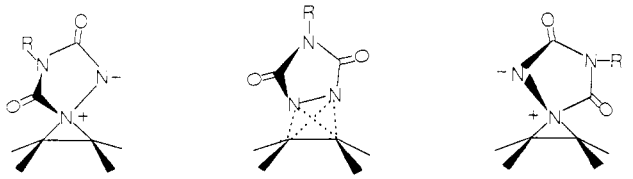
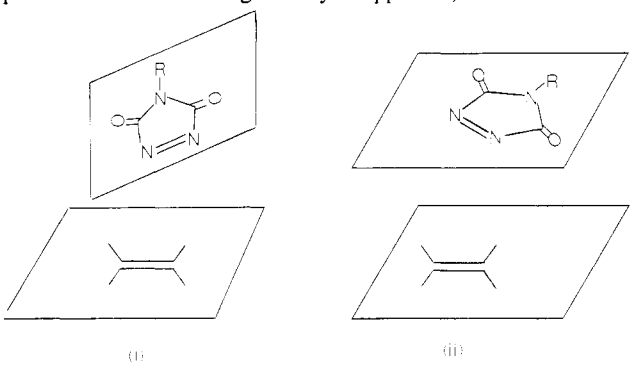
of **6a** to product, **5**, must proceed more rapidly than reversal of **6a** to TAD and olefin, or than isomerization of **6a** to **6c**.



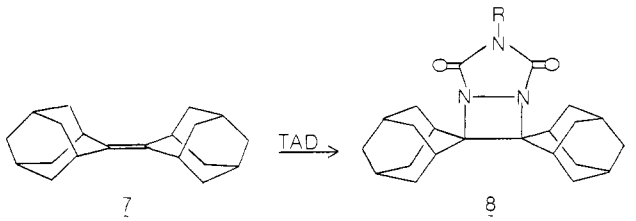
6a 6b 6c

A further point of interest concerns the path for conversion of olefin and TAD to **6a**. Two major possibilities shown below are (i) approach in perpendicular planes and (ii) approach in parallel planes. As a test of the geometry of approach, we have examined



(i) (ii)

the reaction of TAD with adamantylideneadamantane (**7**).[7] Indeed, TAD reacts with **7** at room temperature to afford a colorless 1:1 adduct (**8**).[8] When adduct **8** (R = C_6H_5) is heated



7 8

in chloroform containing tetramethylethylene, the system reverts to olefin **7** and TAD, which is then trapped as the ene product **5**.[5] The proton and ^{13}C NMR[8] data reveal a high degree of symmetry in the adduct **8**, and show a single sharp line for the carbonyl carbons. The spectral and chemical observations are consistent with the simple diazetidine structure **8** for the adduct.[9]

In summary, the facile reaction of TAD with the very hindered olefin **7** implies that reaction can proceed by the geometry of approach shown in i, possibly via a 2s (olefin) + 2a (TAD) process or possibly directly to a species such as **6a**.[10,11] The results with tetramethylethylene indicate that an intermediate is formed, possibly an aziridinium imide, **6a**. If adjacent hydrogens are present, the intermediate may collapse to ene product by 5-center Cope elimination; alternatively, it may collapse to a diazetidine, e.g., **8**.

Further evidence on the TAD-olefin reaction (effect of olefin structure, solvent effects, and the role of the lone-pair electrons of the azo nitrogens of TAD) will be reported at a later date.

Acknowledgment. This work has been supported by the National Science Foundation (Grant CHE77-14616). We thank Dr. Piotr M. Starewicz for assistance in the NMR determinations and for discussions.

(7) For synthesis, see: McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krespi, L. R. *J. Org. Chem.* **1978**, *43*, 3255. For some reactions, see: Bolster, J.; Kellogg, R. M.; Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1979**, 285, and references therein.

(8) (a) Compound **8** (R = CH_3): mp 220–221 °C (to a red melt); IR ($CHCl_3$) 1730, 1675 cm^{-1}; ^1H NMR 250 MHz ($CDCl_3$) δ 1.74, 1.79 (d, 4 H), 1.80 (s, 4 H), 1.80, 1.86 (d, 4 H), 1.98 (s, 2 H), 1.99 (s, 2 H), 2.15, 2.10 (d, 4 H), 2.43 (s, 4 H), 2.62, 2.68 (d, 4 H), 3.06 (s, 3 H); ^{13}C NMR 250 MHz ($CDCl_3$) δ 154.4 (2 C), 90.6 (2 C), 38.21 (2 CH_2), 35.4 (4 CH_2), 34.6 (4 CH_2), 32.5 (4 CH), 26.9 (2 CH), 26.7 (2 CH), 26.2 (1 CH_3); anal. C, H, N. (b) Compound **8** (R = C_6H_5): mp 229–231 °C; IR ($CHCl_3$) 1740, 1680 cm^{-1}; anal. C, H, N.

(9) The crystal structure of the adduct formed from singlet oxygen and olefin **7** shows a nonplanar dioxetane ring and skewed adamantyl units (to reduce nonbonded repulsion with each other): Hess, J.; Vos, A. *Acta Crystallogr., Sect. B* **1977**, *33B*, 3527. We expect that adduct **8** also has these features. Rapid interconversion (on the NMR time scale) between the two skewed forms of **8** accounts for the symmetry seen in the NMR results (ref 8), and shown in structural representation **8**. The low carbonyl frequencies of 1730, 1675 cm^{-1} [in contrast to the usual range of 1750–1780, 1700–1730 cm^{-1} (ref 2a)] are also consistent with a skewed ground-state structure for **8**. An alternative structure for **8** would be one of type **6a**; accommodation of the NMR data would require rapid interconversion between the two equivalent aziridinium imides (e.g., see: **6a** ⇄ **6c**) or an unprecedented structure such as **6b**.

(10) This might involve use of the lone pair of electrons of an azo nitrogen in the rate-determining step, in accord with formation of bromonium ion from olefin plus Br_2.

(11) Attention is also called to the difference in isotope effects observed in the ene reaction of dimethyl azodicarboxylate with (*S*)-*cis*-1-deuterio-1-phenyl-4-methyl-2-pentene ($k_H/k_D \simeq 3$) (Stephenson, L. M.; Mattern, D. L. *J. Org. Chem.* **1976**, *41*, 3614) and in the reaction of TAD **1** with (*Z*)-**4** ($k_H/k_D \simeq 1.1$; this study). The simplest explanation for these differences would appear to lie in the approach in parallel planes (and a 4 + 2 transition state) for the azodicarboxylate–olefin pair rather than the approach in perpendicular planes suggested above for reaction of TAD **1** with olefins **4** and **7**, sterically difficult for azodicarboxylate and olefin.

Catherine A. Seymour, Frederick D. Greene*

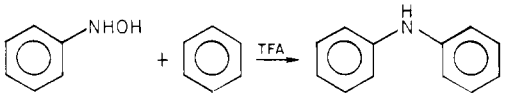
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 23, 1980

Reductive Phenylation of Nitroarenes

Sir:

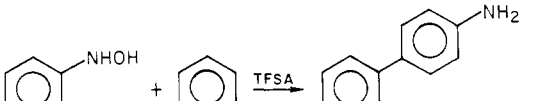
Several methods for the synthesis of diaryl compounds are known.[1] Gomberg, Pschorr, and Ullmann reactions, arylation with aromatic organometallics, photooxidation, and oxidative coupling of phenols are most commonly used for the synthesis. However, they have limitations and restrictions of their own. We have reported the trifluoroacetic acid (TFA) catalyzed reaction of *N*-arylhydroxylamine with benzene, which affords diphenylamine (**1**, eq 1) and the trifluoromethanesulfonic acid (TFSA)



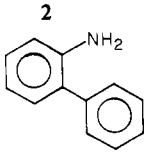
(1)

1

catalyzed reaction with benzene, which affords 4- and 2-aminobiphenyls (**2** and **3**, eq 2).[2-4] These processes seem promising



2



(2)

3

(1) Matieu, J.; Weill-Raynal, J.; "Formation of C–C Bonds"; George Thieme: Stuttgart, 1975; Vol. II, pp 457–477.

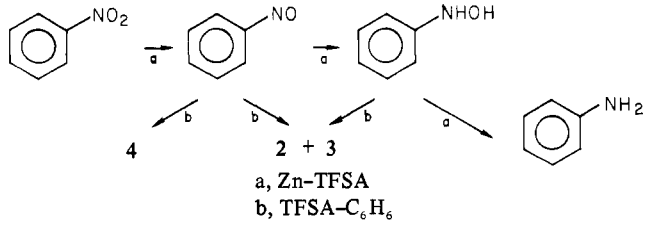
(2) Okamoto, T.; Shudo, K.; Ohta, T. *J. Am. Chem. Soc.* **1975**, *97*, 7184.

(3) Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1973**, 1839.

(4) Bamberger, E. *Justus Liebigs Ann. Chem.* **1912**, *390*, 131. Kliegl, A.; Huber, H. *Chem. Ber.* **1920**, *53*, 1646. Parish, J. H.; Whiting, M. C. *J. Chem. Soc.* **1964**, 4713.

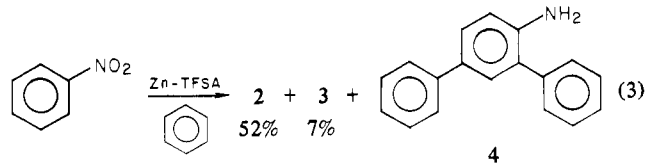
0002-7863/80/1502-6385$01.00/0

Scheme I



as general methods for synthesizing diphenylamine and aminobiphenyl. However, the availability of *N*-arylhydroxylamine is limited. In this work, we extended the phenylation reactions to the reductive phenylation of nitroarenes, which are far better synthetic precursors than *N*-arylhydroxylamines. Metal–acid reduction of a nitroarene to an amine is known to involve nitroso and hydroxylamine intermediates. Therefore, we expected that phenylation of nitroarenes would occur when they are reduced with metal–TFA or metal–TFSA in benzene. Since this was proved to be so, we were able to develop a practical method for the synthesis of diphenylamines and aminobiphenyls.

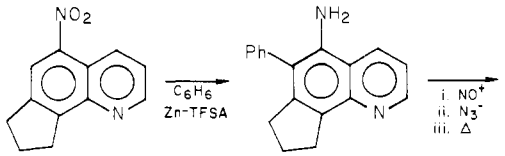
Zinc dust (30 mmol) was added with stirring in three portions over a period of 3 h to an ice-cold mixture of nitrobenzene (5 mmol) in benzene (150 mmol) and TFSA (75 mmol) (eq 3). The



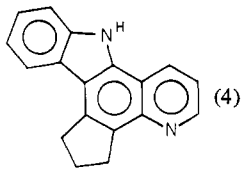
(3)

products isolated were 4-aminobiphenyl (**2**, 52%), 2-aminobiphenyl (**3**, 7%), 4′-amino-*m*-terphenyl (**4**, 2%), and aniline (30%). A possible phenylation process is shown in Scheme I. Nitrobenzene is reduced to nitrosobenzene and *N*-phenylhydroxylamine. Then, consecutively, nitrosobenzene reacts with benzene in the presence of TFSA, giving **2**, **3**, and **4**,[5] and *N*-phenylhydroxylamine reacts with benzene, giving **2** and **3**.[2]

Nitrobiphenyls and nitronaphthalenes were similarly phenylated with benzene. For example, 2-nitronaphthalene was reductively phenylated by benzene–Zn–TFSA to yield 1-phenyl-2-aminonaphthalene in 51% yield. The intermolecular reductive phenylation has been successfully applied to the synthesis of 5-amino-6-phenylquinoline (**6**) from 5-nitro-7,8-cyclopentenoquinoline (**5**)



5 **6**

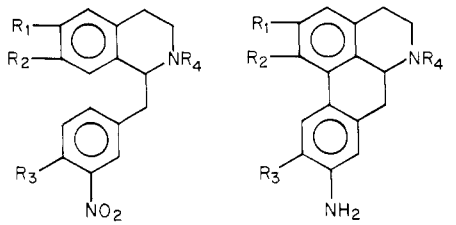


(4)

7

at the key step in the synthesis of a potent mutagen, 3,4-cyclopentenopyrido[3,2-*a*]carbazole (**7**), isolated from L-lysine pyrolysate (eq 4).[6]

This process was very effective in intramolecular phenyl–phenyl bond formation. We applied this method to the synthesis of aminoaporphines. Zinc dust (10 mmol) was added to a solution of 1-(3′-nitro-4′-methoxybenzyl)tetrahydroisoquinoline (**8a**, 2 mmol) in TFA (60 mmol) and TFSA (60 mmol) with stirring at 0 °C in three portions over a period of 3 h. After a simple workup, 9-amino-1,2,10-trimethoxy-6-methylaporphine (**9a**) was isolated in 68% yield. The structure of **9a** was confirmed by its

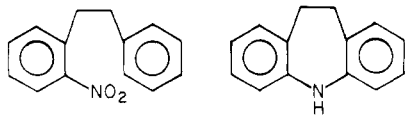


8 **9**

a, $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = OCH_3$, $R_4 = CH_3$ (yield 68%)
b, $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = OCH_3$, $R_4 = H$ (yield 61%)
c, $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = OCH_3$, $R_4 = COCH_3$ (yield 82%)
d, $R_1 = OCH_3$, $R_2 = OCH_3$, $R_3 = H$, $R_4 = CH_3$ (yield 52%)

conversion to (±)-*N*-methyllaurotetanine[7] by hydroxydediazotization. As a reducing agent, catalytic hydrogenation over Pd–C also worked well. Several aporphines (**9b–d**) were prepared.

The TFA-catalyzed reductive phenylation should give a diphenylamine. Zinc dust (60 mmol) was added to an ice-cold mixture of nitrobenzene (10 mmol) in benzene (100 mmol) and TFA (100 mmol) with stirring for 2 h, and diphenylamine was isolated in 31% yield. This process was applied to an intramolecular cyclization. Thus, 2-nitrodibenzyl (**10**), on the reductive *N*-phenylation in TFA, gave dihydrodibenz[*b*,*f*]azepine (**11**) in 38–45% yield.



10 **11**

The new method presented here has several merits: The starting nitro compound is readily prepared; the reaction conditions are mild enough to keep a functional group such as amine, phenol, amide, ether, and methylenedioxy groups intact; activation of a benzene ring or the presence of a special group except a nitro group is not required; intramolecular as well as intermolecular reactions work well; workup procedure is simple. The limitations are the following: The acid-sensitive group must be masked; phenylation at the meta position to the amino group is impossible. Although we only examined a few syntheses of biphenyl derivatives, we believe this is a useful general method for the synthesis of biaryl derivatives.

(5) Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1977**, 101.
(6) Wakabayashi, K.; Tsuji, K.; Kosuge, T.; Takeda, K.; Yamaguchi, K.; Shudo, K.; Iitaka, Y.; Okamoto, T.; Yahagi, T.; Nagao, M.; Sugimura, T. *Proc. Jpn. Acad., Ser. B* **1978**, *54*, 569.
(7) Kikkawa, J. *Yakugaku Zasshi* **1959**, *79*, 83.

Toshiharu Ohta, Ryosuke Machida, Kei Takeda
Yasuyuki Endo, Koichi Shudo,* Toshihiko Okamoto
Faculty of Pharmaceutical Sciences
University of Tokyo, Hongo, Tokyo, Japan
Received April 14, 1980

Intramolecular [2 + 2] Cycloaddition Reactions of Indene Derivatives as a Route to Polycyclic Strained Ring Systems[1]

Sir:

Strained bicyclic and polycyclic compounds continue to play an important role in the understanding of many aspects of organic chemistry.[2-6] For this reason, synthetic efforts in this area have

(1) Photochemical Transformations of Small Ring Coupounds. 115. For part 114, see A. Padwa, T. J. Blacklock, D. M. Cordova, and R. Loza, *J. Am. Chem. Soc.*, **102**, 5648 (1980).

0002-7863/80/1502-6386$01.00/0