

Action of Sodium and Lithium Chlorodifluoroacetates on Phenanthrene-9,10-quinone

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Thermal decomposition of sodium chlorodifluoroacetate in the presence of phenanthrene-9,10-quinone leads to the formation of phenanthrene-9,10-diyl carbonate. Thermal decomposition of lithium chlorodifluoroacetate in the presence of the same quinone gives 10-chlorodifluoromethyl-10-hydroxyphenanthren-9(10*H*)-one.

THE reactions of diazoalkanes with *o*-quinones have been extensively studied.¹ In many cases 1,4-adducts are obtained. For example, diphenyldiazomethane reacts with phenanthrene-9,10-quinone to give the dioxole (I).² There are few reports of other carbenes or carbenoids reacting with *o*-quinones.³ We now report that sodium chlorodifluoroacetate reacts with phenanthrene-9,10-quinone to give the carbonate (II), whereas lithium

chlorodifluoroacetate reacts with the same quinone to give the hydroxy-ketone (III).

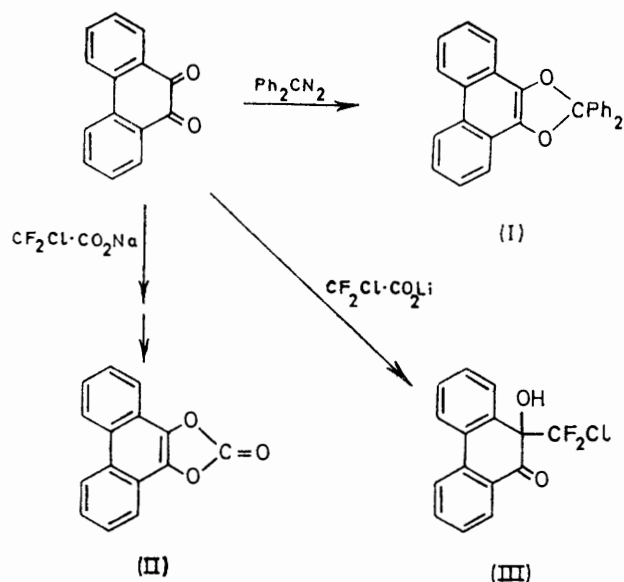
Phenanthrene-9,10-quinone in refluxing triglyme (*ca.* 216°) was treated with sodium chlorodifluoroacetate (50 equiv.). The major product was identified as phenanthrene-9,10-diyl carbonate (II) (40% yield), mainly from the i.r., u.v., and mass spectra. The i.r. spectrum

² A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 1946, 746; B. Eistert, R. Wollheim, G. Fink, H. Minas, and L. Klein, *Chem. Ber.*, 1968, **101**, 84.

³ Ref. 1, p. 390.

¹ G. Pfundt and G. O. Schenck in '1,4-Cycloaddition Reactions,' ed. by J. Hamer, Academic Press, London, 1967, pp. 389—401.

had absorption bands in the region 1800—1900 cm^{-1} , the number of bands depending on whether the spectrum was measured for a carbon tetrachloride solution or a Nujol mull. Five-membered ring carbonates generally have bands in this region,⁴ and in some cases the number of bands has been observed to depend on the physical



state of the sample.⁴ The u.v. spectrum was similar to that of phenanthrene.⁵ Apart from the molecular ion at m/e 236, the mass spectrum contained a peak at m/e 192 ($M - \text{CO}_2$); the mass spectra of carbonates generally contain such a peak.⁶

The last step in the formation of the carbonate is probably the hydrolysis of the 1,4-adduct (IV). We know of no precedent for the hydrolysis of a difluoromethylenedioxy-group, but compounds containing a dichloromethylenedioxy-group react readily with water to give carbonates.⁷ I.r. and u.v. analysis of the final reaction mixture indicated that the carbonate was present prior to work-up. For hydrolysis to occur, the triglyme need contain only 0.05% of water.

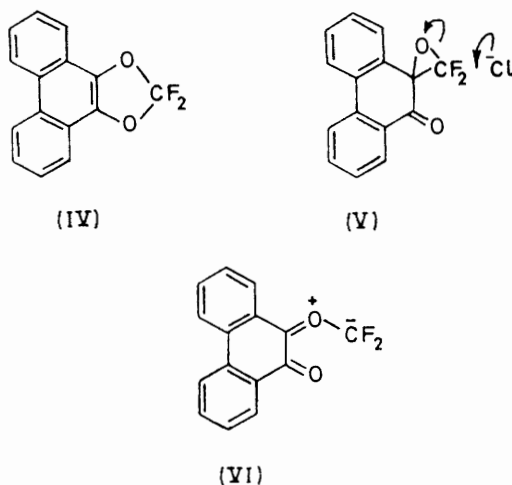
Phenanthrene-9,10-quinone was treated with lithium chlorodifluoroacetate (50 equiv.) under similar conditions. The major product was identified as the hydroxy-ketone (III) (40% yield), mainly on the basis of elemental analyses (C, H, and F) and i.r. and mass spectra. Analyses and molecular ion peaks at m/e 294 and 296 (ratio of intensities, 3 : 1) indicated that the molecular formula of the compound was that of starting material plus CHClF_2 . The base peak in the mass spectrum (m/e 209) corresponded to $M - \text{CCl}_2\text{F}$. The i.r. spectrum had hydroxy- (3468 cm^{-1}) and carbonyl (1702 cm^{-1}) bands. T.l.c. analysis of the final reaction mixture indicated the presence of hydroxy-ketone (III) prior to work-up.

⁴ J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 1957, 618.

⁵ See, e.g., A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon, Oxford, 1964, p. 128.

The crude products from the two reactions were compared. The reaction with the sodium salt did not produce any detectable (t.l.c. and i.r. spectrum) amount of the hydroxy-ketone (III) and that with the lithium salt did not produce any detectable (t.l.c.; i.r. and u.v. spectra) amount of the carbonate (II). Slagel found that the use of lithium and sodium chlorodifluoroacetates as 'difluorocarbene' precursors afforded different results.⁸ He treated diethyl cyclohexene-4,5-dicarboxylate (stereochemistry not specified) with the salts in both refluxing diglyme and triglyme. The reactions with the lithium salt were cleaner and gave substantially higher yields of difluoromethylene adducts than those with the sodium salt. We also found that the reaction with the lithium salt was cleaner than that with the sodium salt.

It is not clear why the reactions with the quinone take different courses. One possible explanation is as follows. Both salts may decompose to give difluorocarbene, and this may react with the quinone to give the epoxide (V). Decomposition of the chlorodifluoroacetates affords the metal chlorides. Lithium chloride may react with the epoxide (V) as shown to give, after work-up, the hydroxy-ketone (III). Lithium chloride would be expected to react more rapidly than sodium chloride: in aprotic solvents lithium halides are generally the more reactive, and lithium chloride is almost certainly more soluble than sodium chloride. When the sodium salt is used the epoxide (V) might thermally rearrange to give the 1,4-adduct (IV) which could then react further to give the carbonate (II). Attempts to detect the involvement of lithium chloride by treating lithium chlorodifluoroacetate with the quinone in the presence of



Li^{36}Cl were inconclusive; it was found that exchange occurred when the hydroxy-ketone (III) alone was treated with Li^{36}Cl in refluxing triglyme.

⁶ E.g., H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, pp. 484—493; P. Brown and C. Djerassi, *Tetrahedron*, 1968, **24**, 2949.

⁷ I. R. C. Bick and R. A. Russell, *Austral. J. Chem.*, 1969, **22**, 1563.

⁸ R. C. Slagel, *Chem. and Ind.*, 1968, 848.

A second possible explanation is that the sodium and lithium salts may decompose by different mechanisms, the sodium salt by a one-step α -elimination⁹ and the lithium salt by a two-step process, the intermediate being the chlorodifluoromethyl carbanion. This anion might attack one of the carbonyl groups to give, after work-up, the hydroxy-ketone (III). If this explanation is correct the 1,4-adduct (IV) might arise as already discussed, *via* the charged species (VI), or directly by 1,4-addition.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ¹H N.m.r. spectra were recorded at 60 MHz for *ca.* 10% solutions in carbon tetrachloride containing tetramethylsilane as internal reference. Mass spectra were obtained with a Varian-MAT CH7 single-focusing instrument. Only the principal peaks are reported.

Triglyme (2,5,8,11-tetraoxadodecane) was distilled from calcium hydride and stored over molecular sieves. Organic solutions were dried with magnesium sulphate.

The radioactivities of samples were determined with a Tritium Scintillation Counter (Isotope Developments Ltd., type 6012A). The scintillator solution was Nuclear Enterprises Ltd., number NE 220. For each sample 10,000 counts were taken, so that the statistical error was $\pm 1.64\%$ (90% probability). Activity was considered to be constant when readings agreed within 2%.

Action of Sodium Chlorodifluoroacetate on Phenanthrene-9,10-quinone.—A solution of sodium chlorodifluoroacetate (20 g) in triglyme (50 ml) was added dropwise to a vigorously stirred solution of the quinone (500 mg) in triglyme (25 ml) heated at reflux temperature under nitrogen. Addition was continued until u.v. spectral analysis indicated that the starting material had largely been consumed; 50 equiv. of the salt had then been added. The mixture was heated and stirred for a further 10 min then cooled and filtered. The filtrate was evaporated under reduced pressure and the dark brown syrup obtained dissolved in ether. The solution was washed with water, dried, and evaporated to give the crude product. T.l.c. analysis indicated the presence of one major component, several minor components, and starting material. Crystallisation of the crude product from ether gave *phenanthrene-9,10-diyl carbonate* (II) (228 mg, 40%), m.p. 186—187°. Recrystallisation from carbon tetrachloride or hexane gave white needles, m.p. 189—192°, ν_{\max} (CCl₄) 1880m, 1848s, and 1815m cm⁻¹; ν_{\max} (Nujol) 1882w, 1877w, 1852m, 1845m, 1825s, and 1815s cm⁻¹; λ_{\max} (EtOH) 219 (log ϵ 4.19), 248 (4.64), 255 (4.74), 269sh (4.01), 279 (3.85), 291 (3.86), 304 (3.97), 325 (2.81), 341

(2.95), and 359 nm (2.95); δ 7.28—7.75 p.p.m. (m, ArH); *m/e* 236 (*M*⁺, 15%), 235 (*M*⁺ - H, 73), 192 (*M*⁺ - CO₂, 10), 180 (27), 164 (100), 163 (41), and 152 (15) (Found: C, 76.0; H, 3.6. C₁₅H₈O₃ requires C, 76.3; H, 3.4%).

Compound (II) appeared to decompose on preparative t.l.c. or column chromatography. With work-up procedures employing these techniques much smaller yields were obtained.

Action of Lithium Chlorodifluoroacetate on Phenanthrene-9,10-quinone.—The quinone (500 mg) was treated with the lithium salt as described in the previous experiment. Again 50 equiv. of salt were required. The crude product was a pale yellow syrup. T.l.c. analysis indicated the presence of one major product, numerous minor products, and starting material. Preparative t.l.c. of the crude product gave 10-chlorodifluoromethyl-10-hydroxyphenanthrene-9(10H)-one (III) (283 mg, 40%), m.p. 111—112°. After recrystallisation from hexane it had m.p. 115—117°, ν_{\max} (CCl₄) 3468 and 1702 cm⁻¹; λ_{\max} (EtOH) 246 (log 4.60), 253 (4.58), 275 (3.93), 283sh (3.86), and 333 nm (3.60); δ 4.80 (OH) and 7.20—8.00 p.p.m. (8H, m, ArH); *m/e* 296 (*M*⁺, 3%), 294 (*M*⁺, 9), 209 (100), 181 (40), and 152 (40) (Found: C, 61.0; H, 3.2; F, 12.0. C₁₅H₉ClF₂O₂ requires C, 61.1; H, 3.1; F, 12.9%).

Treatment of Hydroxy-ketone (III) with Lithium [³⁶Cl]-Chloride.—Aqueous labelled hydrochloric acid (3.55 N; 0.5 ml containing 5 μ Ci of ³⁶Cl) was diluted to 25 ml with triglyme. A sample (0.20 ml) of this solution was added to scintillator solution (4 ml) and the count rate was determined.

Another sample (1.00 ml) was added to a vigorously stirred mixture of anhydrous lithium chloride (100 mg) and triglyme (20 ml) and the mixture was heated under reflux for 30 min. The hydroxy-ketone (III) (50 mg) was then added, and heating and stirring were continued for a further 1 h. The solvent was evaporated off under reduced pressure and the residue dissolved in ether. The washed ethereal solution was dried and evaporated. Preparative t.l.c. of the residue gave the hydroxy-ketone (35 mg, 70% recovered). This was recrystallised from hexane several times, and after each recrystallisation a sample (2 mg) was dissolved in scintillator solution (4 ml) and counted. After the first recrystallisation the activity remained constant. Quenching was shown to be negligible by measuring the count rate of a sample prepared by adding one drop of the original aqueous solution of labelled hydrochloric acid to scintillator solution (4 ml), adding inactive hydroxy-ketone (4 mg), and recounting.

On the assumption that the ³⁶Cl added in the hydrochloric acid became statistically distributed between the hydrogen chloride and the lithium chloride, the molar activity of the recovered hydroxy-ketone was 70% of that of the lithium chloride.

⁹ J. Hine and D. C. Duffey, *J. Amer. Chem. Soc.*, 1959, **81**, 1131.