treated with 20 mmol of sodium methoxide or 20 mmol of tetrabutylammonium hydroxide (25% in methanol). The resulting colorless solution was evaporated under reduced pressure to give the salt. The sodium salts (**2a**, **3a**, **4a**) are white, microcrystalline solids melting above 300°. The tetrabutylammonium salts are hygroscopic but may be recrystallized with difficulty from ethyl acetate-hexane mixtures. Unpurified salts were used for the photolytic work.

Photolysis. General Procedure.—A solution of 2.0–2.5 mmol of the bis salt in 100–120 ml of methanol was placed in a cylindrical quartz tube fitted with a purging inlet and an outlet connected to a gas buret. Purified nitrogen was passed through the solution (*ca.* 20 min), and the reaction tube and gas buret were closed under a nitrogen atmosphere. The magnetically stirred solution was irradiated (254 mμ) in a Rayonet Chamber reactor until greater than 65% reaction, as measured by evolved nitrogen. Photolyses ran from 48 to 80 hr.

After removal of methanol under reduced pressure, the resulting paste or oil was suspended in 20 ml of water and extracted with three 15-ml portions of diethyl ether. The combined extracts were washed with saturated sodium chloride solution (dilute HCl washing was included with **2b**, **3b**, **4b**), dried (MgSO$_4$), and evaporated to give the product. Yields of α α'-bismethoxyxylenes ranged from 85% (**5**, **6**) to 45% (**7**). Only trace amounts of additional products were detected by vpc.

α,α'-Bismethoxyxylenes (5, 6, 7).—Compound **5** was purchased (Aldrich Chemical Co.). Compounds **6**[11] and **7**[12] were prepared by conventional Williamson synthesis from 1,3- and 1,2-bischloromethylbenzene and sodium methoxide in methanol.

Registry No.—**2a**, 36631-14-8; **2b**, 36608-46-5; **3a**, 36608-47-6; **3b**, 36608-48-7; **4a**, 36608-49-8; **4b**, 36631-38-6; 1,2-di(tetrazolyl)benzene, 36631-39-7.

[11] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954).

[12] L. A. Errede, U. S. Patent 3,242,205 (Cl 260-475) (March 22, 1966); S. Murahashi, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **30**, 180 (1936).

A Novel Photochemical Reaction of *p*-Benzoquinone with a Nitroalkene[1]

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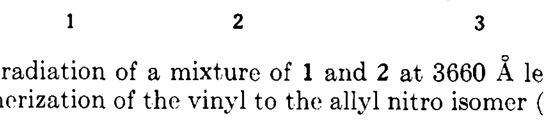
The chromophoric resemblance of nitro olefins to unsaturated ketones makes them potentially interesting substrates in photochemical reactions. Yet only few studies on the photochemical behavior of nitro compounds are available.[2] In a study of the properties of vinyl and allyl nitro olefins (*i.e.*, **1** and **2**), we examined their photochemical lability as well as their reactions with carbonyl compounds leading to possible oxetan formation (*i.e.*, **2** → **3**).

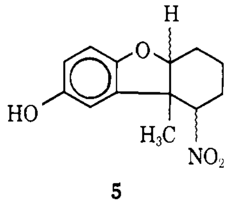


1 2 3

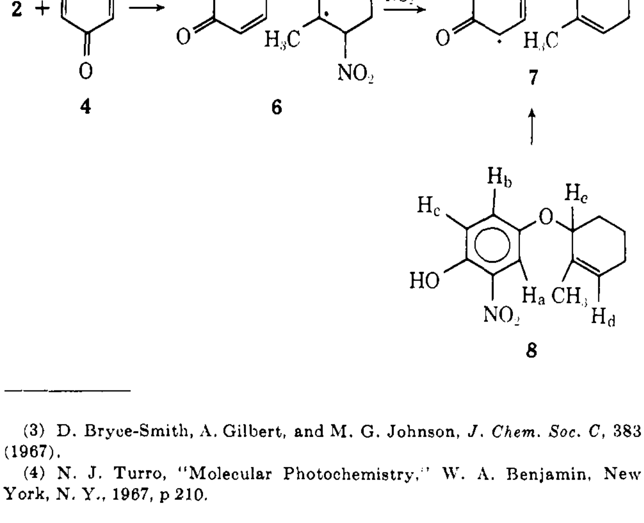
Irradiation of a mixture of **1** and **2** at 3660 Å led to isomerization of the vinyl to the allyl nitro isomer (**1** → **2**) and formation of polymer. When nitro olefin **2** was irradiated in deoxygenated benzene solution in the presence of *p*-benzoquinone (**4**) (either a Hanovia 450-W medium-pressure lamp with a Pyrex immersion well or a Rayonet reactor using 3100- or 3600-Å lamps was used), a yellow-orange product was found by tlc. Separation from excess *p*-benzoquinone and **2** yielded, after column chromatography on silica gel, a yellow-orange solid, mp 57–58°, in *ca.* 4% yield (ignoring recovered nitro olefin). The analysis and mass spectrum were consistent with a 1:1 adduct but the other spectral properties showed that the product was not the expected oxetan.

Although it is well known that *p*-benzoquinone reacts with olefins such as cyclohexene to form isolable oxetans,[3] several factors limit the generality of this reaction.[4] One factor is the triplet energy of the olefinic component, which is expected to be low in the case of **1** or **2**; another is a steric factor during ring closure of intermediate **6**. No reaction was observed even when benzophenone was irradiated with **2**.

The nmr spectrum of the 1:1 photoadduct showed three aromatic protons which were in a 1,2,4 relationship [τ 2.45 (d, J = 3 Hz, H$_a$ deshielded by -NO$_2$), 2.77 (q, J = 3 and 10 Hz, H$_b$), 3.00 (d, J = 10 Hz, H$_c$)]. A dienone–phenol type rearrangement to yield **4** was ruled out because the phenolic proton occurs at τ −0.18, indicating intramolecular hydrogen bonding. Further, one vinyl proton (H$_d$) is present (τ 4.32) and the methyl singlet at τ 8.25 is characteristic of a methyl group on a double bond. The allylic proton α to the ether oxygen (H$_e$) appears at τ 5.47. The infrared spectrum (KBr disk) defined one major structural feature. The nitro group is still present, but it absorbs at *ca.* 1500 cm^{-1}, typical of an aromatic or highly conjugated -NO$_2$. On the basis of this evidence we propose structure **8** for the adduct. The mass spectrum



5



4 6 7

8

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[1] Chemistry of Nitro Compounds. VIII. For Paper VII see A. Hassner, J. E. Kropp, and G. J. Kent, *J. Org. Chem.*, **34**, 2628 (1969).

[2] See, for instance, O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, **9**, 585 (1964); O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Commun.*, 101 (1966); J. T. Pinhey and E. Rizzardo, *ibid.*, 362 (1965).

[3] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).

[4] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 210.

is consistent with this structure, showing a parent peak at *m/e* 249 and the base peak at *m/e* 95 (the allylic methylcyclohexenyl cation).

Initial excitation of the *p*-benzoquinone and intersystem crossing to the triplet is probably followed by O–C coupling to produce the more favorable "diradical species" **6** (or a similar intermediate).[5] Instead of undergoing ring closure to an oxetan, **6** loses a $NO_2\cdot$, which is immediately trapped by the phenoxy radical **7**. It is not known whether the NO_2 radical becomes attached directly to the benzene ring or to the oxygen to yield a phenyl nitrate, which rearranges to the *o*-nitrophenyl compound **8**. The low yield may be partially attributed to loss of NO_2 from the solvent cage before recombination can occur.

Although photolytic fragmentation of nitro compounds has been observed before, this photochemical addition reaction appears to be the first case involving transfer of a nitro group.

Experimental Section

3-Nitro-2-methylcyclohexene (2).—Nitration of 29 g of 1-methylcyclohexene with nitric acid–acetic anhydride as described by Bordwell and Garbisch[6] led to 22.4 g of a mixture of nitro acetate and nitro nitrate, as well as of nitro olefin **2**, which on refluxing with a benzene solution of 1,4-diazabicyclooctane fractional distillation, monitored by glc, afforded 8.9 g of 3-nitro-2-methylcyclohexene (**2**), bp 48–49° (0.3 mm), and a mixture of nitro acetate and nitro nitrate. The latter (8.5 g) was refluxed with a benzene solution of 1,4-diazabicyclooctane to yield, after work-up with water, 2.7 g of a 2:3 mixture of nitro olefins **1** and **2**, bp 42–44° (0.2 mm), as determined by glc.

Irradiation of Nitro Olefins 1 and 2.—A solution of 150 mg of a 2:3 mixture of **1** and **2** (see above) in 10 ml of cyclohexane was irradiated at 3660 Å and the course of the reaction was monitored by glc, using triglyme as an internal standard. Initial conversion of **1** and **2** was evident during the first 6 hr; then polymer formation was observed with concomitant slow disappearance of **1** and **2**.

4-(2′-Methylcyclohex-2′-enoxy)-2-nitrophenol (8).—3-Nitro-2-methylcyclohexene (**2**, 5.3 g) and *p*-benzoquinone (7.8 g) were dissolved in benzene (110 ml). The solution was deoxygenated by bubbling through N_2 and then irradiated at 3130 Å in the Rayonet reactor. The reaction was followed by tlc [silica gel/50% CH_2Cl_2:50% petroleum ether (bp 60–70°)]. After 47 hr the solution was evaporated to a dark oil containing some solid. Pentane was added and the mixture was filtered to yield a yellow-brown solution, containing the product, and an almost black solid. Distillation of the solution under reduced pressure removed the solvent and unchanged nitro olefin. The residue was chromatographed on silica gel in petroleum ether containing increasing concentrations of benzene. The yellow-orange solution was evaporated to an oil which was crystallized by dissolution in petroleum ether and cooling to Dry Ice temperature. The yield of yellow crystalline **8** was 365 mg (4%).

Anal. Calcd: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.37; H, 6.02; N, 5.46.

Registry No.—**1**, 36601-70-4; **2**, 36291-55-1; **4**, 106-51-4; **8**, 36601-72-6.

Acknowledgment.—We thank the U. S. Public Health Service, National Air Pollution Control Administration Grant AP-00596, for support of this work.

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(5) The photosensitized conversion of **2** to **1** followed by photoaddition of benzoquinone has not been ruled out.

(6) F. G. Bordwell and E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **82**, 3588 (1960).

Photooxidative Synthesis of *p*-Methoxycarbonylperbenzoic Acid, a Stable and Convenient Reagent for Epoxidation and Baeyer–Villiger Oxidation[1]

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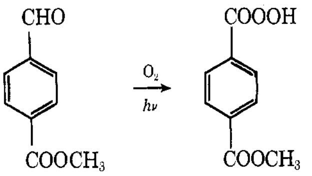
During the course of the photooxidation study of methyl *p*-formylbenzoate (**1**), a simple synthesis of *p*-methoxycarbonylperbenzoic acid (**2**) has been found.



1 **2**

The present note describes the synthesis and chemical behavior of **2** as one of the useful reagents for epoxidation of olefins and Baeyer–Villiger oxidation of carbonyl compounds.

Photooxidation of benzaldehyde is well known as a typical autooxidation, yielding benzoic acid readily.[2] Jorissen and van der Beek first succeeded in isolating perbenzoic acid in 63% yield, by exposing a solution of benzaldehyde in acetone to sunlight.[3] Swern, Findley, and Scanlan prepared perbenzoic acid in 40% yield by employing ultraviolet radiation and carbon tetrachloride.[4] *p*-Bromobenzaldehyde, *p*-chlorobenzaldehyde, and *m*-chlorobenzaldehyde, however, yield little or no peracid when similarly treated.[5]

The photooxidation of **1** afforded mainly *p*-methoxycarbonylbenzoic acid along with a trace of the peracid in the solvents such as acetic acid, formic acid, chloroform, acetone, and benzene, consuming about 0.5 molar equiv of oxygen. However, 1 molar equiv of oxygen was rapidly consumed in the case of carbon tetrachloride,[6] and the reaction product consisted of essentially *p*-methoxycarbonylperbenzoic acid (**2**) which was isolated in a pure crystalline form. The yield was 80–95%.

Differential thermal analysis showed that the peracid began to decompose at 125°, the exothermic decomposition reached its maximum at 134°, and the endothermic point was at 218°, corresponding to the melting point[7] of *p*-methoxycarbonylbenzoic acid. The peracid **2** is as stable as *m*-chloroperbenzoic acid, and showed less than 5% decomposition after 1-year storage at 10°.

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(1) Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April 1968.

(2) H. J. L. Bächström, *J. Amer. Chem. Soc.*, **49**, 1460 (1927).

(3) W. P. Jorissen and P. A. A. van der Beek, *Recl. Trav. Chim. Pays-Bas*, **46**, 42 (1927).

(4) D. Swern, T. W. Findley, and J. T. Scanlan, *J. Amer. Chem. Soc.*, **66**, 1925 (1944).

(5) P. A. A. van der Beek, *Recl. Trav. Chim. Pays-Bas*, **51**, 411 (1932).

(6) It is very important to remove any trace of heavy metal ion from the solvent and the starting aldehyde. Otherwise, the yield of **2** is markedly decreased by autooxidation of the aldehyde with heavy metal ions.

(7) M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).