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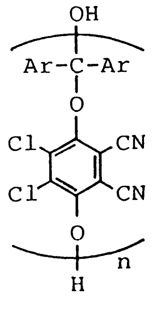
Formation of an Oxirane by the Reaction of 9-Diazofluorene with 2,3-Dichloro-5,6-dicyanobenzoquinone and Inclusion of Some Solvents in the Oxirane

Tadao SHINGAKI, Mitsuji TSUJITA, and Toshikazu NAGAI*
College of General Education, Osaka University,
Toyonaka, Osaka 560

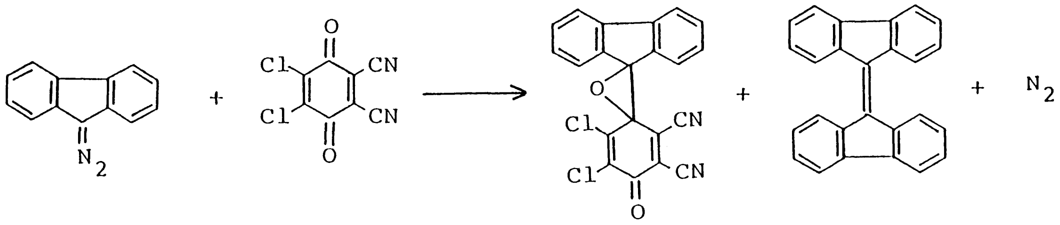
Reaction of 9-diazofluorene with 2,3-dichloro-5,6-dicyanobenzoquinone gave an oxirane. It was found that the oxirane formed 1 : 1 molecular complexes with solvents on recrystallizing from some solvents such as acetone, acetonitrile, 1,4-dioxane, and benzene.

It has been reported that the reaction of substituted diphenyldiazomethanes with an equimolar amount of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene at 30 °C gives resinous substances which establish the structure of the 1 : 1 reaction products (1) having a hydroquinone polyether linkage made up by the successive combination of intermediary diazonium betaines or carbenium betaines.[1)] Employing 9-diazofluorene (9-DF) as a diazo compound, an oxirane[2)] was obtained by intramolecular ring closure probably from a betaine intermediate in the reaction with DDQ. The present letter reports on the formation of the oxirane and its behaviors.



1, n=5— 7

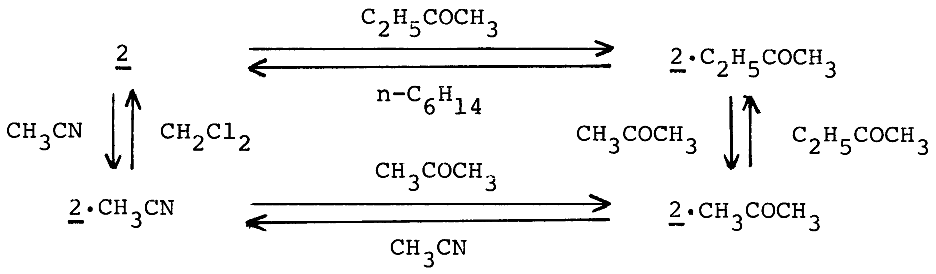
A solution of 9-DF (15 mmol)[3)] in acetonitrile (100 ml) was added dropwise to a solution of DDQ (16 mmol)[4)] in acetonitrile (50 ml) on stirring at 22—27 °C over 2 h. Immediately, an evolution of nitrogen was observed. The reaction gave 9-fluorenylidene-1'-(4'-oxo-2',3'-dichloro-5',6'-dicyano)-2',5'-cyclohexadienylidene 9,1'-oxide (2), yellow powder mp 183 °C (decomp)(from CH_2Cl_2), in a 93% yield beside 9,9'-bifluorenylidene (3), evolving nitrogen quantitatively. Employing acetone,



9-DF DDQ 2 3

dichloromethane, and benzene as the reaction solvent, the reactions gave the results similar to the case of acetonitrile in 70—90% yields of 2. Confirmation of the structure as 2 was done on the basis of the following data: elementary analysis; Found: C, 64.39; H, 2.12; N, 7.16%. Calcd for $C_{21}H_8O_2N_2Cl_2$; C, 64.47; H, 2.06; N, 7.16%. IR (KBr) 1710 cm^{-1} (C=O): MS m/z 390 (M^+): ^{13}C NMR ($(CD_3)_2CO$) δ=40.97, 53.93 (each s, epoxide), 112.60, 122.10 (each s, CN), 175.73 (s, CO), 125.08, 130.62, 134.41, 136.28, 136.43, 142.09, 144.27, 147.39 (each s), 122.37, 123.50, 123.83, 126.66, 129.37, 130.24 (each d), and 132.70 (d, 2C).

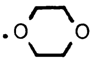
Interestingly, it was found that 2 included certain solvents used for recrystallization of 2 in molar ratio of 1 : 1. The recrystallization of 2 from ethyl methyl ketone gave big yellowish-orange columnar crystals, which exhibited the values of elementary analysis for a molecular compound consisting of one molecule of 2 and one molecule of ethyl methyl ketone ($2 \cdot C_2H_5COCH_3$).[5] The mass spectra of the molecular complex revealed m/z 390 ($M^+-72(C_4H_8O)$) as the highest peak. The ^1H NMR spectra of the molecular complex (in $CDCl_3$, δ ppm) was as follows: 1.20 (t, $CH_2\underline{CH_3}$), 2.12 (s, CH_3), 2.44 (q, CH_2), and 7.0—8.2 (8H, aromatic H). The above resonance signals of the aromatic protons and of the aliphatic ones showed complete agreement with those of ^1H NMR spectra obtained from 2 and from ethyl methyl ketone, respectively; any of the peak shifts attributable to the molecular complex formation were not observed. Consequently, the molecular complex completely dissociates into the components in the solvent because of a weak interaction between 2 and the ketone. Moreover, it was found also that 2 was able to give the corresponding 1 : 1 molecular complex upon recrystallization from acetone, acetonitrile, pyran, 1,4-dioxane, and benzene respectively, but not from hexane, dichloromethane, and chloroform. On the other hand, these molecular complexes play guest-exchange, when they are recrystallized from a solvent different than the solvent used for the original molecular complex formation, as shown in the following Scheme 1.



Scheme 1.

As described above, the ^1H NMR spectra of $\underline{2}\cdot C_2H_5COCH_3$ showed that the molecular complex had dissociated into the components in the solution. And so, differential thermal analysis (DTA) was attempted with each of the molecular complexes. The results of these determinations[6)] are presented in Table 1.

Table 1. Thermal parameters of the molecular complexes

Molecular complex	$\underline{2}\cdot C_6H_6$	$\underline{2}\cdot C_2H_5COC_2H_5$	$\underline{2}\cdot$ 
DTA peak temp/°C	74	88	91
Molecular complex	$\underline{2}\cdot CH_3CN$	$\underline{2}\cdot CH_3COCH_3$	$\underline{2}\cdot C_2H_5COCH_3$
DTA peak temp/°C	95	96	107

In the DTA curve, every one of the molecular complexes showed an endothermic peak at the temperature given in the Table and all of the complexes indicated the start of the exothermic peaks at temperatures between 183 and 185 °C. The endothermic peaks are attributable to elimination of the additives from these complexes, the beginning of the exothermic peaks mean that $\underline{2}$ starts to decompose at the melting point. As seen in Table 1, the molecular complexes with polar additives (nitrile and ketone) have a tendency to indicate higher DTA endothermic peak points than the boiling points of these additives, however, any relationship between the peak points and the natures of the solvents is not found out at the present time.

Every electronic spectrum obtained from the molecular complexes mixed with Nujol showed a slight blue shift (4—5 nm at λ_{max}) compared with that from $\underline{2}$ (λ_{max}

292 nm), the shapes of the curves being virtually the same. On the other hand, the broad absorptions in the visible region (as far as 500 nm) of the complexes displayed a slight bathochromic effect. Further work on these molecular complexes is in progress.

References

1) T. Oshima, R. Nishioka, and T. Nagai., Tetrahedron Lett., 1980, 3919; T. Oshima and T. Nagai, Bull. Chem. Soc. Jpn., 54, 2039 (1981).
2) H-D. Becker, J. Org. Chem., 34, 1203 (1969). This report gave an oxirane structure for the compound obtained from the reaction of diazomethane with DDQ. After that, the structure was cancelled to give a cyclopropane structure which was provided by addition of methylene to the cyano-substituted double bond in the following report: H-D. Becker, B. W. Skelton, and A. H. White, Aust. J. Chem., 34, 2189 (1981).
3) T. Baltzly, N.B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky, and A. M. Steinberg, J. Org. Chem., 26, 3669 (1961).
4) A. B. Turner, "2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ)," in "Synthetic Reagents," ed by J. S. Pizey, John Wiley & Sons (1977), Vol. 3, p. 193, and references quoted therein.
5) Elementary analysis: Found: C, 64.81; H, 3.48; N, 6.05; Cl, 15.31%. Calcd for $C_{25}H_{16}O_3N_2Cl_2$: C, 64.79; H, 3.31; N, 5.90; Cl, 15.21%.
6) Heating was adjusted to a 10 °C/min rise rate, the samples were heated from room temperature to 190 °C.

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