500-ml flask equipped with mechanical stirrer, Dry Ice condenser, nitrogen inlet–outlet, and an addition funnel. The addition of methyl iodide to lithium was performed at ice–salt temperature in about 2 hr. After an additional 2 hr all lithium had reacted. The methyllithium solution was cooled in an acetone–Dry Ice bath and a solution of a 60:40 mixture of ethyl 2,2-dimethyl-3-vinyl- and ethyl 3-ethylidene-2,2-dimethylcyclobutaneacetate (19.6 g, 0.1 mol) in anhydrous ether (25 ml) was added dropwise with rapid stirring. After addition was complete, the mixture was allowed to warm to room temperature and stirred in a nitrogen atmosphere overnight. The reaction slurry was poured onto 300 g of crushed ice containing 100 ml of concentrated ammonia. The mixture was stirred rapidly for 1 hr. The ether layer was separated and the aqueous layer was extracted with 2 × 100 ml of ether. The combined ether solutions were washed with water and dried over anhydrous sodium sulfate. Removal of ether under reduced pressure yielded a colorless liquid (17.5 g, 96% yield). Distillation of this liquid afforded 16.3 g, bp 58° (0.4 mm). The infrared spectrum of this liquid exhibited hydroxyl absorption at 3400 cm^{-1} and absorptions due to *gem*-dimethyl groups at 1355 and 1375 cm^{-1}; the nmr ($CDCl_3$) was consistent for the mixture of alcohols.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.05; H, 12.16. Found: C, 78.80; H, 12.01.

Mixture of 1-(2,2-Dimethylvinyl)-3-vinyl-2,2-dimethylcyclobutane (VI) and 1-(2,2-Dimethylvinyl)-3-ethylidene-2,2-dimethylcyclobutane (VII).—To a mixture of alcohols (12.0 g) contained in a 50-ml distilling flask was added anhydrous oxalic acid (4.5 g). The flask was fitted with a 4 by 0.5 ft Vigreux column equipped with distillation head, condenser, and receiving flask. The system was connected to the water aspirator and the pressure was held at 45–50 mm. The reaction flask was heated and the water began to distil. After water ceased to distil the reaction flask was cooled and the residue in the pot was taken up in ether. The ether extract was washed with sodium bicarbonate solution and then with water and finally dried over anhydrous sodium sulfate. Removal of ether and distillation of the residual liquid afforded colorless liquid, 10.3 g (94% yield), bp 94–96° (42 mm). The infrared spectrum exhibited no hydroxyl absorption and had bands at 3050 (m, vinyl CH), 1668 (m, C=C), and 1375 and 1355 cm^{-1} (s, *gem*-dimethyl doublet).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.64; H, 12.48.

Ozonolysis of This Mixture of Diolefins (VI and VII).—A mixture of diolefins (9.0 g) was taken up in 150 ml of ethyl acetate and ozonized oxygen was passed through the solution at 0° for 2 hr until the exit gas turned acidified potassium iodide solution brown. To this solution was added acetic acid (15 ml) and hydrogen peroxide (30%, 10 ml) and this mixture was allowed to stand at room temperature overnight. The reaction mixture was taken up in ether and the acidic components were extracted with 2 *N* Na_2CO_3 solution. The ether layer yielded a neutral fraction of 3.2 g, whereas acidification of the sodium carbonate extract with sulfuric acid and extraction with ether gave a viscous oil, 4.5 g. The infrared spectrum of this oil exhibited carboxylic acid absorption at 2900–2550 cm^{-1} (broad) and two different bands due to keto absorption as well as the acid carbonyl. On standing with a small amount of ether this oil afforded 1.2 g of white powder, mp 160–163° (mp of *cis*-norpinic acid ~170°). The residual oil in its ir exhibited two different carbonyls at 1785 and 1740 cm^{-1}.

Ethyl 3-Oxo-2,2-dimethylcyclobutanecarboxylate (I) and Diethyl Norpinate (X).—The mixture of diolefins (11.1 g, 0.068 mol) in *tert*-butyl alcohol (50 ml) was added dropwise to a stirred mixture of sodium bicarbonate (33.6 g, 0.39 mol), sodium periodate (150 g, 0.069 mol), and potassium permanganate (3 g) in water (1000 ml). After this mixture was stirred for 48 hr, it was acidified with dilute sulfuric acid and filtered to remove insoluble salts and the oxidate was extracted with ether. The ether solution was extracted with 2 *N* Na_2CO_3 solution. The ether layer yielded a neutral 2.2 g, identified as unreacted starting material, whereas acidification of the sodium carbonate extract with sulfuric acid and extraction with ether gave viscous oil (5.8 g). The infrared spectrum of this oil exhibited absorptions due to carboxylic acid and two carbonyl absorptions at 1780 and 1730 cm^{-1}. This crude acid (4.5 g) was dissolved in benzene (75 ml) and esterified with ethanol using *p*-toluenesulfonic acid (0.50 g) as catalyst. Benzene was removed and the crude product was taken up in ether. The ether solution was washed with sodium carbonate solution and then with water and finally dried over anhydrous sodium sulfate. Removal of ether afforded brownish colored liquid (4.2 g). The infrared spectrum exhibited two different carbonyl absorptions at 1790 and 1735 cm^{-1}. This liquid (3.65 g) was distilled to give two main fractions: (1) 1.02 g of ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I), bp 57–60° (0.3 mm), and (2) 2.20 g of diethyl norpinate (X), bp 86–89° (0.3 mm).

Ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I) in its ir spectrum exhibited two carbonyl absorptions at 1805 (keto) and 1755 cm^{-1} (ester). Its nmr spectrum ($CDCl_3$) exhibited signals at δ 4.1 (octet, 2 H, $-CH_2-$), 3.4 (m, 2 H, $CH_2C{=}O$), 2.2–1.6 [m, 1 H, $-CHC(=O)O$], and 1.1–1.4 (m, 9 H, *gem*-methyls, $-CH_3$).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.53; H, 8.24. Found: C, 64.01; H, 9.10.

These analyses indicates that the keto ester may contain a small amount of the diester.

The 2,4-dinitrophenylhydrazone was obtained as a yellow precipitate, mp 118–120°, which was purified by chromatography on alumina, using benzene as an eluent. The yellow band was eluted with benzene. After removal of benzene, crystallization from ethanol gave a yellowish powder, mp 122–123°.

Anal. Calcd for $C_{15}H_{18}N_4O_6$: C, 51.43; H, 5.14; N, 16.00. Found: C, 51.68; H, 5.37; N, 15.81.

Registry No.—I, 36611-75-3; I DNP, 36611-76-4; IV, 36611-77-5; V, 36611-78-6; VI, 36611-79-7; VII, 36611-80-0.

Acknowledgments.—This is a partial report of the work done under the contract with the Western and Southern Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act of 1946. The contract is supervised by Dr. Glen Hedrick of Naval Stores Research Laboratory, Olustee, Fla. The authors wish to thank Dr. Glen Hedrick for a generous sample of the mixture of ethyl pinenates which was used in these experiments.

Ditetrazolylbenzene Dianions. Potential Precursors of the Phenylenedimethylenes[1]

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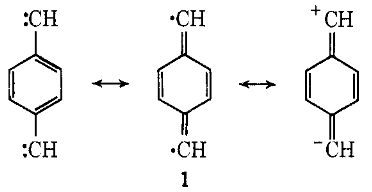
Arylmethylenes have received attention from the synthetic[2] and theoretical[3] viewpoints. Of particular interest are arylpolycarbene systems, few of which have as yet been generated.[3] Molecule 1 (*p*-phenylenedimethylene), for example, presents intriguing possibilities with regard to electronic distribution,



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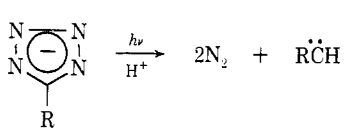
[1] This research was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society, and the Research Foundation of the City University of New York.

[2] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 5.

[3] A. M. Trozzolo, *Accounts Chem. Res.*, **1**, 329 (1968).

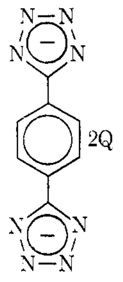
configuration, and consequent chemical reactivity. Attempts to prepare structures such as **1** or its isomers have been hindered by lack of suitable precursors. Convenient starting materials amenable to the requisite low-temperature esr, emission, and absorption spectroscopic investigations have not been generally available.

Recently Griffin and coworkers demonstrated the feasibility of 1,4-bis(2,3-diphenyloxiranyl)benzene as a new precursor for *p*-phenylene bis(phenylmethylene).[4] Photolysis of the bisoxirane in methanol produced the bismethyl ether (OH insertion product) and benzaldehyde, indicating a stepwise fragmentation through carbene intermediates. We report similar evidence for a photolytic route to the simplest aryldicarbenes, the isomeric *o*-, *m*-, and *p*-phenylenedimethylenes.



Previous work has shown that 5-phenyltetrazolide anion photolyzes with loss of 2 equiv of nitrogen to phenylcarbene.[5,6] This mode of photolysis is general and has served as a source of several monosubstituted carbenes.[7] It therefore appeared likely that under suitable conditions dicarbenes could be produced by irradiation of ditetrazolide anions.

The required 1,2-, 1,3-,[8] and 1,4-di(5-tetrazolyl)benzenes[9] were readily obtained by the addition of azide to the corresponding dicyanobenzenes. Treatment of the di(5-tetrazolyl)benzenes with 2 equiv of sodium methoxide gave the bissodium salts (**2a**, **3a**, **4a**); similarly, the bistetrabutylammonium salts (**2b**, **3b**, **4b**) were prepared with tetrabutylammonium hydroxide. The latter, owing to their appreciable solubility, were investigated in anticipation of synthetic and spectroscopic work in less polar organic solvents.



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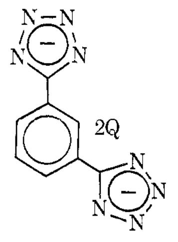

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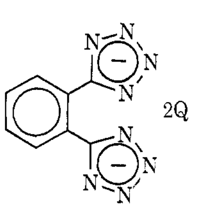

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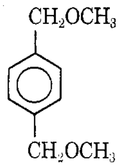
a, Q = Na^+
b, Q = $N^+(C_4H_9)_4$

Deoxygenated methanol solutions (0.020–0.017 *M*) of the salts (**2**, **3**, **4**) irradiated with 254-mμ light produced 4 equiv of nitrogen per ditetrazolide anion. The simple work-up (removal of solvent, dilution with water, and ether extraction) afforded satisfactory yields of essentially pure product, the corresponding α,α′-bismethoxyxylenes (**5**, **6**, **7**). The products were



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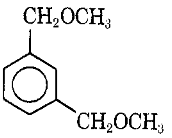

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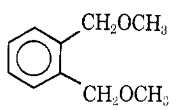

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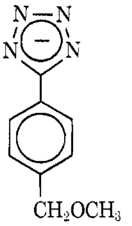
identified by comparison (ir and vpc retention time) with authentic samples. Identical results were obtained with either the sodium or the tetrabutylammonium salts.

Formation of methyl ethers by insertion into methanol has frequently served as a diagnostic for carbene formation.[10] However, it is unlikely that dicarbenes were present in the room-temperature photolyses described above. These reactions most probably proceeded in a stepwise fashion, first giving α-methoxytolyl-5-tetrazolides (*e.g.*, **8**) *via* carbene intermediates.



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Subsequent photolysis through a second monocarbene intermediate would then result in the observed products. Nevertheless, as Griffin has pointed out,[4] the possibility of observing dicarbenes exists in rigid matrices at −196° or lower, where bimolecular reactions are excluded. The results obtained indicate that phenylenedimethylenes are probable intermediates under such conditions. Spectroscopic observation will depend on the inherent lifetimes of these species. Work in this area and synthetic applications of di(5-tetrazolyl)benzene dianion photolysis are in progress.

Experimental Section

Ir spectra were obtained on 5% chloroform solutions with a Perkin-Elmer 700 spectrophotometer. Vpc analyses were made with a Varian Aerograph Model 700 using a 5 ft, 3% SE-30 column at 140° and He carrier gas.

1,2-Di(5-tetrazolyl)benzene.—A suspension of 25.6 g (0.20 mol) of *o*-dicyanobenzene, 28.6 g (0.44 mol) of sodium azide, and 7.0 g of ammonium chloride in 200 ml of anhydrous DMF was stirred and maintained at 110–115° for 4 days. Solvent was removed under reduced pressure. The residue was dissolved in 220 ml of water and acidified with concentrated hydrochloric acid. Caution: HN_3 was evolved. Following aspiration (20 min) to remove HN_3, the white precipitate was collected and washed with water. Recrystallization from 60% aqueous methanol gave 26.2 g (61%) of 1,2-di(5-tetrazolyl)benzene hemihydrate, mp 233–234° dec. Five additional crystallizations gave the analytical sample, mp 236–237° dec.

Anal. Calcd for $C_8H_6N_8 \cdot {}^1/_2H_2O$: C, 43.05; H, 3.16; N, 50.20; mol wt, 223.2. Found: C, 43.19; H, 3.10; N, 50.28; mol wt, 226.6 (titration).

Salts of Di(5-tetrazolyl)benzenes.—Ten millimoles of the di(5-tetrazolyl)benzene suspended in 100 ml of methanol was

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[4] N. R. Bertoniere, S. P. Rowland, and G. W. Griffin, *J. Org. Chem.*, **36**, 2956 (1971).

[5] (a) P. Scheiner, *J. Org. Chem.*, **34**, 199 (1969); (b) P. Scheiner, *Tetrahedron Lett.*, 4863 (1969).

[6] Substituted tetrazoles photolyze in an entirely different manner. See P. Scheiner and J. F. Dinda, *Tetrahedron*, **26**, 2619 (1970), and ref 5a.

[7] P. Scheiner, *Tetrahedron Lett.*, 4489 (1971).

[8] R. Huisgen, C. Axen, and H. Seidl, *Chem. Ber.*, **98**, 2966 (1965).

[9] W. G. Finnegan, R. A. Henry, and R. Loftquist, *J. Amer. Chem. Soc.*, **80**, 3908 (1958).

[10] W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958).

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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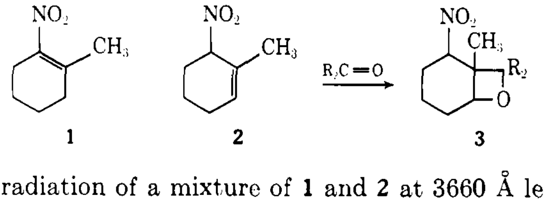
Received June 2, 1972

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**).



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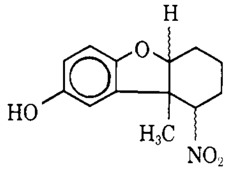
Irradiation of a mixture of **1** and **2** at 3660 Å led to isomerization of the vinyl to the allyl nitro isomer (**1** → **2**) and formation of polymer. When nitro olefin **2** was irradiated in deoxygenated benzene solution in the presence of *p*-benzoquinone (**4**) (either a Hanovia 450-W medium-pressure 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



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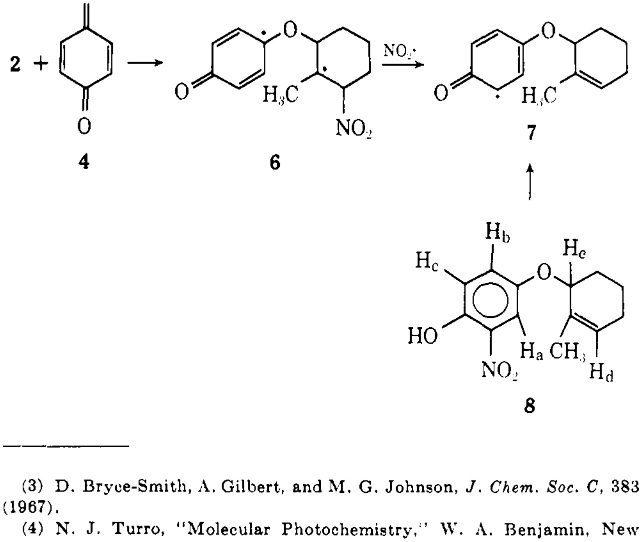

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(1) Chemistry of Nitro Compounds. VIII. For Paper VII see A. Hassner, J. E. Kropp, and G. J. Kent, *J. Org. Chem.*, **34**, 2628 (1969).

(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.