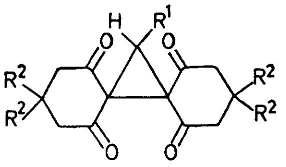
Syntheses and Reactions of 1,1,2,2-Tetra-acylcyclopropanes

By Katsuo Ohkata, Takashi Sakai, Yasuo Kubo, and Terukiyo Hanafusa*
(*Chemistry Department, Faculty of Science, Hiroshima University, Higashi-senda-cho, Hiroshima* 730, *Japan*)

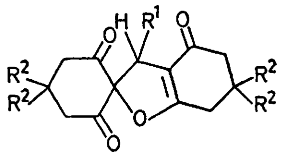
Summary The title compounds (**1**, **3**) were prepared by photochemical isomerisation of 2,3-dihydrofurans (**2**, **4**) and reacted with pyridines or pyrazine to give zwitterionic products (**5**) which are thought to be intramolecular charge-transfer complexes.

Recently, attention has been focused on the physical properties[1] and chemical reactivity[2] of cyclopropanes having four electron withdrawing groups. We now report a general synthesis of some 1,1,2,2-tetra-acylcyclopropanes by photochemical isomerisation of the corresponding dihydrofurans, and their reactions with pyridine and its analogues.



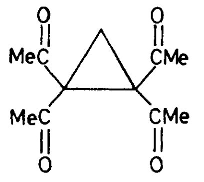
(1)

	R^1	R^2	m.p/°C
a,	H	Me	147-148
b,	Me	Me	109-110
c,	Et	Me	136-137
d,	H	H	

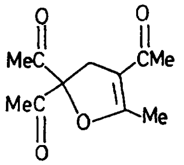


(2)

	R^1	R^2
a;	H	Me
b,	Me	Me
c,	Et	Me

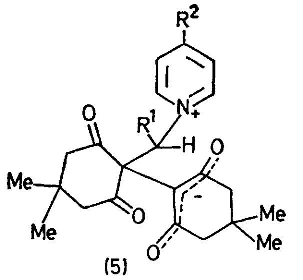


(3) m.p./°C 96-97



(4)

By treating the disodio-derivative of a formaldehyde-dimedone adduct with iodine in absolute ethanol, Radulescu and Georgescu obtained a crystalline solid (m.p. 211–212°) for which the tetra-acylcyclopropane structure (**1a**) was postulated.[3] This compound was, however, identified by Greenberg as the dihydrofuran derivative (**2a**) on the basis of spectroscopic evidence,[4] and some of its homologues (**2b,c**) have been prepared by the treatment of the corresponding dimedone adducts with bromine in acetic acid. Mattsson and his co-workers obtained the tetra-acylcyclopropane derivative (**1d**) by the oxidation of methylene-bis-1,3-cyclohexadione with Fe[Fe(CN)$_6$] followed by dehydration under reduced pressure at 140°.[5]



(5)

	R^1	R^2	m.p.(decomp.)/°C
a;	H	H	181-182
b;	Me	H	113-116
c;	H	Me	188-189

Some tetra-acylcyclopropane derivatives have now been obtained quite readily by the following procedure. An ethereal suspension of a dihydrofuran (**2a**—**c**, **4**)[4] was irradiated by a low pressure mercury lamp through a quartz wall under nitrogen for 1 h to give a yellow solution, from which a colourless crystalline product was obtained (65—68%) identified with a 1,1,2,2-tetra-acylcyclopropane derivative from spectral data.† [**1a**) m/e^+, 290; i.r. (Nujol), 1710, 1720 cm^{-1}; λ_{max} (EtOH), 283 nm, ϵ 320; ^{1}H n.m.r. δ (CDCl$_3$), 1·04 (3H, s), 1·15 (3H, s), 2·23 (2H, s), 2·62 (8H, s); Fourier transform ^{13}C n.m.r., (CDCl$_3$), from Me$_4$Si, 199, 56·6, 55·3, 31·0, 29·0, 28·0, 23·0[6]].

Contrary to the usual cyclopropyl compounds, the tetra-acyl derivatives are resistant to acidic reagents but react easily with basic reagents. (**1a**) was recovered in more than 90% yield by treatment with a small amount of toluene-*p*-sulphonic acid in benzene at room temperature for

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† All new compounds were characterised by i.r. and n.m.r. spectra and had elemental analyses or mass spectra in agreement with the reported structures.

12 h, but it reacted with pyridine in chloroform even at room temperature to give a stable yellow crystalline product, characterised as (**5a**) by spectroscopic analysis [m/e^+, 290, 79; λ_{max} (CH_2Cl_2), 401 (774), 288 nm (ϵ 13900); i.r., (Nujol) 1715, 1680, 1625 cm^{-1}; ^{1}H n.m.r., δ ($CDCl_3$), 0·80 (3H, s), 1·03 (3H, s), 1·09 (6H, s), 1·95 (4H, s), 2·17, 2·94 (4H, ABq, J 12 Hz), 7·71 (2H, m), 8·23 (1H, m), 8·75, (2H, m)]. In a similar manner (**5b**,**c**) and a pyrazinium compound with (**1a**), m.p. 140—142°, were obtained.‡ This reaction may be regarded as a nucleophilic substitution at CH_2 in the cyclopropane ring, the leaving group being an enolate anion of the 1,3-diketone.

The characteristic absorption bands in the visible spectra of these products were very subject to solvent effects. The plots of the transition energies, E_T, of (**5a**) against the solvent polarity parameter, Z, were linear with a slope of *ca.* 0·57.[7] The difference of transition energy, ΔET between (**5a**) and (**5c**) was 3·1 kcal mol^{-1} in CH_2Cl_2 which is the same as the value between methylpyridinium iodide and its 4-methyl derivative. The latter have been identified with a charge-transfer complex.[8] Analogous results were obtained for the pyrazinium complex. Thus, the products are characterised as an intramolecular charge-transfer complex, in which a donor and an acceptor interact with each other through space without conjugation.

Several reports have been published with regard to analogous nucleophilic reactions of cyclopropane derivatives which are provided with powerful electron-attracting groups.[9] The formation of a stable, charge-transfer complex might take part in the driving force for the easy cyclopropane ring opening.

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‡ These compounds were so hygroscopic that the elemental analyses were not satisfactory. In their mass spectra, the spectrum of a tetraketone was superimposed on that of a base.

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[6] We are indebted for the measurement of ^{13}C n.m.r. to Dr. S. Sato and Mr. K. Kushida of Nichiden-Varian Inc., Tokyo.

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