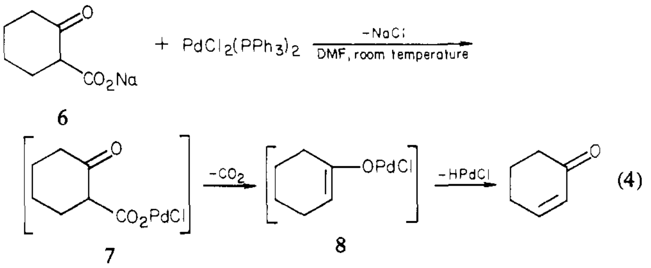
cyclohexenone in 91% yield, presumably via a palladium(II) chloride–enolate complex (**8**) (eq 4). In the presence of $CuCl_2$, cyclohexenone was produced with a catalytic amount of $PdCl_2(PPh_3)_2$.



As the starting $\beta$-ketocarboxylates are accessible,[8] the decarboxylation of palladium(II) $\beta$-ketocarboxylates provides a convenient way to produce the synthetically useful palladium(II) enolate intermediates. Other low-valent transition-metal complexes such as $Ni(PPh_3)_4$ and $RhCl(PPh_3)_3$ also caused the decarboxylation of **1** to produce 2-allylcyclohexanone.

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[8] Rathke, M. W.; Deitch, J. *Tetrahedron Lett.* **1971**, 2953. Ainsworth, C.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 73. Wierenga, W.; Skulnich, H. I. *J. Org. Chem.* **1979**, *44*, 310.

**Tetsuo Tsuda, Yoshiki Chujo, Sei-ichi Nishi, Kunio Tawara**
**Takeo Saegusa***

*Department of Synthetic Chemistry, Faculty of Engineering*
*Kyoto University, Kyoto, Japan 606*

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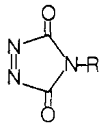
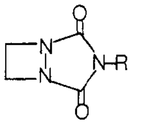
## Mechanism of Triazolinedione–Olefin Reactions. Ene and Cycloaddition

*Sir:*

In the course of efforts to synthesize diazetines[1] (four-membered ring cyclic azo compounds), we have been attracted to the reactions of triazolinediones, TAD (**1**). These species react with dienes to afford Diels–Alder adducts,[2a] with mono olefins to afford products of an ene reaction,[2b,c] and occasionally with olefins to afford products corresponding to [2 + 2] cycloaddition, diazetidine derivatives **2**.[2d,e]

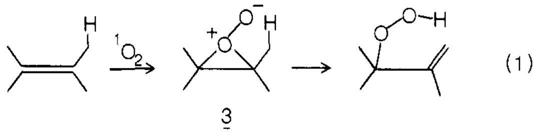


1

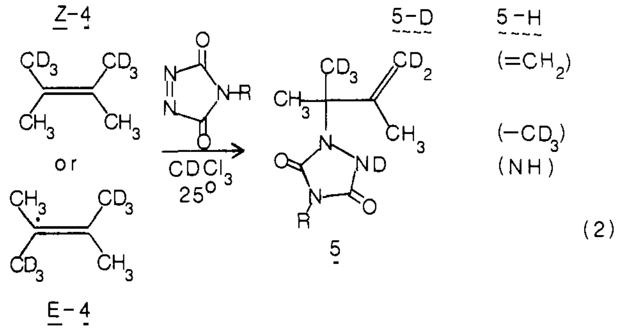


2

We have been struck by the variety of reactions of TAD, and by similarities in reactions of TAD and singlet oxygen, which also undergoes the above three reactions.[3] By an elegant isotope effect experiment, Stephenson has provided evidence for an intermediate, a perepoxide **3** or a complex with the structural characteristics of a perepoxide,[4a] in the ene reaction (eq 1) of singlet oxygen with (*Z*)- and (*E*)-2,3-bis(trideuteriomethyl)-2-butene (**4**).[4b]

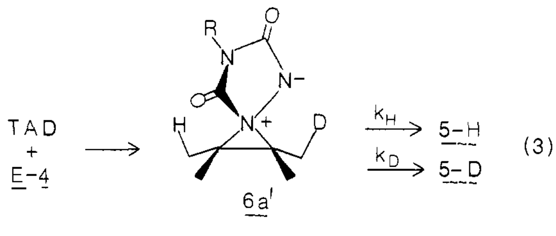


We have applied this Stephenson test to the reaction of TAD with (*Z*)- and (*E*)-**4** (eq 2). Reaction of TAD with **4** affords the ene product **5**.[5] Determination of the location and amount of deuterium is easily made by NMR,[5] leading to the following isotope effects.



| | TAD, 1 | $k_H/k_D$ |
|---|---|---|
| (*Z*)-4 | $R = CH_3$ | 1.08 ± 0.1 |
| | $R = C_6H_5$ | 1.1 |
| (*E*)-4 | $R = CH_3$ | 3.8 ± 0.2 |
| | $R = C_6H_5$ | 3.7 |

The observation of an isotope effect only when $CH_3$ is cis to $CD_3$ [olefin (*E*)-**4**] but not when $CH_3$ is trans or geminal to $CD_3$ implies rate-determining conversion of olefin **4** and TAD to an intermediate in which little or no breaking of an allylic carbon–protium bond has taken place. In a subsequent step, isotopic discrimination occurs if the "allylic" carbon–protium atoms are cis to each other (eq 3). Species **6a**, an aziridinium imide,[6] appears to be a possible representation for the intermediate. The isotope effects place some further restrictions on **6a**: conversion



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[1] White, D. K.; Greene, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 6760.

[2] (a) See: Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325, and references therein. (b) See: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (c) See: Gopalan, A.; Moerck, R.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1979**, 548, and references therein. (d) von Gustorf, E. K.; White, D. V.; Kim, B.; Hess, D.; Leitich, J. *J. Org. Chem.* **1970**, *35*, 1155. (e) Pasto, D. J.; Chen, F-T. *Tetrahedron Lett.* **1973**, 713.

[3] (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 439. (c) Schulte-Elte, K. H.; Rautenstrauch, V. *Ibid.* **1980**, *102*, 1738.

[4] (a) Stephenson, L. M. *Tetrahedron Lett.* **1980**, *21*, 1005. (b) Grdina, B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111.

[5] Compound **5**, undeuterated ($R = CH_3$); mp 95–96 °C. Pirkle, W. H.; Stickler, J. C. *Chem. Commun.* **1967**, 760. $^1$H NMR ($CDCl_3$): $\delta$ 1.58 (s, 6 H), 1.82 (s, 3 H), 3.04 (s, 3 H), 4.99 (s, 2 H), 7.90 (s, br, 1 H). Compound **5** ($R = C_6H_5$): mp 127–128 °C; IR 1760, 1695 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.60 (s, 6 H), 1.82 (s, 3 H), 4.95 (s, 1 H), 4.99 (s, 1 H), 7.38 (m, 5 H), 7.90 (s, br, 1 H); anal. C, H, N.

[6] An isolable species of known structure (X-ray analysis) and bearing some resemblance to **6a** has been reported; 1-(diphenylhydrazono)-3,5-dioxo-4-phenyl-1,2,4-triazolidinium hydroxide, inner salt: Weidenborner, J. E.; Fahr, E.; Richter, M. J.; Koch, K.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 236.

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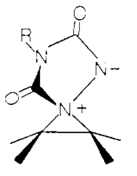
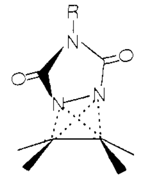
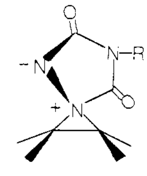
of **6a** to product, **5**, must proceed more rapidly than reversal of **6a** to TAD and olefin, or than isomerization of **6a** to **6c**.



6a

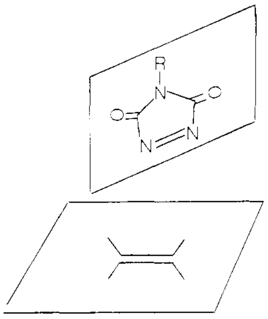


6b

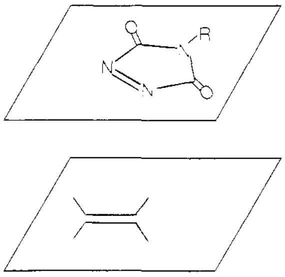


6c

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

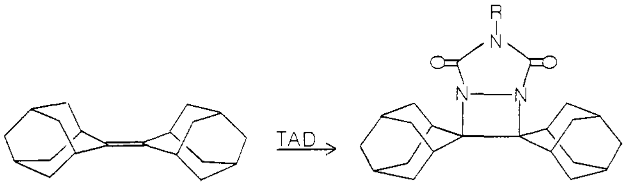


(i)



(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.

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[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 ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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: $\mathbf{6a} \rightleftarrows \mathbf{6c}$) 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*

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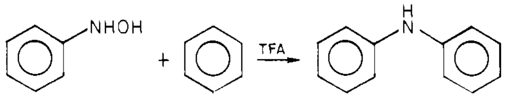
## Reductive Phenylation of Nitroarenes

*Sir:*

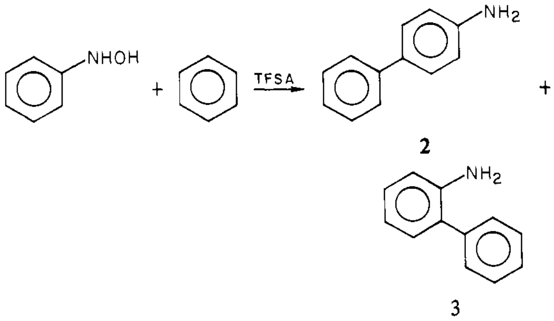
Several methods for the synthesis of diaryl compounds are known.[1] Gomberg, Pschorr, and Ullmann reactions, arylation with aromatic organomethalics, photooxidation, and oxidative coupling of phenols are most commonly used for the synthesis. However, they have limitations and restrictions of their own. 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

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[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.