Table I. Bakers' Yeast Reduction of Esters of Phenacyl Alcohol (3a)

substrate	incubation time, h	recovery, %	products: 1-acyl[b] compd	1-acyl[b] yield,[a] %	diol 4[b] yield,[a] %	diol 4[b] ee,[c] %	2-acyl[b] compd	2-acyl[b] yield,[a] %	2-acyl[b] ee,[d] %
5c	8	97	**7a**	7	13	58	**6a**	70	94
5d	8	85	**7b**	8	4	48	**6b**	50	91
5d	20	82	**7b**	15	19	*e*	**6b**	40	*e*
5e	24	30	**7c**	2	5	21	**6c**	14	*e*

[a] Yields of products purified by silica gel column chromatography. [b] Configuration *S* for all products. [c] Optical purities determined by comparison with the literature values (ref 10). [d] Determined by 200-MHz ^{1}H-NMR analysis of (*R*)-(+)-MTPA esters. [e] Not determined for lack of pure material.

of the methoxy group centered at 3.47 and 3.58 ppm.

1-Phenyl-1,2-ethanediol (4) from (*S*)-(+)-6a. A sample of the (*S*)-(+)-2-acetate **6a** (0.09 g, 0.5 mmol) was reduced in anhydrous tetrahydrofuran (2 mL) with $LiAlH_4$ (0.06 g, 1.5 mmol) at −5 °C. After 0.5 h, 0.06 mL of water, 0.06 mL of 15% sodium hydroxide, 0.18 mL of water, were sequentially added, and the mixture was stirred for 10 min. The mixture was filtered and the precipitate washed with anhydrous diethyl ether. The filtrates were dried over sodium sulfate and evaporated. Benzene (2 mL) was added, and evaporation of the solvent gave dry *S*-diol **4** (0.075 g), pure by TLC and GLC: α_D +40° (*c* 2, acetone).

(+)-2-Acetoxy-2-phenylethanol (7a): yield, 0.048 g (8%); ^{1}H NMr δ 2.03 (3 H, s), 2.8 (1 H, br s), 3.8 (2 H, t, *J* = 6 Hz), 5.8 (1 H, t, *J* = 6 Hz), 7.3 (5 H, s); α_D +43° (*c* 2, acetone).

(*S*)-(+)-1-Phenyl-1,2-ethanediol (4): yield, 0.07 g (13%); α_D +28° (*c* 2, acetone); chromatographic and spectroscopic data identical with those of an authentic sample.

2-(Propanoyloxy)-1-phenylethanone (5d). A solution of phenacyl alcohol **3a** (1.5 g, 11 mmol) and propionic anhydride (1.5 mL) in dry pyridine (15 mL) was kept at room temperature (12 h). After being poured into water (50 mL), the ester **5d** was recovered by decanting the water layer and taken up with diethyl ether (80 mL). After washing with 0.5 N HCl (10 mL) and brine (10 mL), the organic extract was dried over sodium sulfate and evaporated. The residue was purified by filtration through a short silica gel column, by eluting with petroleum ether/ethyl acetate (95:5). Pure propanoate **5d** was obtained (1.7 g, 80%). A sample for analytical purposes was distilled: bp 210 °C (14 mmHg); IR (neat) 1750, 1705 cm^{-1}; ^{1}H NMR δ 1.17 (3 H, t, *J* = 8 Hz), 2.44 (2 H, q, *J* = 8 Hz), 5.24 (2 H, s), 7.40–8.20 (5 H, Ar). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.7; H, 6.3. Found: C, 68.85; H, 6.4.

Bakers' Yeast Incubation of 2-(Propanoyloxy)-1-phenylethanone (5d). Incubation conditions were as for the acetate **5c**, with incubation time of 8 h. Starting from 0.72 g of compound **5d**, after workup and silica gel chromatography (petroleum ether/ethyl acetate, from 85:15 to 1:1 as eluant), yields of purified products were as follows.

2-(Propanoyloxy)-1-phenylethanone (5d): yield, 0.122 g (17%) physical and chemical characteristics corresponding to those of an authentic sample.

2-Hydroxy-1-phenylethanone (3a): yield, 0.03 g (6%); physical and chemical characteristics corresponding to those of an authentic sample.

(*S*)-(+)-2-(Propanoyloxy)-1-phenylethanol (6b): yield, 0.365 g (50%); bp 180–185 °C (14 mmHg); IR (neat) 3450, 1725 cm^{-1}; ^{1}H NMR δ 1.10 (3 H, t, *J* = 7 Hz), 2.30 (2 H, q, *J* = 7 Hz), 3.30 (1 H, br s), 4.05–4.28 (2 H, m), 4.87 (1 H, m), 7.30 (5 H, s, Ar); α_D +23° (*c* 2, acetone). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.0; H, 7.25. Found: C, 68.15; H, 7.4.

A sample of the compound **6b** was transformed into the (*R*)-(+)-MTPA ester[13] and 91% ee was established from integrations of the signals of methoxy group in its 200-MHz ^{1}H NMR spectrum. Two multiplets at δ 3.47 and 3.58 were present for the derivative from the racemic and optically active **4d** at ratio 1:1 and 95.5:4.5, respectively.

(+)-2-(Propanoyloxy)-2-phenylethanol (7b): yield, 0.06 g (8%); ^{1}H NMR δ 1.12 (3 H, t, *J* = 7 Hz), 2.40 (2 H, q, *J* = 7 Hz), 2.60 (1 H, br s), 3.75 (2 H, d, *J* = 6 Hz), 5.85 (1 H, t, *J* = 6 Hz), 7.34 (5 H, s, Ar); α_D +58° (*c* 2, acetone).

(*S*)-(+)-1-Phenyl-1,2-ethanediol (4): yield, 0.02 g (4%); identical with an authentic sample; α_D +23° (*c* 2, acetone).

Acknowledgment. We thank Ministero della Pubblica Istruzione for financial help.

Registry No. **3a**, 582-24-1; **3b**, 70-11-1; **4**, 16355-00-3; **5c**, 2243-35-8; **5d**, 54797-42-1; **5e**, 54797-43-2; **6a**, 103574-67-0; **6b**, 115482-82-1; **6c**, 115482-83-2; **7a**, 115482-84-3; **7b**, 115482-85-4; **7c**, 115482-86-5.

Unusual Structure in Meisenheimer Complex Formation from the Highly Electrophilic 4,6-Dinitrobenzofuroxan

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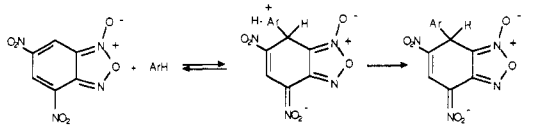
4,6-Dinitrobenzofuroxan (DNBF) exhibits an extremely high electrophilic character which is very useful to assess the reactivity of very weak nucleophiles.[1] Thus, many aromatic amines which have a very low carbon basicity undergo facile addition to DNBF to yield carbon-bonded σ-adducts as the thermodynamically stable species.[2,3] 1,8-Bis(dimethylamino)naphthalene, i.e., the Proton Sponge, is the most spectacular example in the series.[4] Also, weakly basic aromatics (ArH) like 1,3,5-trimethoxybenzene or indoles react with DNBF, affording the stable σ-adducts **1** according to eq 1.[5a] In these latter instances, the reactions proceed so readily that a detailed kinetic analysis of the formation of **1** could be made.[5b]



1

With the aim at assessing the reactivity of indene, we have looked at the interaction of this derivative with

(1) Terrier, F. *Chem. Rev.* **1982**, *82*, 77.
(2) (a) Strauss, M. J.; Renfrow, R. A.; Buncel, E. *J. Am. Chem. Soc.* **1983**, *105*, 2473. (b) Buncel, E.; Renfrow, R. A.; Strauss, M. J. *J. Org. Chem.* **1987**, *52*, 488.
(3) (a) Spear, R. J.; Norris, W. P.; Read, R. W. *Tetrahedron Lett.* **1983**, *24*, 1555. (b) Read, R. W.; Spear, R. J.; Norris, W. P. *Aust. J. Chem.* **1984**, *37*, 985. (c) Norris, W. P.; Spear, R. J.; Read, R. W. *Aust. J. Chem.* **1983**, *36*, 297.
(4) Terrier, F.; Hallé, J. C.; Pouet, M. J.; Simonnin, M. P. *J. Org. Chem.* **1986**, *51*, 409.
(5) (a) Hallé, J. C.; Pouet, M. J.; Simonnin, M. P.; Terrier, F. *Tetrahedron Lett.* **1985**, *26*, 1307. (b) Terrier, F.; Kizilian, E., Unpublished results.

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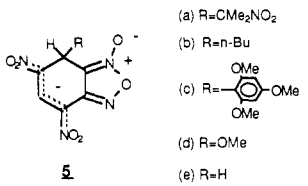
Table I. UV-Visible and NMR Parameters for DNBF and Compounds 3–5[a,b]

compd	λ_{max}	^1H[b,c] H_5	H_7	$H_{1'}$	^{13}C[b,c] C_4	C_5	^{15}N:[b,c] J_{N_6-H}
DNBF	420[d]	8.95	9.27	–	136.7[e]	126.5[e]	$J_{N_6-H_5}$ = 1.6, $J_{N_6-H_7}$ = 2.4
3	395	7.93	4.71	6.47	135.3	127.2	$J_{N_6-H_5}$ = 1.9, $J_{N_6-H_7}$ = 3.1, $J_{N_6-H_{1'}}$ = 7.1
	397[f]	8.11[f]	4.40[f]	6.32[f]			$J_{N_6-H_5}$ = 1.9, $J_{N_6-H_7}$ = 2.9, $J_{N_6-H_{1'}}$ = 7.1
4	480	8.64	4.79	5.33	–[g]	132.6	
5a[h]	484	8.69	5.27	–	110.6	133.3	
5b[h]	492	8.65	4.41	–	109.4	131.5	
5c	490	8.65[i]	5.83[i]	–	110.6	131.0	
5d[h]	470	8.70[j]	5.89[j]	–	109.5	131.4	$J_{N_6-H_5}$ = 2.6, $J_{N_6-H_7}$ = 0.7
5e[h]	487	8.52	3.79	–	109.8	130.6	

[a] Solvent Me_2SO or Me_2SO-d_6 unless otherwise indicated. [b] See structures 3–5 in the text for numbering of hydrogen, carbon, and nitrogen atoms. [c] Chemical shifts (ppm) relative to Me_4Si as internal standard; J in hertz. [d] λ_{max} in the presence of a strong acid in H_2O–Me_2SO, 10:90 (v/v). [e] An INADEQUATE analysis of DNBF will be reported elsewhere. [f] In CH_2Cl_2 or CD_2Cl_2. [g] Unambiguous assignment of C_4 could not be made because of the relative instability of 4 in Me_2SO which causes the appearance of overlapping resonances due to unidentified products. [h] Unpublished results. [i] Reference 5a. [j] Similar values have been reported in ref 3c.

DNBF. This paper deals with the isolation and structure elucidation of the neutral dihydrooxazine *N*-oxide **3** as the resulting product. The formation of a derivative like **3** has never been observed in σ-complex chemistry, and it represents a rare example of neighboring nitro group participation in the field.[6-8]

The following key observations have been made. (1) The addition of indene to 1 equiv of DNBF in Me_2SO or methanol resulted in the formation of a product, X, with UV–visible and NMR parameters that are very different from those reported for common DNBF π- or σ-adducts.[2-5] In particular, we note in Table I that X has λ_{max} 395 nm in Me_2SO, as compared with λ_{max} in the range 465–490 nm for a number of fairly well identified σ-adducts **5**. Similarly, the H_5 signals for **5** all lie in the narrow range of 8.52–8.70 ppm while the H_5 signal for X is seen at higher field (δ 7.93). Also revealing are the ^{13}C spectra since the C_4 and C_5 chemical shifts for X closely resemble those for neutral DNBF rather than those for **5**.



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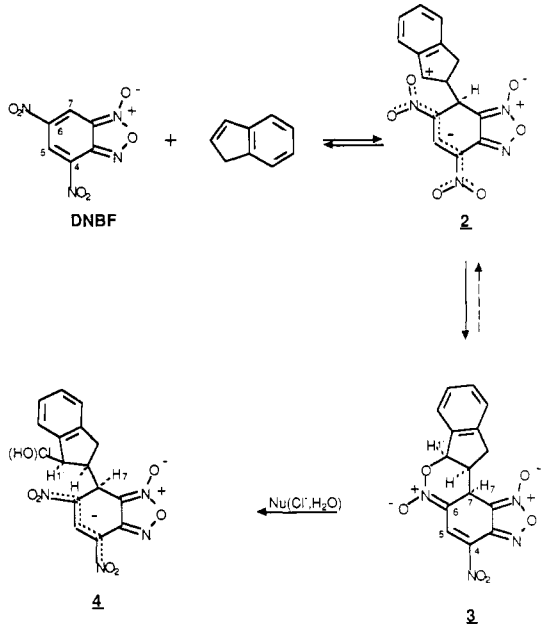
(2) The addition of other weak nucleophiles in the reaction mixture, e.g., H_2O, Cl^-, resulted in conversion of X into new products whose visible and ^1H NMR characteristics are consistent with the structure of the C-adducts **4**. The C_5 signal also agreed with structure **4**.

(3) The addition of indene to DNBF also proceeded in relatively weak polar solvents, e.g., CH_2Cl_2. In marked contrast with the adducts **5**, the resulting product was notably soluble in these media, where it exhibits the same spectral characteristics as those found for X in Me_2SO (Table I). This finding also rules out the possibility of dealing with a π-complex.[3c] X was readily obtained as yellow crystals which are stable at room temperature.

The above observations are difficult to reconcile with X being the expected zwitterionic σ-adduct **2**, although our original feeling was that the negatively and positively charged moieties of **2** could be appropriately located for direct stabilizing interaction. Evidence for such effective stabilization in zwitterionic σ-adducts has been obtained for amidine adducts of 1,3,5-trinitrobenzene and 1,3-dinitronaphthalene.[9] Here, we suggest the mechanism depicted in Scheme I, which is based on the well-known fact that the negative charge of the arenide or hetarenide moiety of σ-adducts is largely localized onto the NO_2 groups in very activated systems.[1,7,8] Then, the possibility arises for intramolecular nucleophilic attack of an oxygen atom of the ortho-like 6-NO_2 group of the DNBF moiety of **2** at the positively charged carbon of the indene ring, yielding the neutral dihydrooxazine *N*-oxide **3** as the X product. A concerted mechanism avoiding the formation of **2** and involving a cyclic transition state may also account for the formation of **3**. On this ground, formation of **4** will occur via a S_N2-like substitution by Cl^- or H_2O at $C_{1'}$ of **3**. Interestingly, such nitro group interaction was suggested, but not demonstrated, to occur in the bicarbonate-catalyzed S_NAr displacement of a NO_2 group of 1,3,5-trinitrobenzene.[10]

Scheme I



While elemental analysis data agreed with **3**, the oxazine *N*-oxide structure was unambiguously established from NMR experiments with a sample of DNBF that we have ^{15}N-labeled in the 6-position. Then a large coupling constant between $H_{1'}$ and the labeled nitrogen atom is observed by ^1H and ^{15}N NMR spectroscopy: $^3J_{^{15}N-H_{1'}}$ = 7.1

(6) Preston, P. N.; Tennant, G. *Chem. Rev.* **1972**, *72*, 627.
(7) Strauss, M. J. *Acc. Chem. Res.* **1974**, *7*, 181.
(8) Artamkina, G. A.; Egorov, M. P.; Beletskaya, I. P. *Chem. Rev.* **1982**, *82*, 427.
(9) (a) Bard, R. R.; Strauss, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 3789; (b) *J. Org. Chem.* **1976**, *41*, 2421.
(10) Izzo, P. T. *J. Org. Chem.* **1959**, *24*, 2026.

Hz. In addition, Table I shows that the $^3J_{^{15}N-H_5}$ and $^3J_{^{15}N-H_7}$ coupling constants for **3** look like those for DNBF rather than those for the adducts **5**.

Experimental Section

General. All melting points were determined on a Reichert Kofler block and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Brucker AM-250 spectrometer equipped with an ASPECT 3000 Computer. Chemical shifts are reported in parts per million (δ, J in hertz) relative to internal Me_4Si, and UV-visible spectra were recorded on a Beckman Acta III spectrophotometer. Electron-impact mass spectra were recorded on a Nermag R10-10C instrument. Elemental analyses were performed by the INSCIR Microanalytical Laboratory, Mont-Saint-Aignan, France.

Materials. 4-Nitrobenzofuroxan and 4,6-dinitrobenzofuroxan were prepared according to previously reported methods. 4-Nitrobenzofuroxan: mp 143 °C (lit.[11,12] mp 143 °C); DNBF, mp 173 °C (lit.[3b,c,11] mp 172-174.5 °C). Indene (Aldrich) was freshly distilled prior to use.

[6-^{15}N]-4,6-Dinitrobenzofuroxan. A solution of 1 mL of $H^{15}NO_3$, 40% (Aldrich, 98% ^{15}N), in 4 mL of sulfuric acid (d = 1.84) was added dropwise to a stirred solution of 1.1 g of 4-nitrobenzofuroxan (6.1 mmol) in 8 mL of sulfuric acid (d = 1.84) at 0 °C. The resulting mixture was kept at 0 °C for 30 min, heated at 50-60 °C for 3 h, and then allowed to return to room temperature. After the mixture was poured onto cracked ice, the resulting orange crystals were filtered, washed with water, and vacuum dried over P_2O_5 to yield 1.1 g of [6-^{15}N]DNBF (80%): mp 173 °C; mass spectrum (obsd), m/e 227, 211, 197, 151, 121, 87; for comparison, DNBF mass spectrum (obsd), m/e 226, 210, 196, 150, 120, 87.

Preparation of 3. The oxazine *N*-oxide **3** was prepared by the addition of DNBF (226 mg, 1 mmol) to a stirred solution of indene (128 mg, 1.1 mmol) in methylene chloride (2 mL) at room temperature. The solution turned orange and some precipitate was formed after 2 h. After 24 h at room temperature, the resulting yellow crystals were filtered, washed with diethyl ether, and vacuum dried over P_2O_5: mp 165 °C dec. Anal. Calcd for $C_{15}H_{10}N_4O_6$: C, 52.64; H, 2.94; N, 16.37. Found: C, 52.18; H, 2.76; N, 16.18. The same method was used to prepare **3** from ^{15}N-labeled DNBF.

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(11) Drost, P. *Justus Liebigs Ann. Chem.* **1899**, *307*, 49.
(12) Ghosh, P. B.; Whitehouse, M. W. *J. Med. Chem.* **1968**, *11*, 305.

Reinvestigation of the Metalation of Phenylcyclopropane: Does the Phenylcyclopropyl Anion Undergo Ring-Opening?

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There are several examples of ring-opening reactions of cyclopropanes with base that give allyl anions.[1-7] In the light of orbital-symmetry considerations,[8] these were thought to be examples of pericyclic reactions[1-3] with thermally allowed conrotatory ring-opening. Since acyclic allyl anions are not configurationally stable, the stereochemistry of the product and the sense of the ring-opening were uncertain. Later examples were shown to give symmetry-forbidden products in a tricyclic system.[4-7] It was then proposed that the reaction proceeds through a single electron transfer process from the base to the tricyclic carbon acid.[5] This reaction has since been shown to proceed by initial deprotonation of the acid rather than initial electron transfer from the metalating agent to the acceptor.[7] A universal requirement for the ring-opening to occur is that the incipient allyl anion must have at least one group on the allyl termini which is capable of stabilizing the charge.[1] Both symmetry-allowed and symmetry-forbidden ring-openings are observed; the mechanistic pathway is uncertain.

We are interested in cyclopropyl anion ring-openings as a synthetic route to cross-conjugated carbanions. The ring-opening of 1-vinylcyclopropyl carbanion[9] and spiropentyl carbanion[10] would lead to the simplest carbanion of this type, the as yet unknown isoprenyl carbanion.[11] As a model for the ring-opening of the conjugated cyclopropyl carbanions, we selected the 1-phenylcyclopropyl carbanion, which is readily prepared from commercially available cyclopropylbenzene.[12] We report herein the results of a study of the 1-phenylcyclopropyl anion and the subsequent ring-opening of a cyclopropyl anion species.

Table I. Product Distribution from Eq 1 under Various Conditions

entry no.	equiv of base	temp, °C	time	1:2
1	1.1	20	4 h	>100:1
2	1.1	70	4 h	5:1[a]
3	4.0	70	4 h	2:1
4	4.0	70	1 day	1:1
5	4.0	20	2 days	30:1
6	4.0	20	14 days	14:1
7	4.0	20	25 days	11:1
8	4.0	20	60 days	8:1

[a] Deuterium oxide quench of this was analyzed by electron-impact mass spectroscopy. As calculated by using the program HEAVY, **1b** had from 0.2 to 1.0 deuteriums per molecule and **2b** had from 1.6 to 1.8 deuteriums per molecule.

Results and Discussion

The results of the metalation studies of cyclopropylbenzene (**1a**) with Lochmann's base (*n*-butyllithium/potassium *tert*-butoxide in hexane)[13] are shown in Table I. Metalation at room temperature followed by quenching with D_2O gives rise to **1b** with an average of 0.8 deuterium

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(1) Boche, G.; Walborsky, H. M. *The Chemistry of Functional Groups*; Rappoport, Z., Ed.; Wiley: New York, 1987; pp 701-808 and references cited therein.
(2) Mulvaney, J. E.; Savage, D. *J. Org. Chem.* **1971**, *36*, 2592-6 and references cited therein.
(3) Boche, G.; Martens, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 724-5. Boche, G.; Martens, D.; Danzer, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 984.
(4) Londrigan, M. E.; Mulvaney, J. E. *J. Org. Chem.* **1972**, *37*, 2823-6.
(5) Newcomb, M.; Seidel, T.; McPherson, M. B. *J. Am. Chem. Soc.* **1979**, *101*, 777-8.
(6) Mulvaney, J. E.; Londrigan, M. E.; Savage, D. J. *J. Org. Chem.* **1981**, *46*, 4592-4.
(7) Boche, G.; Marsch, M. *Tetrahedron Lett.* **1983**, *24*, 3225-8.
(8) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395-7.
(9) Beavers, W. A.; Wilson, S. E.; Gordon, B.; Bates, R. B.; Romano, A. R. *Tetrahedron Lett.* **1979**, 1675-8.
(10) Applequist, D. E.; Fanta, G. F. *J. Am. Chem. Soc.* **1960**, *82*, 6393-7.
(11) Bahl, J. J.; Bates, R. B.; Gordon, B. *J. Org. Chem.* **1979**, *44*, 2290-1.
(12) Schlosser, M.; Schneider, P. *Helv. Chim. Acta* **1980**, *63*, 2404-10.
(13) Lochmann, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 257-8.

0022-3263/88/1953-4409$01.50/0