Oxidation of Nitrobenzylic Carbanions with Dimethyldioxirane. New Synthesis of Quinomethanes and Nitrobenzylic Carbinols. First Examples of Methylation of Carbanions with Dimethyldioxirane

Mieczysław Mąkosza,*,† Waldemar Adam,‡ Cong-Gui Zhao,‡ and Marek Surowiec†

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland, and Institut für Organische Chemie, Universit Würzburg, Am Hubland, D-97074 Würzburg, Germany

icho-s@icho.edu.pl

Received January 17, 2001

The reaction of nitrobenzylic carbanions with dimethyldioxirane (DMD) results in oxidation at the carbanion center or at the nitronate center to give nitrobenzylic carbinols or quinomethanes, respectively. Minor amounts of the methylation products are also formed. Both of these processes were observed for carbanions of (*p*-nitroaryl)diarylmethanes. The outcome of the oxidation process is very sensitive to the reaction conditions.

Introduction

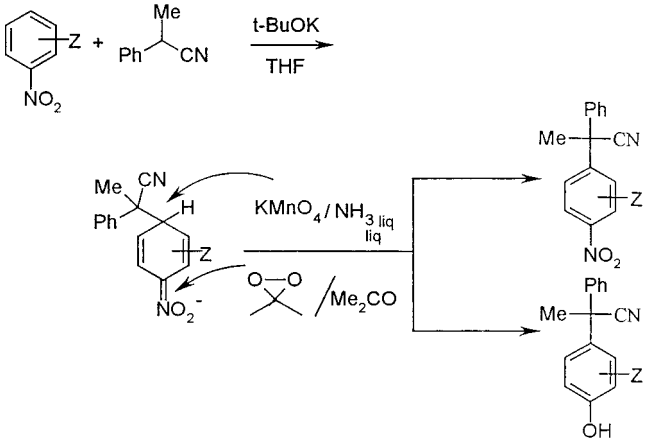
The oxidation of σ^H adducts of the 2-phenylpropionitrile carbanion with nitroarenes by potassium permanganate in liquid ammonia results in the formation of *p*-nitroarylated nitriles—products of the oxidative nucleophilic substitution of hydrogen in nitroarenes.[1] In contrast, the oxidation of these σ^H adducts by dimethyldioxirane (DMD) in THF affords para-substituted phenols (Scheme 1).[2]

In the case of the oxidation with permanganate, the oxidation process takes place at the site at which the nucleophile was added to the nitrobenzene ring. This process is sensitive to the steric hindrance of the substituents located in the vicinity of the addition site and proceeds with a large kinetic isotope effect $k_H/k_D = 9.79$ (at −70 °C).[3] Both of these experimental observations indicate that the oxidation of the σ^H adducts with $KMnO_4$ proceeds via attack of the oxidant on the site of the nucleophilic addition. In contrast, the bulky substituents in the vicinity of the addition site do not affect the oxidation of the σ^H adducts by DMD, and the kinetic isotope effect for the oxidation of the σ^H and σ^D adducts is negligible, that is $k_H/k_D = 1.01$.[2] These observations indicate that the DMD oxidant, contrary to $KMnO_4$, attacks the negatively charged nitronate group of the σ^H adducts. A similar reactivity has been proposed for the oxidation of nitronate anions to ketones by DMD, an oxidative variant of the Nef reaction.[4]

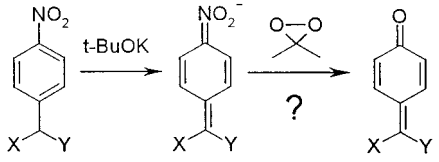
Since the distribution of the negative charge in the *p*-nitrobenzylic carbanions should be similar to that in the anionic σ^H adducts, we expected that the oxidation of the former by DMD should convert the nitronate functionality into a carbonyl group and, thus, give quinomethane derivatives (Scheme 2).

Previously it was observed that typical oxidants such as O_2, H_2O_2, and MnO_4^- react with these carbanions to give hydroxy compounds and products of their further transformations, such as alcohols, aldehydes, ketones, carboxylic acids, etc.[5,6] Herein we report our results on

Scheme 1. Oxidation of the σ^H Adducts Derived from the 2-Phenylpropionitrile Carbanion and Nitroarenes by Potassium Permanganate in Liquid Ammonia or by DMD



Scheme 2. Expected Oxidation of Nitrobenzylic Carbanions to Quinomethanes by DMD



* To whom correspondence should be addressed. Fax +48(22)-6326681.

† Polish Academy of Sciences.

‡ Universit Würzburg. Fax: +499318884756. http://www-organik.chemie.uni-wuerzburg.de.

(1) (a) Mąkosza, M.; Staliński, K. *Chem. Eur. J.* **1997**, *3*, 2025. (b) Mąkosza, M.; Staliński, K. *Tetrahedron* **1998**, *54*, 8797. (c) Mąkosza, M.; Staliński, K. *Synthesis* **1998**, *11*, 1631.

(2) Adam, W.; Mąkosza, M.; Staliński, K.; Zhao, C.-G. *J. Org. Chem.* **1998**, *63*, 4390. (b) Adam, W.; Mąkosza, M.; Zhao, C.-G.; Surowiec, M. *J. Org. Chem.* **2000**, *65*, 1099.

(3) Mąkosza, M.; Staliński, K. *Tetrahedron Lett.* **1998**, *39*, 3575.

(4) Adam, W.; Mąkosza, M.; Saha-Moller, C. R.; Zhao, C.-G. *Synlett* **1998**, *124*, 1335.

(5) Lawrence, N. J.; Lamarche, O.; Thurrab, N. *J. Chem. Soc., Chem. Commun.* **1999**, 689.

(6) Mąkosza, M., unpublished results.

10.1021/jo010055z CCC: $20.00
Published on Web 06/22/2001

Scheme 3. Oxidation of Nitrobenzylic Carbanions to the Corresponding Hydroxy Compounds by DMD

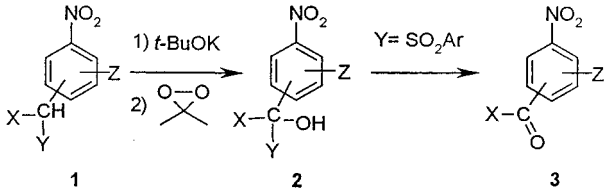


Table 1. Oxidation of Nitrobenzylic Carbanions with DMD to the Corresponding Hydroxy Compounds[a]

	nitroarene						
	Z	position of CHXY	X	Y	convn (%)	product	yield (%)
1a	H	4	H	SO_2Ph	63	**3a**	60
1b	H	4	Me	SO_2Ph	50	**3b**	33
1c	$(CH)_4$[b]	2	H	SO_2Tol	74	**3c**	30
1d	4-Cl	2	H	SO_2Ph	78	**3d**	43
1e	H	4	Me	Me	87	**2e**	85
1f	H	4	Ph	COOMe	100	**2f**	63
1g	H	4	9-fluorenyl		99	**2g**	99

[a] Run in THF at ambient temperature (ca. 20 °C). [b](1-Nitro-2-naphthyl)methyl 4-tolyl sulfone.

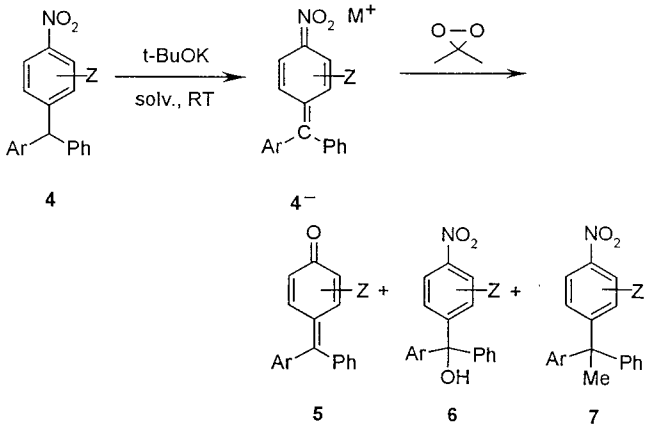
the DMD oxidation of nitrobenzylic carbanions which results in the formation of hydroxy compounds and the corresponding quinomethanes.

Results and Discussion

The precursors of the nitrobenzylic carbanions **1** are readily available from nitroarenes by vicarious nucleophilic substitution, VNS with chloroalkyl sulfones, esters of α-chloroalkanoic acids, etc.[7] The carbanions were generated from the substituted nitroarenes **1** by reaction with *t*-BuOK (2 equiv of the base were advantageous, as assessed through optimization of the experimental conditions) and submitted to oxidation by DMD (Scheme 3), which was prepared in the standard way.[8] The results of these experiments are summarized in Table 1.

Thus, when the carbanions of *p*-nitrobenzyl phenyl sulfone (**1a)** and 1-(4-nitrophenyl)ethyl phenyl sulfone (**1b**) were treated with DMD, instead of the expected quinomethanes, *p*-nitrobenzaldehyde (**3a**) and *p*-nitroacetophenone (**3b**) were obtained as main products. Clearly, similar to the oxidation of these carbanions with other oxidants, the reaction proceeded at the carbanionic site with the formation of corresponding hydroxy derivatives **2**. After the elimination of the sufinic acid from the intermediates **2**, aldehydes and ketones **3** are formed as final products.[6] The oxidation of these carbanions by the 3,3-pentamethyleneoxaziridine, an analogue of DMD, took place also at the carbanionic site.[9] The oxidation of the carbanions of methyl α-(4-nitrophenyl)-α-phenylacetate (**1f)**, 4-isopropyl-nitrobenzene (**1e**), and 9-(4-nitrophenyl)fluorene (**1g**) by DMD result in the formation of the corresponding hydroxy compounds **2f**, **2e**, and **2g** (Table 1).

Scheme 4. Oxidation of Diphenyl(4-nitrophenyl)methanes by DMD



On the other hand, treatment of the carbanion of (4-nitrophenyl)diphenylmethane (**4a)** with DMD (Scheme 4) results in the formation of the expected quinonemethane **5a** as the major product. Additionally, (4-nitrophenyl)diphenyl carbinol (**6a)**, product of the oxidation of the carbanion and, suprisingly, 1,1-diphenyl-1-(4-nitrophenyl)ethane (**7a)**, were also isolated. The unusual methylation of the carbanion by dimethyldioxirane will be discussed later.

Although the structure of the carbanion **4a**$^-$ is similar to that derived from the 9-fluorenyl derivative **1g**, the latter is oxidized by DMD only to the corresponding carbinol **2g** (Table 1), whereas under the same conditions, carbanion **4a**$^-$ produces the quinomethane **5a** as the major product. In the carbanion derived from **1g**, the fluorenyl structure obliges a planar geometry of the two benzene rings, while in the benzhydryl carbanion **4a**$^-$, the phenyl groups are twisted out from planarity. The different behavior of these rather similar carbanions, **4a**$^-$ and **1g**$^-$, suggests that the oxidation by DMD is sensitive to the steric hindrance at the reaction site. It appears that the oxidation of the benzylic carbanions by DMD at the carbanionic center is a facile process when it is planar, as is the case of substrate **1g**. In contrast, for the carbanion **4a**$^-$, the phenyl groups are twisted out of planarity, and therefore the oxidation of the carbanion center by DMD is hindered due to steric reasons, and DMD reacts preferentially at the more exposed nitronate functionality.

Since there are a few competing reactions proceeding when the nitrobenzylic carbanion of **4a** is treated with DMD, we could expect that the final outcome of the oxidation process should be sensitive to the reaction conditions. For this purpose, the products distribution pattern of the nitrobenzylic carbanion **4a**$^-$ oxidation with DMD was examined as a function of the solvent and countercation (Table 2).

As the data in Table 2 indicate, the nature of the carbanion−cation pair affects substantially the product distribution, however, in a complex way. Thus, the oxidation of the K^+ salt gave the highest yield of the quinomethane **5a** in the nonpolar toluene (entry 8) and in moderately polar THF (entry 3) solvents. On the other hand, the oxidation of the carbanion **4a**$^-$ in THF with Bu_4N^+ and $ClMg^+$ as countercations gave only the hydroxylation product **6a** (entries 5 and 4), whereas the oxidation of the Na^+ and Li^+ salts in THF gave appreciate

(7) Goliński, J.; Mąkosza, M. *Tetrahedron Lett.* **1978**, 3495. (b) Mąkosza, M.; Glinka, T. *J. Org. Chem.* **1983**, *48*, 3860. (c) Mudryk, B.; Mąkosza, M. *Synthesis* **1988**, 1007. (d) Mąkosza, M.; Winiarski, J. *Acc. Chem. Res.* **1987**, *20*, 282. (e) Mąkosza, M.; Wojciechowski, K. *Liebigs Ann. Rec.* **1997**, 1805.

(8) Adam, W.; Białas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.

(9) Wulf, J. P.; Sienkiwicz, K.; Mąkosza, M.; Schmitz, E. *Liebigs Ann. Chem.* **1991**, 537.

Table 2. The Product Ratio in the DMD Oxidation of the Nitrobenzylic Carbanion of 4a[a]

				product/yield (%)[b]		
entry	cation M^+	solvent	convn	**5a**	**6a**	**7a**
1	Li^+	THF	83	17	63	16
2	Na^+	THF	88	33	47	16
3	K^+	THF	95	48	26	17
4	$ClMg^+$	THF	96	traces	80	3
5	$^nBu_4N^+$	THF	97	0	95	0
6	K^+	DMF	93	29	60	8
7	K^+	3:1 THF/DMF	91	37	45	14
8	K^+	toluene	90	51	33	15

[a] Run at ambient temperature (ca. 20 °C). [b]Isolated products by preparative TLC and calculated for complete conversion.

Table 3. Oxidation of Potassium Salts of Diphenyl(nitroaryl)methanes Carbanions 4 by DMD[a]

substrates				products/yields (%)[b]	
	Ar	Z	convn (%)	**5**	**6**
4a	Ph	H	95	**5a**/51	**6a**/28[c]
4b[d]	Ph	$(CH)_4$	100	**5b**/91	**6b**/traces
4c	Ph	2-I	94	**5c**/33	**6c**/38
4d	Ph	2-MeO	86	**5d**/58	**6d**/36
4e	Ph	2-Cl	93	**5e**/58	**6e**/30
4f	Ph	3-MeO	99	**5f**/44	**6f**/13[e]
4g	Ph	3-Cl	83	**5g**/61	**6g**/10
4h	Ph	3-CN	100	**5h**/64	–
4i	4-Cl-phenyl	3-MeO	100	**5i**/40	**6i**/26 [f]
4j	1-naphthyl	H	80	**5j**/75	**6j**/20

[a] Run in THF at ambient temperature (ca. 20 °C). [b]Isolated products by preparative TLC, calculated for complete conversion. [c]Also 18% of **7a**. [d]Reaction performed in DMF. [e]Also 30% of **7f**. [f]Also 33% of **7i**.

Table 4. Oxidation of $4a^-$ with Various Oxidants

oxidant	convn (%)	products/yields[a] (%)	
DMD	95	**5a**/51	**6a**/26
3,3-pentamethylene-oxaziridine	98	**5a**/0	**6a**/76
H_2O_2	85	**5a**/0	**6a**/91
$^nBu_4N^+ MnO_4^-$	99	**5a**/0	**6a**/95

[a] Isolated products by preparative TLC, calculated for complete conversion.

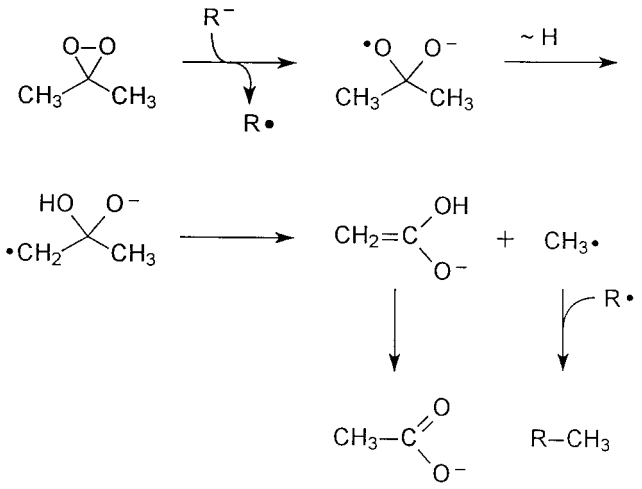
amounts of the quinomethane **5a**, in parallel with carbinol **6a** as a main product (entries 1 and 2).

Since the carbanion $\mathbf{4a}^-$ upon the oxidation with DMD gave the expected quinomethane **5a** as the major product, a number of other (4-nitroarene)diarylmethanes **4b**–**j** were prepared,[10] in anticipation that the corresponding carbanions would give the desired quinomethanes upon the oxidation by DMD. Indeed, the treatment of the carbanions **4b**–**j** with DMD, under the conditions in which the oxidation of $\mathbf{4a}^-$ gave mainly **5a**, led to the corresponding quinomethanes **5** as the major products (Table 3). Particularly the carbanions $\mathbf{4b}^-$ and $\mathbf{4j}^-$ afforded the expected quinomethanes **5b** and **5j** in high yields.

Oxidation of carbanion $\mathbf{4a}^-$ with other oxidants proceeds only at the carbanion center to give the corresponding carbinol **6a**, without even traces of the quinomethane **5a** (Table 4). This emphasizes the unique oxidative nature of the DMD, which can react at the nitronate functionality and the nitrobenzylic carbanion site. The quinomethane/carbinol product ratio provides a delicate measure of these two competitive oxidation processes.

(10) Mąkosza, M.; Voskresenski, S.; Surowiec, M. *Synthesis* **2000**, 1237.

Scheme 5. Proposed Mechanism for the Methylation of Nitrobenzylic Carbanions by DMD



In a few cases, the oxidation of the nitrobenzylic carbanions by DMD was accompanied by the formation of significant quantity (up to 16%) of 1,1-diaryl-1-(4-nitroarene)ethane **7**, the methylation product of the carbanions (Table 3). In three cases, the methylation products **7a**, **7f**, and **7i** were isolated and fully characterized. A similar unusual reaction has been reported in the case of oxidation by the nitroxide radical of methyl(trifluoromethyl)dioxirane and by hydrazine derivatives of DMD.[11,12] Presumably, this reaction proceeds via single electron transfer (SET) from the carbanion to DMD, followed by further transformations of the intermediary radical species, as shown in Scheme 5.

Conclusions

Oxidation of the nitrobenzylic carbanions with dimethyldioxirane proceeds at the carbanion center giving hydroxy compouds and at the nitronate group producing quinomethanes. The reaction course is governed by the substituents at the carbanion center and the reaction conditions: solvents and countercation. In some cases a peculiar reaction of methylation of the carbanions was observed.

Experimental Section

General Aspects. Melting points were uncorrected. ^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Bruker AMX (500 MHz) instruments. Chemical shifts are reported in ppm relative to TMS as internal standard; coupling constants *J* are in Hz. EIMS HR were measured on a AMD 604 spectrometer. THF was distilled over potassium benzophenone ketyl before reaction, and DMF was distilled over calcium hydride and stored over molecules sieves. Potassium *tert*-butoxide was reagent grade, purchased from Fluka, and was handled in a drybox under argon gas. Starting nitroarenes: **1a**–**d** and **1g** were prepared according to the standard procedure,[7] **1h** was prepared according procedure described by Wojciechowski,[13] **1e** was a commercial sample, and **4a**–**j** were prepared according to the reported procedure.[10] Dimethyldioxirane (DMD) was prepared according to standard procedure.[8]

(11) Adam, W.; Bottle, S. E., Mello, R. *J. Chem. Soc., Chem. Commun.* **1991**, 771.
(12) Nelsen, S. F.; Scamehorn, R. G.; De Felippis, J.; Wang, Y. *J. Org. Chem.* **1993**, *58*, 1657.
(13) Wojciechowski, K. *Bull. Pol. Ac. Chem.* **1988**, *36*235.

General Procedure for the Oxidation of the Nitrobenzylic Carbanions by DMD. The appropriate carbanion precursor (1 mmol) was added to a solution of *t*-BuOK (2 mmol, 224 mg) in THF (DMF, 3:1 THF:DMF or toluene) (10 mL) with stirring under argon gas at ambient temperature (ca. 20 °C). The deep violet, blue, or red solution was stirred for 5 min, and an acetone solution of DMD (ca. 2.5 mmol, 42 mL of ca. 0.06 M) was added to the mixture in one portion. The color changed to bright yellow. After 5 min of further stirring, saturated aqueous NH_4Cl (0.2 mL) was added, and the solution was dried over anhydrous $MgSO_4$. The solid phase was removed by filtration and washed with acetone (20 mL). The solvents were evaporated (25 °C, 15 Torr), and the residue was dissolved in 20 mL of methylene chloride, and passed through a short silica gel column (ca. 5 g). After evaporation of the solvent (25 °C, 15 Torr), the products were purified by preparative TLC with hexane/ethyl acetate (20:1) as the eluent. The solid products were additionally recrystallized.

***p*-Nitrobenzaldehyde[9] (3a):** 91.0 mg (60%) of yellow powder; mp 102−103 °C (EtOH).

***p*-Nitroacetophenone[9] (3b):** 55.0 mg (33%) of colorless powder; mp 80−81 °C (EtOH).

1-Nitronaphthalene-2-carbaldehyde[14] (3c): 61.0 mg (30%) of colorless powder; mp 95−96 °C (EtOH).

2-Nitro-5-chlorobenzaldehyde[14] (3d): 80.0 mg (43%) of colorless needles; mp 75−76 °C (EtOH).

2-(4-Nitrophenyl)-propan-2-ol[15] (2e): 154 mg (85%) of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.13−8.22 (m, 2H), 7.62−7.70 (m, 2H), 2.18 (s br. 1H), 1.62 (s, 6H). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.28; H, 6.49; N, 7.31.

Methyl α-hydroxy-α-(4-nitrophenyl)-α-phenylacetate (2f): 181 mg (63%) of an orange oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ =8.15−8.25 (m, 2H), 7.72−7.83 (m, 2H), 7.38−7.33 (m, 5H), 4.38 (s broad, 1H), 3.89 (s, 3H). Anal. Calcd for $C_{15}H_{13}NO_5$: C, 62.72; H, 4.56; N, 4.88. Found: C, 62.79; H, 4.49; N, 4.84.

9-(4-Nitrophenyl)-9*H*-fluoren-9-ol[16] (2g): 300 mg (99%) of yellow cubes; mp 160−161 °C (EtOH).

4-Benzhydrylidenecyclohexa-2,5-dienone[17] (5a): 127 mg (49%) of orange cubes; mp 165−166 °C (benzene).

(4-Nitrophenyl)diphenylcarbinol[18] (6a): 83.0 mg (27%) of colorless cubes; mp 96−97 °C (cyclohexane).

1,1-Diphenyl-1-(4-nitrophenyl)ethane (7a): 52.0 mg (17%) of colorless cubes; mp 97−98 °C (EtOH). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.10−8.19 (m, 2H), 7.42−7.28 (m, 8H), 7.18−7.08 (m, 4H), 2.27 (s, 3H). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.18; H, 5.47; N, 4.51.

4-Benzhydrylidene-4a,8a-dihydro-4H-naphthalen-1-one[19] (5b): 281 mg (91%) of an orange powder; mp 185−186 °C (benzene).

4-Benzhydrylidene-2-iodocyclohexa-2,5-dienone (5c): 120 mg (31%) of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.55−7.20 (m, 10H), 7.08 (dd, 1H, *J* = 8.5, *J* = 2.2), 6.90 (d, 1H, *J* = 8.6), 6.58 (d, 1H, *J* = 2.2). EIMS(+) HR: calcd for $C_{19}H_{13}OI$ $(M)^{+\bullet}$ 384.00112; found: 384.00217.

(3-Iodo-4-nitrophenyl)diphenyl carbinol (6c): 156.0 mg (36%) of a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.15 (d, 1H, *J* = 1.9), 7.76 (d, 1H, *J* = 8.5), 7.42−7.19 (m, 11H), 2.90 (s, 1H). Anal. Calcd for $C_{19}H_{14}NO_3I$: C, 52.92; H, 3.27; N, 3.25. Found: C, 52.94; H, 3.29; N, 3.11.

4-Benzhydrylidene-2-methoxycyclohexa-2,5-dienone[17] (5d): 144 mg (50%) of orange plates; mp 185−186 °C (benzene).

(3-Methoxy-4-nitrophenyl)diphenylcarbinol (6d): 104 mg (31%) of colorless cubes; mp 133−135 °C (cyclohexane). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.80 (d, 1H, *J* = 8.4), 7.45−7.23 (m, 11H), 6.91 (dd, 1H, *J* = 8.5, *J* = 1.7), 3.89 (s, 3H), 3.19 (s broad, 1H). Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.53; H, 5.08; N, 3.95.

4-Benzhydrylidene-2-chlorocyclohexa-2,5-dienone (5e): 158 mg (54%) of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40−7.20 (m, 11H), 7.05 (dd, 1H, *J* = 8.6, *J* = 2.2), 6.93 (d, 1H, *J* = 8.5). EIMS(+) HR: calcd for $C_{19}H_{13}35ClO$ $(M)^{+\bullet}$: 292.06549; found: 292.06768.

(3-Chloro-4-nitrophenyl)diphenylcarbinol (6e): 96.0 mg (28%) of a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.80 (d, 1H, *J* = 8.5), 7.64 (d, 1H, *J* = 1.9), 7.39−7.31 (m, 7H), 7.28−7.20 (m, 4H), 2.94 (s, 1H). Anal. Calcd for $C_{19}H_{14}NO_3Cl$: C, 67.16; H, 4.15; N, 4.12. Found: C, 67.12; H, 4.45; N, 4.01.

4-Benzhydrylidene-3-methoxycyclohexa-2,5-dienone (5f): 127 mg (44%) of orange needles; mp 109−110 °C (cyclohexane/CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.52−7.10 (m, 10H), 6.51 (d, 1H, *J* = 2.2), 6.30 (s, 1H), 6.27 (d, 1H, *J* = 2.2), 3.62 (s, 3H). EIMS(+) HR: calcd for $C_{20}H_{16}O_2$ $(M)^{+\bullet}$: 288.11503; found: 288.11483.

(2-Methoxy-4-nitrophenyl)diphenylcarbinol (6f): 44.0 mg (13%) of a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.80 (d, 1H, *J* = 2.2), 7.71 (dd, 1H, *J* = 8.5, *J* = 2.2), 7.35−7.27 (m, 6H), 7.26−7.17 (m, 4H), 6.74 (d, 1H, *J* = 8.5), 3.84 (s, 1H), 3.77 (s, 3H). Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.63; H, 4.97; N, 4.04.

1,1-Diphenyl-1-(2-methoxy-4-nitrophenyl)ethane (7f): 100 mg (30%) of colorless cubes; mp 105−106 °C (EtOH). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.65−7.80 (m, 2H), 7.38−7.19 (m, 6H), 7.13−7.03 (m, 4H), 6.88 (d, 1H, *J* = 8.8), 3.56 (s, 3H), 2.25 (s, 3H). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.53; H, 5.79; N, 4.12.

4-Benzhydrylidene-3-chlorocyclohexa-2,5-dienone (5g): 150 mg (51%) of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.37−7.21 (m, 10H), 6.91 (dd, 1H, *J* = 2.0, *J* = 0.9), 6.54 (d, 1H, *J* = 2.0), 6.53 (s, 1H). EIMS(+) HR: calcd for $C_{19}H_{13}O^{35}Cl$ $(M)^{+\bullet}$ 292.06549; found: 292.06599.

(2-Chloro-4-nitrophenyl)diphenylcarbinol (6g): 28.0 mg (8%) of a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.27 (d, 1H, *J* = 2.3), 7.97 (dd, 1H, *J* = 8.7, *J* = 2.4), 7.41−7.20 (m, 10H), 7.03 (d, 1H, *J* = 8.7), 4.21 (s, 1H). Anal. Calcd for $C_{19}H_{14}ClNO_2$: C, 67.16; H, 4.15; N, 4.12. Found: C, 67.12; H, 4.00; N, 3.99.

4-Benzhydrylidene-3-cyanocyclohexa-2,5-dienone (5h): 182 mg (64%) of an orange powder; mp 112−113 °C (cyclohexane/CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.95 (d, 1H, *J* = 2.2), 8.35 (dd, 1H, *J* = 8.4, *J* = 2.2), 7.40−6.60 (m, 10H), 6.33 (d, 1H, *J* = 8.5). EIMS(+) HR: calcd for $C_{20}H_{13}ON$ $(M)^{+\bullet}$: 283.09971; found: 283.09910.

4-[(4-Chloro-phenyl)phenylmethylene]-3-methoxycyclohexa-2,5-dienone (5i): 130 mg (40%) of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.12−7.33 (m, 9H), 6.47 (d, 1H, *J* = 2.1), 6.27 (s, 1H), 6.25 (d, 1H, *J* = 2.2), 3.61 (s, 3H). EIMS(+) HR: calcd for $C_{20}H_{15}O_235Cl$ $(M)^{+\bullet}$: 322.07606; found: 322.07676.

(4-Chlorophenyl)−(2-methoxy-4-nitrophenyl)phenylcarbinol (6i): 97.0 mg (26%) of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.81 (d, 1H, *J* = 2.2), 7.72 (dd, 1H, *J* = 8.5, *J* = 2.2), 7.10−7.37 (m, 9H), 6.73 (d,1H, *J* = 8.5), 4.99 (s, 1H), 3.80 (s, 3H). Anal. Calcd for $C_{20}H_{16}NO_4Cl$: C, 64.96; H, 4.36; N, 3.79. Found: C, 65.09; H, 4.20; N, 3.63.

1-(4-Chlorophenyl)-1-(2-methoxy-4-nitrophenyl)-1-phenylethane (7i): 122 mg (33%) of a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.66−7.72 (m, 2H), 7.18−7.35 (m, 5H), 6.97−7.08 (m, 4H), 6.88 (d, 1H, *J* = 9.0), 3.60 (s, 3H), 2.22 (s, 3H). Anal. Calcd for $C_{21}H_{18}NO_3Cl$: C, 68.57; H, 4.93; N, 3.81. Found: C, 68.17; H, 4.62; N, 3.46.

4-(Naphthalen-1-yl-phenylmethylene)cyclohexa-2,5-dienone (5j): 186 mg (60%) of an orange powder; mp 168−170 °C (cyclohexane/CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.95 (d, 1H, *J* = 8.3), 7.90 (d, 1H, *J* = 8.2), 7.65 (dd, 1H, *J* = 10.1, *J* = 2.7), 7.61 (d, 1H, *J* = 8.5), 7.54 (t, 1H, *J* = 7.7), 7.45 (t, 1H, *J* = 7.5), 7.32−7.42 (m, 7H), 6.98 (dd, 1H, *J* = 10.0, *J* = 2.7), 6.53 (dd, 1H, *J* = 10.1, *J* = 2.0), 6.28 (dd, 1H, *J* = 10.0, *J* = 2.1). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.36; H, 4.98.

(14) Mąkosza, M.; Owczarczyk, Z. *J. Org. Chem.* **1989**, *54*, 5094.
(15) Kornblum, N.; Ackermann, P. S.; Swiger, R. T. *J. Org. Chem.* **1980**, *45*, 5294.
(16) Von Wittig, G.; Doser, H.; Lorenz, I. *Liebigs Ann. Chem.* **1949**, 192.
(17) Ioffe, I. S.; Chawin, Z. J. *Zh. Obsch. Khim.* **1949**, *19*, 917.
(18) Starnes, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 1807.
(19) Gomberg, M.; Sullivan, F. W. *J. Am. Chem. Soc.* **1920**, *42*, 1867.

(4-Nitrophenyl)−(1-naphthyl)phenylcarbinol (6j): 57.0 mg (16%) of a colorless powder; mp 150−151 °C (cyclohexane/CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11−8.15 (m, 2H), 7.95 (d, 1H, J = 8.6), 7.81−7.87 (m, 2H), 7.49−7.53 (m, 2H), 7.38−7.43 (m, 1H), 7.22−7.36 (m, 7H), 6.84 (dd, 1H, J = 7.3, J = 1.0), 3.58 (s, 1H). Anal. Calcd for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.41; H, 4.87; N, 3.66.

Oxidation of Nitrobenzylic Salts (Except the Potassium Salt) by DMD. The nitroarene **4a** (1.0 mmol, 289 mg) was added to a solution of *t*-BuOK (2.0 mmol, 224 mg) in dry THF (10 mL) while stirring under argon gas at ambient temperature (ca. 20 °C). The deep red solution was stirred for another 5 min, the appropriate salt was added (LiCl or $MgCl_2$, 5 mmol), and the solution was stirred for 15 min. Then an acetone solution of DMD (ca. 2.5 mmol, 42 mL of ca. 0.06 M) was added to the mixture in one portion, and the color changed to yellow. After 5 min of further stirring, saturated aqueous NH_4Cl (1 mL) was added, and the workup was conducted as described in the preceding procedure.

The sodium salt was prepared analogously with *t*-BuONa as base.

The ^{n}Bu$_4$N$^+$ salt was prepared analogously with ^{n}Bu$_4$N$^+$OH$^-$ solution in dioxane as base.

Acknowledgment. The work in Warsaw was generously suported by the State Committee for Scientific Research (grant no. PBZ 6. 01), the work in Würzburg by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm “Peroxidchemie”) and the Founds der Chemischen Industrie. This cooperative project was initiated during the stay of M. Mąkosza in Würzburg as an Alexander-von-Humboldt Awardee. C.-G. Zhao thanks the Deutsche Akademische Austauschdienst (DAAD) for a doctoral fellowship.

Supporting Information Available: ^{1}H NMR spectral and elemental analyses data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010055Z