6-mercapto-8-methylpurine, 57379-36-9; 3-methyl-2-buten-1-ol, 556-82-1; chloromethyl pivalate, 18997-19-8.

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Reaction of 7,7,8,8-Tetracyanoquinodimethane with Sodium Benzoate and Acetone

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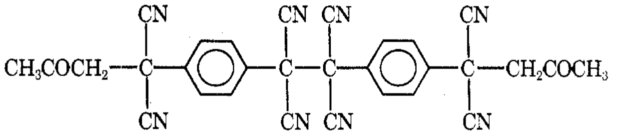
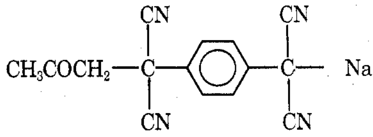
Complexes and anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) exhibit unusual electrical conductivity properties.[1] TCNQ forms π complexes[1,2] with Lewis bases, simple anion radical salts ($M^+TCNQ\cdot^-$) with metal iodides [except for $Cs_2(TCNQ\cdot^-)_2(TCNQ)$], and complex salts with organic iodides. Tropylium iodide reacts with $Li^+TCNQ\cdot^-$ to yield α,α'-ditropyl-$\alpha,\alpha,\alpha',\alpha'$-tetracyano-*p*-xylene. TCNQ undergoes 1,6 addition with sulfurous acid and with chlorine. When TCNQ reacts with primary and secondary amines, one or two cyano groups are replaced by amine.[3]

Although acetone has been used as a solvent in some of these reactions, no reaction of TCNQ with acetone has been reported. This work describes a unique reaction which produces an acetone-substituted dimer of TCNQ, I. It appears that carboxylate anion is oxidized by TCNQ because sodium benzoate, sodium salicylate, and sodium acetate reduced TCNQ to $Na^+TCNQ\cdot^-$ in acetone and generated acetonyl radical. However, little or no CO_2 was evolved in these reactions.

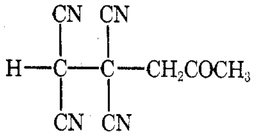


I

In a typical experiment TCNQ (20.0 mmol) and sodium benzoate (20.0 mmol) in 500 ml of dry acetone were stirred vigorously at room temperature in the dark for 48 hr. Results were the same in air and under nitrogen. $Na^+TCNQ\cdot^-$ (6.7 mmol) and benzoic acid (10.0 mmol) were obtained, as well as 0.319 g of compound I (dimer) and 1.736 g of compound II. The latter was soluble in ethyl acetate, ethanol, and acetonitrile with a light green color. II had strong absorption at 320 nm and very weak, broad absorption at 500–600 nm. II had strong infrared absorption (KBr disk) at 2130 and 2170 cm^{-1} (substituted malononitrile anion as in sodium pentacyanoethane and potassium phenylmalononitrile),[4] weak absorption at 2250 cm^{-1} (unconjugated nitrile with electronegative groups on carbon), strong absorption at 1720 cm^{-1} (ketone), and peaks at 1610, 1520, 825 (para-substituted phenyl with strong π overlap), 1420, 1360 cm^{-1} (methyl and methylene). The NMR spectrum in acetone-d_6 showed two coupled doublets, 7.3 (2 H) and 7.0 ppm (2 H), and two singlets, 3.8 (2 H) and 2.3 ppm (3 H). When TCNQ was added to II, $Na^+TCNQ\cdot^-$ was formed. We assign to II the structure i on the basis of evidence described above, the conversion to dimer described below, and the fact that ii is formed from tetracyanoethylene and acetone by a free-radical mechanism.[5,6] II is also formed when sodium acetate and sodium salicylate were used instead of sodium benzoate.



i



ii

An equimolar mixture of II and TCNQ in ethyl acetate yielded $Na^+TCNQ\cdot^-$ and I. I was purified by washing with ethanol and recrystallization from acetone, white needles, mp 279.9–280.1°C. I had a maximum at 320 nm in ethanol. The infrared spectrum (KBr disk) showed strong absorption at 1730 cm^{-1} (ketone) and very weak absorption at 2250 and 2350 (unconjugated nitrile with electronegative groups on α carbon as in *p*-phenylenemalononitrile, which has a band at 2270 cm^{-1}), 1510 and 805 (para-substituted phenyl), and 1425 and 1355 cm^{-1} (methyl and methylene). The NMR spectrum in acetone-d_6 showed two coupled doublets, 7.9 (2 H) and 7.6 ppm (2 H), and singlets at 4.0 (2 H) and 2.3 ppm (3 H). Anal. Calcd for $C_{30}H_{18}O_2N_8$: C, 69.0; H, 3.5; N, 21.5. Found: C, 68.8; H, 3.4; N, 21.4. Mol wt: calcd, 522; found, 483. The mass spectrum at high gain shows a peak at *m/e* 522.

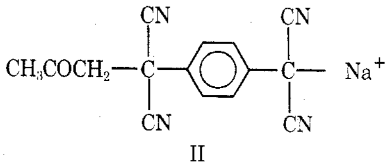
When acetonitrile was used as solvent in this reaction, $Na^+TCNQ\cdot^-$ was produced along with a material with broad absorption at 365 and 390 nm which resisted purification. With sodium carbonate and acetone or acetonitrile, TCNQ was converted to the sodium salt of α,α-dicyano-*p*-toluoyl cyanide.[3]

We assign to I the structure of the dimer rather than monomer primarily because of the molecular weight determination. We propose that the reaction proceeds in the following way.

$$C_6H_5COO^-Na^+ + TCNQ \longrightarrow C_6H_5COO + Na^+TCNQ\cdot^-$$

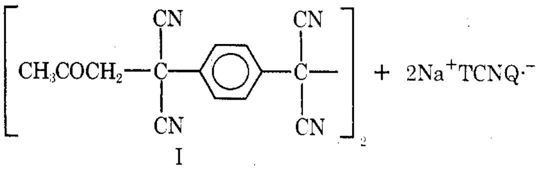
$$C_6H_5COO\cdot + CH_3COCH_3 \longrightarrow C_6H_5COOH + CH_3COCH_2\cdot$$

$$CH_3COCH_2\cdot + Na^+TCNQ\cdot^- \longrightarrow$$



II

$$2II + 2TCNQ \longrightarrow$$



I

While there are many examples of one-electron transfers from various donors to TCNQ, electron transfer from carboxylate ion is less common. In fact only the Kolbe synthesis unequivocally involves such a process. TCNQ appears to be a strong enough oxidant for carboxylate anion. Little or no decarboxylation is observed in agreement with the observation of others[7,8] on the fate of benzoyloxy radicals in solution. The isolation of dimer I suggests hydrogen abstraction from solvent, acetone.

Acknowledgment. One of the authors (M.F.) thanks Professor P. v. R. Schleyer for the opportunity to perform some experiments in his laboratory at Princeton University and for helpful discussions.

Registry No.—I, 57362-36-4; II, 57379-37-0; TCNQ, 1518-16-7; sodium benzoate, 532-32-1; acetone, 67-64-1; $Na^+TCNQ\cdot^-$, 12153-63-8; sodium acetate, 127-09-3; sodium salicylate, 54-21-7; sodium carbonate, 144-55-8; α,α-dicyano-*p*-toluoyl cyanide sodium salt, 57379-38-1.

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Photochemistry of 2,2,4,4-Tetraphenyloxetan-3-one. Intermediates in the Photofragmentation of Aryl Substituted Oxiranes

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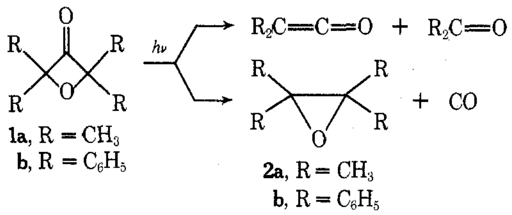
The photochromic behavior of vicinally substituted aryloxiranes has been investigated in rigid glasses[2] and the intervention of ionic and free-radical intermediates has been proposed for the fragmentation of these oxiranes to arylcarbenes and carbonyl compounds.[3] During these investigations the development of a blue-colored species (λ_{max} 610 nm) was observed upon irradiating tetraphenyloxirane (**2b**) at 254 nm in hydrocarbon glasses (77K). That carbon–carbon bond cleavage is associated with this phenomenon was confirmed by low-temperature rigid matrix studies on 2,2,4,4-tetraphenyloxetan-3-one (**1b**).[4] The colored intermediate that forms from the oxetanone on decarbonylation at 350 nm, under conditions in which the oxirane is photostable, was shown to be spectroscopically identical with that obtained from **2b** at 254 nm. We now wish to report additional photochemical results obtained on **1b** in solution.

Hammond and co-workers[5a,b] studied the solution photolysis of a related compound, 2,2,4,4-tetramethyloxetan-3-one (**1a**). In polar solvents, the principal reaction path involved cycloelimination to give dimethylketene and acetone, rather than decarbonylation to tetramethyloxirane. In nonpolar solvents, both reactions were found to occur (Scheme I). An acyl–alkyl biradical intermediate which decomposes by two different solvent-dependent paths was proposed for these processes, although complete product identification was not achieved.

Scheme I

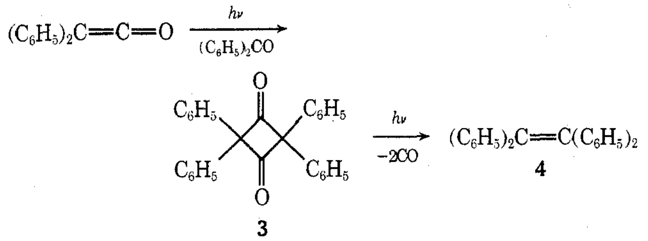


The results with **1a** suggested that the tetraphenyl analogue **1b** would photolyze in a similar manner upon irradiation above 300 nm to give tetraphenyloxirane (**2b**). Under these conditions the oxirane is known to be photostable and, if formed, should be isolable.

Irradiation of **1b** in benzene (350 nm, Pyrex, *c* 20 mmol/l.) for 17 hr resulted in the conversion of the starting material (76%) to a mixture of the expected oxirane **2b** (36%), carbon monoxide (detected by gas-phase infrared spectroscopy), benzophenone (55%), and diphenylketene (Scheme I), as well as tetraphenylethylene (10%). Diphenylketene was shown to be present among the primary photoproducts by infrared spectroscopy ($\nu_{C=C=O}$ 2080 cm^{-1}) and was trapped as methyl diphenylacetate (13%) by quenching the benzene solution with methanol after irradiation. The benzophenone and methyl diphenylacetate were separated from unreacted **1b** and other photoproducts by elution chromatography on silica gel. The relative amounts of the two components were established by NMR.

The formation of tetraphenylethylene (**4**) was noted with great interest. 2,2,4,4-Tetraphenylcyclobutane-1,3-dione (**3**), the head-to-tail dimer of diphenylketene which is known to decarbonylate to **4**,[6] appeared to be a reasonable precursor[7a] (Scheme II). While benzene solutions of diphenylketene are stable to irradiation at 350 nm for prolonged periods (90 hr) in the absence of benzophenone (92% recovery), tetraphenylethylene (66%) and traces of biphenyl are formed when benzophenone is added to the solution. Since both benzophenone and diphenylketene are primary cycloelimination products obtained from **1b**, the proposed mechanism for the formation of **4** is clearly consistent with the experimental results. Benzophenone presumably behaves as a sensitizer for the dimerization of diphenylketene and experiments designed to test this proposal are in progress. An alternative route to **4** involving dimerization of diphenylcarbene, formed from diphenylketene in a sensitized process, is unlikely, at least in solution, at the wavelength employed.[7b,c]

Scheme II



In an attempt to trap diphenylcarbene, a potential primary photoproduct of **1b**, irradiation of a solution of **1b** in methanol (*c* 3.3 mmol/l.) was undertaken.[8] After 18 hr ex-