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HALOGENATED KETENES. XIX. 2-ALKYLTROPONES: A NEW SYNTHESIS[1]

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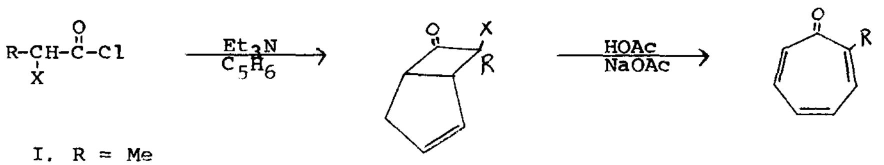
Tropolone has been synthesized by the solvolysis of the cycloadduct of dichloroketene and cyclopentadiene and, 4,5-benzotropolone obtained from the cycloadduct of dichloroketene and indene in a similar manner.[2,3] We have extended this solvolysis reaction to the solvolysis of the cycloadducts of alkylhaloketenes and cyclopentadiene and found a new general method for the preparation of 2-alkyltropones.

Thus, the solvolysis of exo-7-chloro-endo-7-methylbicyclo(3.2.0)hept-2-en-6-one (the cycloadduct of methylchloroketene and cyclopentadiene)[4] in 70% aqueous acetic acid at a cycloadduct concentration of 0.3 M and sodium acetate concentration of 0.6 M for 24 hrs. at reflux, afforded a 50% yield of 2-methyltropone, (I): bp 69° at 2 mm; ir, 1575 and 1630 cm.$^{-1}$; nmr (CCl_4) δ 2.1 (s, 3H) and δ 6.9 (m, 5H); mol. wt. (mass spect.) 120 (theory 120). 2-Ethyl- and 2-n-butyltropones (II and III) were obtained in an analogous manner except for longer solvolysis times. (II): bp 78° at 1.5 mm[5]; ir, 1585 and 1635 cm.$^{-1}$; nmr (CCl_4) δ 1.3 (t, 3H), δ 2.8 (q, 2H) and δ 7.1 (m, 5H). (III): bp 115-117° at 2 mm; ir, 1585 and 1635 cm.$^{-1}$; nmr (CCl_4) δ 1.13 (m, 7H), δ 2.4 (t, 2H), and 6.9 (m, 5H); mol. wt. (mass spect.) 162



I, R = Me
II, R = Et
III, R = n-Bu

(theory 162). The reflux time required for the solvolysis depended on the alkyl group· i.e., the larger the group the longer the reflux time required (24-144 hrs.). The progress of the solvolysis was followed by ir, observing the disappearance of the absorption at 1800 cm.$^{-1}$ of the cycloadduct and the appearance of the alkyltropone absorptions at 1575 and 1620 cm.$^{-1}$

This synthesis appears to be quite general and certainly most useful for the synthesis of 2-alkyltropones. The great advantage of this method over previously reported tropone syntheses such as the introduction of unsaturation to cycloheptanones[6] or carbene addition to phenols[7] is the ability to prepare any 2-alkyltropone from readily available starting materials in two steps. Any α-halo-α-alkylacetyl chloride may be used for the preparation of the ketene - cyclopentadiene cycloadduct which is then solvolyzed to the 2-alkyltropone.

The attainment of the aromatic system of tropone is postulated as the driving force for the ring expansion. This is supported by the failure of *exo*-7-chloro-*endo*-7-methylbicyclo(3.2.0)heptan-6-one (cycloadduct of methylchloroketene and cyclopentene)[8] to yield 2-methyl-2,6-cycloheptadien-1-one on solvolysis under identical conditions that lead to 2-methyltropone with the corresponding cyclopentadiene adduct.

It is interesting that only the *endo*-alkyl cycloadduct undergoes ring expansion to form tropones. When the *exo*-cycloadduct is solvolyzed under identical conditions a ring opening reaction occurs producing a mixture of products but no tropone.

Initial attempts to produce 2-phenyltropone by this method have been unsuccessful. The phenylchloroketene - cyclopentadiene adduct undergoes solvolysis but no tropone has been detected.

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