and H5-a. A homoallylic coupling (~2.4 Hz) from H6 to H3-a and a small coupling from H6 to H2 establish the *t*-butyl group at C-6 rather than at C-5.

4-Methylpivalophenone 3 (24 %).

Reduction of cyclopropylphenylketone 4. *4* (2 g) and *36* (10 ml) were reduced at E = −1.60 V, n = 2.08 F mol^{-1}. The ketone in the crude product was converted to the oxime and after filtration the filtrate containing alcohols was purified on a column of silica with a 3:1 mixture of light petroleum–dichloromethane as eluent yielding pure 1-cyclopropyl-2,2-dimethyl-1-phenylpropan-1-ol *21* (25 %) liquid. ^{1}H NMR ($CDCl_3$): δ 0.1–1.8 (5 H, m), 0.95 (9 H, s), 1.40 (1 H, s), 7.2–7.9 (5 H, arom.). MS [*m/e* (%)]: 203 (7), 187 (14), 174 (13), 162 (16), 147 (100), 105 (90), 77 (54), 57 (44). The oxime has m.p. 143.6 °C; the oxime was hydrolyzed and the ketone recrystallized from hexane diethyl ether; cyclopropyl(4-*t*-butylphenyl)ketone *20* m.p. 56.1 °C (47 %). ^{1}H NMR ($CDCl_3$) δ 0.7–1.3 (4 H, m), 1.35 (9 H, s), 2.70 (1 H, m), 7.4–8.1 (4 H, arom.). The relative yields of *20* and *21* are determined by the area of the *t*-butyl ^{1}H NMR signals and the total yields are determined from the total area of aromatic protons in relation to the aromatic protons from *20* and *21*. The relative amounts of *20* and *21* varied in otherwise identical experiments over a rather wide range.

Reduction of benzophenone 5. *5* (2 g) and *11* (10 ml) were reduced at E = −1.30 V, n = 4.1 F mol^{-1}. The crude product was separated by preparative HPLC and the yields were determined by the same method on a 5 μ RP-18 column eluted with a 3:1 mixture of CH_3CN-H_2O. Isolated were:

2,2-Dimethyl-1,1-diphenylpropan-1-ol 22 (61 %), liquid (m.p. 28.5–29.5 °C, b.p. 10 mm 164 °C),[23] attempts to crystallize it were un-

successful. ^{1}H NMR ($CDCl_3$): δ 1.15 (9 H, s), 2.25 (1 H, s), 7.0–7.5 (10 H, arom.).

1-(4-t-Butylphenyl)-2,2-dimethyl-1-phenylpropan-1-ol 23 (29 %) m.p. −10 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (9 H, s); 1.25 (9 H, s), 2.20 (1 H, s), 7.1–7.6 (3 H, arom.). MS [*m/e* (%)]: 295 (0.5), 239 (100), 219 (20), 161 (22), 105 (90), 77 (30), 57 (35).

4,4'-Di-t-butylbenzophenone 24 (2 %), m.p. 132 °C (134.1–135.5).[24]

4-t-Butylbenzophenone 6 (8 %). The ^{1}H NMR spectra were consistent with lit.[17]

Reduction of 4-t-butylbenzophenone 6. *6* (2 g) and *11* (10 ml) were reduced at $E = -1.30$ V, $t = -8$ °C, $n = 2.6$ F mol^{-1}. In the catholyte precipitated 5,6-di-*t*-butyl-2,3-'di-(4-*t*-butylbenzoyl-1,4,5,6,1',4',5',6'-octahydrobiphenyl *25* (10 %) m.p. 258 °C. ^{1}H NMR (270 MHz) ($CDCl_3$): δ 0.65 (9 H, s), 0.80 (9 H, s), 1.28 (18 H, s), 1.69 (1 H, m, 17 Hz broad), 1.75 (1 H, m), 1.97 (1 H, d, *J* 10.8 Hz), 2.00 (1 H, m, 22 Hz broad), 2.44 (2 H, m), 2.83 (1 H, d, *J* 6.5 Hz), 3.07 (1 H, d, *J* 10.8 Hz), 6.97 (1 H, m), 7.10 (1 H, d, *J* 6.5 Hz), 7.46–7.74 (8 H, arom.). The integral in the aliphatic region indicates that some more protons are present, but the signals are unresolved. MS [*m/e* (%)]: 594 (7), 536 (8), 297 (100), 239 (76), 161 (43), 105 (22), 57 (47). The structure was assigned on the basis of the following arguments.

Besides three singlets at δ 0.65, 0.80 and 1.28 (*t*-butyl) 8 one-proton and one two-proton signals were found. Decoupling experiments show that the ethylenic proton δ 7.10 (at C-2) is neighbour to a methine group δ 2.83 (at C-3).

The signal from the ethylenic proton δ 6.97 (at C-2') resembles the X-part of an ABX-system with 4 lines in the X-part. Decoupling confirms this, the AB-part being the methylene group δ 2.44 (at C-3'). A doublet at δ 3.07 can be related to a position β to the carbonyl group, the partner of this doublet is a methine proton at δ 1.97. The shift difference between these seems too large and the coupling constant too small (10.8 Hz) for geminal protons. As there are no other large couplings at δ 3.07 and 1.97, we can conclude that there are substituents in the 4', 5' and 6' positions. The chemical shift of the C-6' proton suggests that the cyclohexene rings are linked through C-6'.

1-(4-t-Butylphenyl)-2,2-dimethyl-1-phenylpropan-1-ol 23 (52 %).

4,4'-Di-t-butylbenzophenone 24 (28 %).

Reduction of 2-cyanobenzophenone 7. *7* (2 g) and *11* (10 ml) were reduced at $E = -1.30$ V, $n = 2.1$ F mol^{-1}. The crude product was separated on a column of silica with a 4:1 mixture of light petroleum and diethyl ether. Isolated were:

2-t-Butylbenzophenone 26 (42 %). ^{1}H NMR spectrum was consistent with literature data.[17]

3-t-Butyl-3-phenylphthalide 27 (22 %), liquid. ^{1}H NMR ($CDCl_3$): δ 1.00 (9 H, s), 7.2–7.8 (9 H, arom.). MS [*m/e* (%)]: 209 (100), 174 (10), 154 (15), 122 (32), 120 (36), 108 (20), 77 (20), 57 (14). IR ($CHCl_3$) cm^{-1} (intensity): 2950 (w), 1750 (s), 1600 (w), 1480 (m), 1380 (w), 1360 (w), 1280 (m), 1110 (m).

6-t-Butyl-3-phenylphthalide 28 (35 %) m.p. 84 °C. ^{1}H NMR ($CDCl_3$): δ 1.40 (9 H, s), 6.40 (1 H, s), 7.5–8.0 (8 H, arom.). MS [*m/e* (%)]: 266 (55), 254 (80), 214 (75), 165 (100), 122 (70), 120 (80), 105 (83), 88 (62), 77 (64), 57 (58). IR ($CHCl_3$) cm^{-1} (intensity): 2950 (m), 1750 (s), 1360 (w), 1295 (m), 1250 (m), 1090 (m), 1050 (m), 900 (w), 855 (w), 820 (w).

Reduction of 3-cyanobenzophenone 8. *8* (2 g) and *11* (10 ml) were reduced at $E = -1.10$ V, $n = 2.2$ F mol^{-1}. The crude product was separated by HPLC on a 5 μ RP-18 column with a 3:1 mixture of CH_3CN:H_2O as eluent. Yields are determined as weight per cent of the injected crude product.

1-(3-Cyanophenyl)-2,2-dimethyl-1-phenylpropan-1-ol 30 (34 %) m.p. 90 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (9 H, s), 2.40 (1 H, s), 7.15–7.75 (9 H, arom.). IR ($CDCl_3$) cm^{-1}: 2210 (w).

4-t-Butyl-3-cyanobenzophenone 31 (53 %), liquid. ^{1}H NMR ($CDCl_3$): δ 1.30 (9 H, s), 7.3–8.1 (8 H, arom.). ^{13}C NMR ($CDCl_3$) ppm (intensity): 157.89 (14), 136.94 (42), 136.64 (18), 135.66 (18), 133.78 (42), 133.62 (12), 132.98 (48), 129.68 (91), 128.59 (75), 126.63 (49), 119.36 (12), 111.13 (16), 36.05 (26), 30.02 (120). MS [*m/e* (%)]: 263 (2), 248 (5), 208 (21), 105 (100), 77 (74), 57 (64). IR ($CDCl_3$) cm^{-1} (intensity): 2900 (m), 2210 (m), 1660 (s), 1600 (m), 1380 (m), 1360 (m), 1270 (s), 790 (s), 720 (s).

Reduction of 4-cyanobenzophenone 9. *9* (2 g) and *11* (10 ml) were reduced at $E = -0.85$ V, $n = 2.1$ F mol^{-1}. The crude product was separated by HPLC on a 10 μ RP-8 column with a 4:1 mixture of CH_3CN-H_2O. Yields in weight per cent of crude product. Products *4-t-butylbenzophenone* 6 (50 %) and *1-(4-cyanophenyl)-2,2-dimethyl-1-phenylpropan-1-ol* 32 (33 %) m.p. 107 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (9 H, s), 2.60 (1 H, s), 7.1–7.8 (9 H, arom.). MS [*m/e* (%)]: 264 (1), 239 (4), 208 (100), 130 (86), 105 (87), 102 (76), 57 (69). IR ($CDCl_3$): 2210 cm^{-1}.

Reduction of 4,4'-dimethoxybenzophenone 10. *10* (2 g) and *11* (10 ml) were reduced at $E = -1.50$ V, $n = 4.9$ F mol^{-1}. Separation and determination of yields by HPLC on a 5 μ RP-18 column with a 3:1 mixture of CH_3CN-H_2O. Isolated were:

1,1-Di-(4-methoxyphenyl-2,2-dimethylpropan-1-ol 33 (72 %), liquid. ^{1}H NMR ($CDCl_3$): δ 1.10 (9 H, s), 2.10 (1 H, s), 3.80 (6 H, s), 6.6–7.5 (8 H, arom.).

4,6-Di-t-butyl-3,4,5,6-tetrahydro-4,4'-dimethoxybenzophenone 34 (5 %). ^{1}H NMR ($CDCl_3$): δ 0.85 (9 H, s), 0.90 (9 H, s), 3.25 (3 H, s), 3.83 (3 H, s), 6.2 (1 H, dd, *J* 8 and 9 Hz). Unresolved signals between 0.8–1.8 indicate 5–6 aliphatic protons. MS [*m/e* (%)]: 257 (2), 301 (14), 269 (3), 243 (5), 213 (14), 212 (17), 161 (18), 135 (100), 92 (21), 77 (34), 57 (46).

1-(2-t-Butyl-4-methoxyphenyl)-1-(4-methoxyphenyl)-2,2-dimethylpropan-1-ol 35 (7 %). ^{1}H

NMR ($CDCl_3$): δ 1.15 (9 H, s), 1.32 (9 H, s), 1.50 (1 H, s), 3.75 (6 H, s), 6.7 – 7.5 (7 H, arom.). MS [*m/e* (%)]: 308 (1), 269 (10), 145 (28), 142 (30), 135 (78), 119 (100), 117 (100), 77 (39), 57 (94).

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