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CONDENSATION OF A p-DIAZOOXIDE WITH DIMETHYL ACETYLENEDICARBOXYLATE: FORMATION OF A SPIRO[4.5]DECATETRAENONE AND A NONENOLIZABLE NAPHTHALENONE IN A SINGLE REACTION

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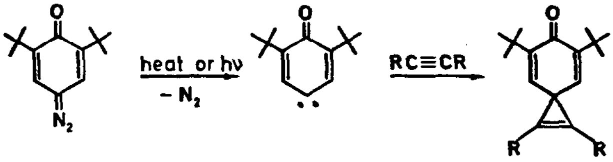
Summary: The condensation of p-diazooxide 1 with dimethyl acetylenedicarboxylate at 90°-100°C yields two $C_{26}H_{32}O_9$ products, corresponding to addition of two molecules of ester to one of the carbene 2. The major product is the novel spirodecatetraenone 4, and the minor product is the remarkable, nonenolizable naphthalenone 5. Spirodecatetraenone 4 is not a precursor of 5, since the former is stable to acids and rearranges only above 200° to give the blocked azulenone 8. A mechanism for the concomitant formation of product 4 and 5 is proposed.

The condensation of p-diazooxide 1 with alkynes is reported to yield cyclopropenes (3) via carbene 2.[1,2,3,4]

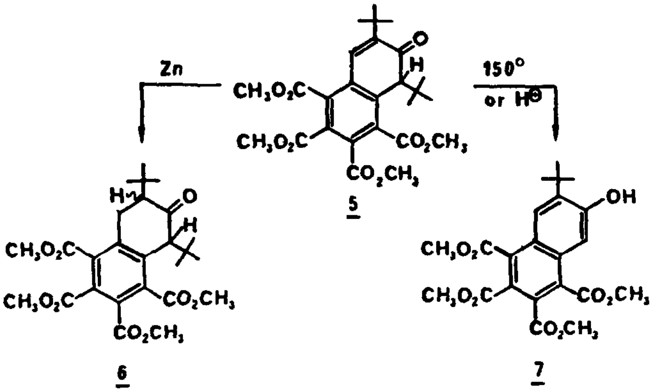


1 2 3

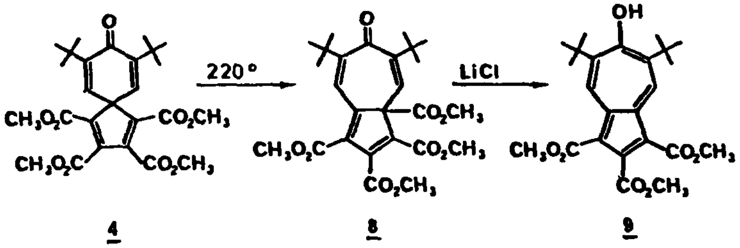
We now report unprecedented chemistry for the reaction of 1 with dimethyl acetylenedicarboxylate (DAD). Thermolysis of 1 in neat DAD (9% 1, 90°-100°C, 20 min) yields 68% of a colorless $C_{26}H_{32}O_9$ product (4, mp 98°-99°C) and 14% of an isomeric pale yellow product (5, mp 130°-131°C). The C_2 symmetry of 4 evident from its ^{1}H-NMR spectra, taken with its IR and UV maxima, were uniquely consistent with the novel spiro[4.5]decatetraenone shown.[5] On the other hand, the minor isomer 5 lacked symmetry by ^{1}H-NMR, and exhibited IR and UV peaks suggesting an aryl-substituted enone.[6] Reduction of 5 with zinc dust (HOAc-NaOAc, 25°, 2 hrs) gave 90% of a $C_{26}H_{34}O_9$ ketone (6, mp 169°-171°; IR, $\nu_{max}^{CHCl_3}$ 1710 cm^{-1}) that was no longer conjugated.[7]

Reaction of adduct 5 with acid, or heating to 150°, led to loss of C_4H_8 to give a fully aromatic $C_{22}H_{24}O_9$ phenol (7, mp 203°-205°C).[8]

These data suggested that the minor isomer might be the naphthalenone 5, and that the Zn-reduction and de-t-butylation products were 6 and 7, respectively. However, structure 5 is the keto tautomer of a 2-naphthol and would normally be unstable relative to its aromatic counterpart. Our concern over this structure was reinforced by the observation that 5 was recovered unchanged and undeuterated after 24 hrs in 0.1 M $NaOCH_3$ in CH_3OD.[9]

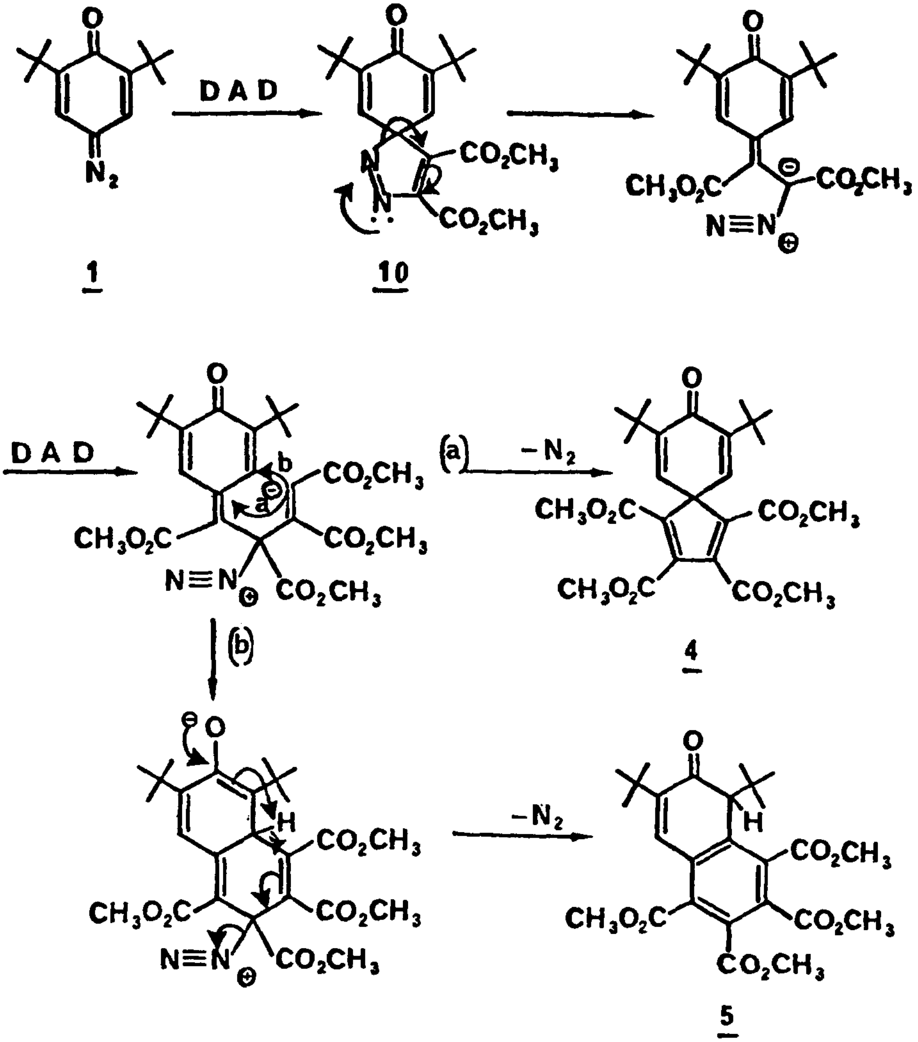


Single crystal X-ray analysis of 5 unambiguously confirmed the structure of this stable naphthalenone and led us to probe its origin. Since 5 is formally the dienone-phenol rearrangement product of 4, we were surprised to find 4 stable to acids or to heating at 150°C (neat or in DAD). At 210°-220°C for 20 min, 4 was converted in 78% yield to a new isomer (mp 125°-127°C; λ_{max}^{MeOH} 361 nm, ε = 8100; 264 nm, ε = 28200) having ^{1}H-NMR and IR spectra consistent with the 1,5-sigmatropic rearrangement product 8.[10] This was confirmed by selective nucleophilic decarboxylation (LiCl, moist DMSO, reflux, 20 min, 48% yd) to the orange hydroxyazulene 9, mp 170°-172°C.[11]



We conclude that 4 and 5 are formed simultaneously in the reaction of 1 with DAD. Since the disappearance of 1 in DAD-heptane is first order with respect to [DAD], we propose that the reaction proceeds by initial formation of a pyrazole (10), analogous to the 1:1 adduct between DAD and 10-diazoanthrone.[4] Subsequent steps that could lead to the products are in Scheme 1. The striking resistance of 5 to aromatization is probably the result of the t-butyl/ester peri interaction that would destabilize the phenol or phenolate form of this remarkable system.[12,13]

Scheme 1



References and Notes

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3. Sviridov, B. D.; Nikiforov, G. A.; Ershov, V. V. Izv. Akad. Nauk. SSSR, Ser. Khim., 1970, 2388. The structure of the carbene aduct with diphenylacetylene given in this paper has been challenged by Pavlickova, L. and Soucek, M. Coll. Czech. Chem. Commun. 1979, 44, 1810.
4. Fleming, J. C.; Schechter, H. J. Org. Chem. 1969, 34, 3962.
5. All isolated compounds gave satisfactory C,H analyses. Compound **4**: ^{1}H-NMR(CDCl$_3$): δ 5.90 (2H,s), 3.87(6H,s), 3.66(6H,s), 1.20(18H,s); IR(CCl$_4$): 1735, 1665 cm^{-1}; UV(CH$_3$OH): λ_{max} 234 nm (ε=21500).
6. Compound **5**: ^{1}H-NMR(CDCl$_3$): δ 7.30(1H,s), 4.17(1H,s), 3.95(3H,s), 3.87(3H,s), 3.85(3H,s), 3.83(3H,s), 1.26(9H,s), 0.88(9H,s); IR(CHCl$_3$): 1740, 1680 cm^{-1}; UV(CH$_3$OH): λ_{max} 306 nm (ε=9000), 253 (17000).
7. The stereochemistry of **6** is not known.
8. Compound **7**: ^{1}H-NMR(CDCl$_3$): δ 7.80(1H,s), 7.36(1H,s), 6.52(1H,s,exch), 3.99(3H,s), 3.95(3H,s), 3.89(3H,s), 3.88(3H,s), 1.40(9H,s).
9. These conditions fully exchange both α-protons of 2,6-dimethylcyclohexanone.
10. Compound **9**: ^{1}H-NMR(CDCl$_3$): δ 7.45(1H,s), 7.12(1H,s), 3.96(3H,s), 3.85(3H,s), 3.73(6H,s), 1.40(18H,s); IR(CCl$_4$): 1745, 1640 cm^{-1}.
11. Compound **10**: ^{1}H-NMR(dmso-d$_6$): δ 8.48(1H,s), 8.43(1H,br,s,exch), 3.67(3H,s), 3.60(6H,s), 1.37(18H,s); UV(CH$_2$Cl$_2$): λ_{max} 465 nm (e=830), 370 (8000), sh 350 (11000), 322 (35000), 283 (18000). *Cf.* Nozoe, T.; Asao, T.; Susumago, H.; Ando, M. Bull. Chem. Soc. Japan 1974, 47, 1471.
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13. Partial support of this research by grant CA-11326, awarded by the National Cancer Institute, USPH, is gratefully acknowledged. We thank Drs. Patrick J. Carroll and Bruce H. Toder for the X-ray crystal analysis.

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