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ACYLATION OF OLEFINS BY ACID REARRANGEMENT OF CYCLOBUTANONES

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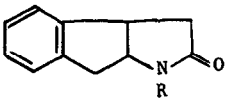
In an attempt to make indenopyrrolidones (e.g. 1) as synthetic intermediates, we examined a possible general approach to this type of compound through ring expansion of the corresponding cyclobutanones (e.g. cis-1,2,2a,7a-tetrahydro-7H-cyclobut[a]inden-1-one, 2).

The adduct, 4, from regiospecific 2 + 2 cycloaddition of dichloroketene to indene is well-known[1], and the chlorine atoms can be removed in stepwise manner to yield 3 and 2 as desired. Under Schmidt conditions (NaN_3, conc. sulphuric acid, 0°), 2 rearranged to a single product (m.p. 62°, 65%) which contained no nitrogen and, from spectroscopic data, was clearly 2-acetylindene, 5, [m/e 158, 143 (M-15), 115 (M-43), δ ($CDCl_3$) 7.58 (t, 1H, olefinic, J2Hz), 7.5-7.2 (4H, aromatic), 3.6 (d, 2H, J2Hz, $-CH_2-$), 2.4 (s, 3H, $-CH_3$)]. The rearrangement took the same course in the absence of NaN_3 and was complete after 5 min. at 0°.

More interestingly, 3 also rearranged rapidly in concentrated sulphuric at 0°C to give 2-α-chloroacetylindene, 6, (m.p. 101-102°C) in 70% yield, while 4 afforded 2-α,α-dichloroacetylindene, 7 (m.p. 120-121°C) in 40% yield after 2 hr. at room temperature[2].

Since dichloroketene adds readily to a variety of olefins and α,β-unsaturated ketones halogenated at the terminal position are not readily accessible by direct methods[3], this rearrangement could have synthetic potential. It augments the results of Huisgen[4] and co-workers who found that the more sterically compressed cyclobutanones derived from addition of diphenyl ketene to olefins often open to give α,β-unsaturated ketones.

Although the spectroscopic evidence left no room for doubt that the rearrangement of 2 had yielded 2-acetylindene, the latter clearly differed from the "2-acetylindene" (m.p. 122°C) obtained by Rupe and Müller[5] by formylation of 8 followed by acid-catalysed cyclisation of the copper complex of the β-ketoaldehyde (9). We have repeated these experiments and their product, m.p. 122°C, is 10 [m/e 474, δ ($CDCl_3$) 8.6 (s, 3H, aromatic), 7.2 (s, 15H, aromatic), 3.18 (centre of two triplets, 12H, methylene groups)], the symmetrical trimer derived from the product of formylation of the methyl group of 8.



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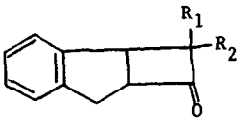
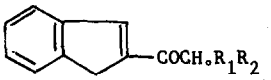




2, $R_1 = R_2 = H$

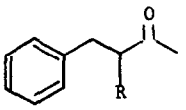
3, $R_1 = H$; $R_2 = Cl$

4, $R_1 = R_2 = Cl$

5, $R_1 = R_2 = H$

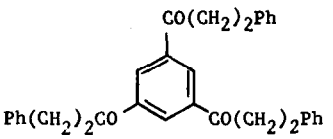
6, $R_1 = H$; $R_2 = Cl$

7, $R_1 = R_2 = Cl$



8, R = H

9, R = CHO



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   R.W. Turner and T.P. Seden, J.C.S. Chem. Comm., 1966, 399.
2. Under the conditions starting material was recovered.
3. Only recently (D.V.C. Awang and S. Wolfe, Canad. J. Chem., 47, 706, 1969) has a direct route to 1-bromo-4-phenylbut-3-en-2-one from benzalacetone been described.
4. (a) R. Huisgen and L.A. Feiler, Ber., 102, 3391, 1969.
   (b) R. Huisgen, L.A. Feiler, and P. Otto, ibid., 102, 3405, 1969.
   (c) R. Huisgen and L.A. Feiler, ibid., 102, 3428, 1969.
5. H. Rupe and H. Müller, Helv. Chim. Acta., 1921, 4, 841.