Novel Rearrangement of the Adduct of 6,6-Dimethylfulvene and Dichloroketen

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Summary Various reactions of the 1 : 1 adduct of 6,6-dimethylfulvene and dichloroketen afforded unexpected tropone derivatives and benzoic acid derivatives.

The synthetic method for tropolone involving the solvolysis of the 1 : 1 adduct of cyclopentadiene and dichloroketen, developed by Stevens *et al.*,[1] has also been applied to the synthesis of 4,5-benzotropolone.[2] The present investigation was undertaken to study the reactivity of fulvene and ketens, with a view to obtaining substituted tropolones.

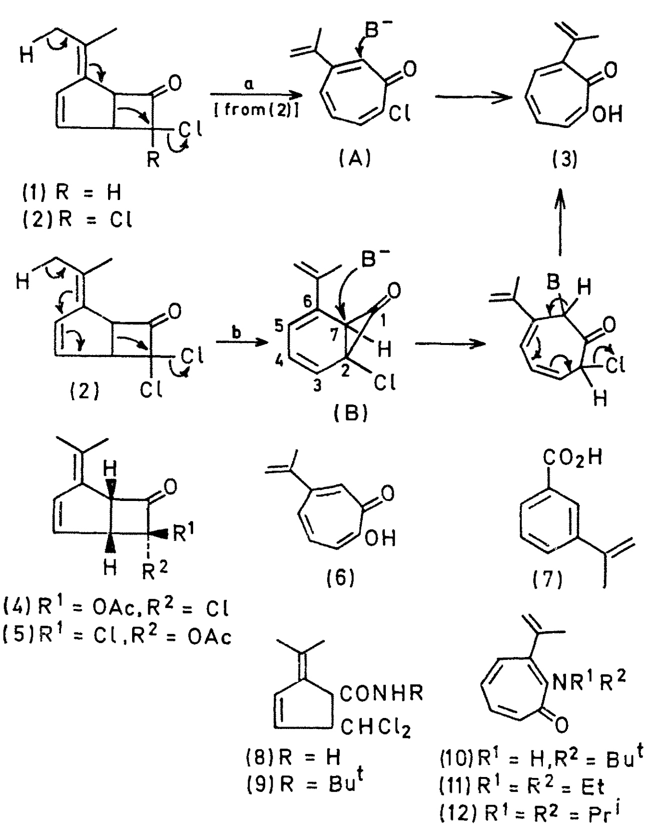
The reaction of 6,6-dimethylfulvene and monochloroketen[3] produced by the reaction of chloroacetyl chloride and triethylamine in boiling n-hexane afforded a 1 : 1 adduct (1), m.p. 63°, as colourless needles in 22% yield, $\lambda_{\max}$ (MeOH) 250 nm (ϵ 17,500); $\nu_{\max}$ (KBr) 1792 cm^{-1}. Similarly, by the reaction of 6,6-dimethylfulvene and dichloroketen, an oily 1 : 1 adduct (2), b.p. 100°/0·7 mm, was obtained in 95·5% yield, $\lambda_{\max}$ (MeOH) 250·5 nm (ϵ 16,600); $\nu_{\max}$ (neat) 1803 cm^{-1}. Structures (1) and (2) were indicated by n.m.r. and double resonance studies† and are in accord with the expected manner of addition of ketens[4] and the electron distribution in fulvene.[5]

Solvolysis of (1) under various conditions gave only polymeric material.[6] In the hope of obtaining β-dolabrin (4-isopropenyltropolone), solvolysis of (2) with potassium acetate in aqueous acetic acid, and with triethylammonium acetate in aqueous acetone, was carried out. However, unexpectedly, α-dolabrin (3-isopropenyltropolone) (3)[7] was obtained in 65·2 and 90·5% yields, respectively.‡ The mixture of dihydro-derivatives obtained by hydrogenation of (2) also yielded α-thujaplicin (3-isopropyltropolone) on similar solvolysis.

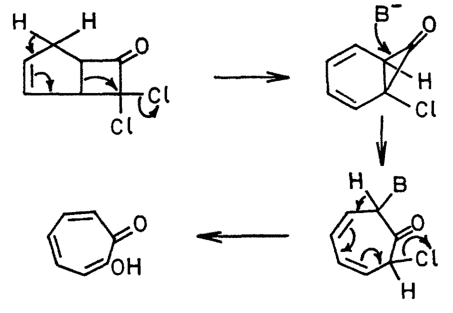
Two mechanisms can be considered for this novel solvolysis; (i) *via* 2-chlorotropone derivative (A) as intermediate followed by abnormal substitution[8] (a); (ii) *via* norcaradienone intermediate (B) (b). Treatment of 2-chloro-6-isopropyltropone under the same solvolytic conditions afforded a minute amount of hinokitiol (4-isopropyltropolone) and starting material. From this evidence, the formation of α-dolabrin seems to proceed *via* route (b).

Reaction of (2) with silver acetate in aqueous acetonitrile gave 22·4% of a mixture of isomeric chloro-acetoxy-compounds;[9] oily (4) and crystalline (5), m.p. 94°, and 6% of β-dolabrin (6).[7,10] This is the only case in which a 4-substituted tropolone is obtained from the adduct (2). Reaction of (2) with silver trifluoroacetate in acetonitrile or acetone afforded *m*-isopropenylbenzoic acid (7), in 32% yield, which may be produced by attack at carbonyl carbon of the norcaradienone intermediate (B) by a nucleophile. When the adduct (2) was allowed to stand at room temperature with acids such as concentrated sulphuric acid (15 min.), 60% HClO$_4$ (2 days), or 75% H$_3$PO$_4$ (2 days), benzoic acid was obtained in about 40% yield.

The reaction of (2) with various amines was studied. Addition of liquid ammonia to (2) afforded the dichloro-amide (8), which must be formed by the initial attack at carbonyl carbon.[11] The more bulky amines would be expected to attack at less sterically hindered chlorine-bearing carbon atoms to give 2-amino-6-isopropenyltropone derivatives. However, when the adduct (2) was treated with t-butylamine in ether, dichloro-amide (9) and 2-t-butylamino-3-isopropenyl tropone (10) were obtained, and the reaction of (2) with diethylamine and di-isopropylamine



(1) R = H
(2) R = Cl
(A)
(3)
(B)
(4) R^1 = OAc, R^2 = Cl
(5) R^1 = Cl, R^2 = OAc
(6)
(7)
(8) R = H
(9) R = Bu^t
(10) R^1 = H, R^2 = Bu^t
(11) R^1 = R^2 = Et
(12) R^1 = R^2 = Pr^i



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† Satisfactory analytical data were obtained for all the new compounds; the detailed analyses of n.m.r. spectra will be reported elsewhere.

‡ A similar result was obtained by the research group of Takasago Perfumery Co., Ltd.

afforded 2-diethylamino- and 2-di-isopropylamino-3-isopropenyltropone (11) and (12), respectively, in good yield. The structures of these 2-aminotropone derivatives (10—12) were demonstrated by hydrolysis with dilute methanolic KOH to give α-dolabrin.

That such sterically hindered amino-tropone derivatives are formed in high yield seems to support a norcaradienone intermediate, attacked from the convex side by nucleophilic reagents only at the 7-position to afford tropone derivatives.

The formation of tropolone from the adduct of cyclopentadiene and dichloroketen can also be considered to proceed by a similar mechanism, as shown below, since 2-chlorotropone is hydrolysed to tropolone extremely slowly under the same solvolytic conditions. Tracer experiments to clarify the mechanisms and further studies on the reactivity of (2) are in progress.

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[1] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, 1965, **87**, 5257.

[2] R. W. Turner and T. Seden, *Chem. Comm.*, 1966, 399.

[3] W. T. Brady and E. F. Hoff, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 6256.

[4] *Cf.* H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, 1967, p. 38.

[5] K. Hafner, *Angew. Chem.*, 1962, **74**, 499.

[6] Tropone was obtained in low yield on solvolysis of the adduct of cyclopentadiene and monochloroketen; Y. Kitahara, M. Funamizu, and M. Tanemura, unpublished work.

[7] T. Nozoe, T. Mukai, and T. Asao, *Bull. Chem. Soc. Japan*, 1960, **33**, 1452.

[8] *Cf.* T. Nozoe, in "Non-Benzenoid Aromatic Compounds," ed. D. Ginsburg, Interscience, New York, 1959, p. 339.

[9] A mixture of the compounds (4) and (5) was also obtained on reaction of (2) with tetramethylammonium acetate or triethylammonium acetate in acetone in 85% yield. Relative configurations of the chloro- and acetoxy-groups were assigned by the analyses of n.m.r. spectra.

[10] T. Nozoe, K. Takase, and M. Ogata, *Chem. and Ind.*, 1957, 1070; S. Seto, S. Matsumura, and K. Ro, *Chem. and Pharm. Bull. Japan*, 1962, **10**, 901.

[11] A similar reaction using methoxide was observed for the adduct of cyclopentadiene and dichloroketen. L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Letters*, 1966, 135.