The Mechanism of the Formation of Tropolone from the Adduct of Cyclopentadiene and Dichloroketene*[1]

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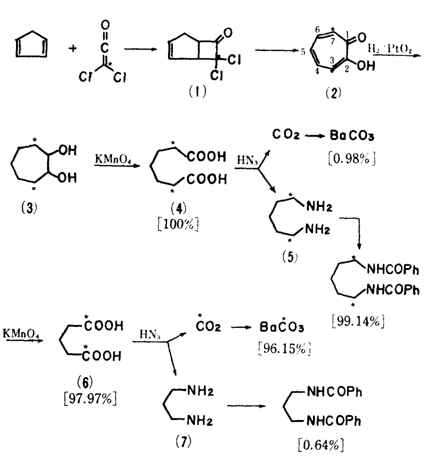
We have previously reported[1)] the novel rearrangements of the adduct of 6,6-dimethylfulvene with dichloroketene, and have proposed a mechanism for the formation of tropone derivatives from the adduct involving a norcaradienone intermediate. We have also proposed a similar mechanism for the rearrangement[2)] of the adduct of cyclopentadiene with dichloroketene to tropolone. This report will present evidence to support the proposed mechanism by a tracer experiment.

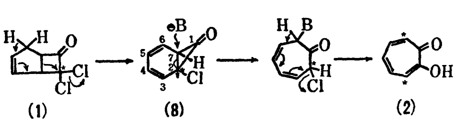
The reaction of cyclopentadiene with dichloroketene-2-^{14}C, produced by the reaction of the dichloroacetyl chloride-2-^{14}C and triethylamine, in boiling *n*-hexane afforded a 1 : 1 adduct (**1**).[2,3)] The adduct (**1**) was rearranged to ^{14}C containing tropolone (**2**) under solvolytic condition (potassium acetate in acetic acid and water) according to the method of Stevens *et al.*[2)]

The tropolone was submitted to catalytic hydrogenation in the presence of the Adams catalyst to give ^{14}C containing cycloheptane-1,2-diol (**3**). The diol (**3**) was degraded to trimethylenediamine (**7**) and carbon dioxide via pimelic acid (**4**), pentamethylenediamine (**5**), and glutaric acid (**6**) by repeated oxidations and Schmidt reactions, as is shown in the following scheme.



Pimelic acid (**4**) shows a radioactivity*[3] of 152,883 dpm/mM; the activities of the consecutive degradation products or their derivatives are shown in parentheses in terms of a percentage of the activity based on the activity of pimelic acid.

It is clear from the above results that all the ^{14}C are located at the 3- or 7-carbon in the tropolone (**2**); this supports the previously-proposed mechanism for the formation of tropolone by way of the attack of the nucleophile at the 7-position of the norcaradienone intermediate (**8**). The details will be reported elsewhere.



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1) T. Asao, T. Machiguchi, T. Kitamura and Y. Kitahara, *Chem. Commun.*, **1970**, 89.

2) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

3) L. Ghosez, R. Montaigne and P. Mollet, *Tetrahedron Lett.*, **1966**, 135.

*[3] The activities of the compounds (**4**), (**6**) and dibenzoate of (**5**) and (**7**) were measured in dioxane, and those of $BaCO_3$ were measured in toluene on TEN Liquid Scintillation Counter GSL-111.