

2-CYCLOBUTEN-1-ONE DERIVATIVES FROM ACETYLENES
AND *t*-BUTYLCYANOKETENE

M.D. Gheorghiu, C. Draghici, Ligia Stănescu and Margareta Avram

Institute of Organic Chemistry, Bucharest, Roumania

(Received in UK 17 November 1972; accepted for publication 30 November 1972)

Recently it was reported that *t*-butylcyanoketene (1) possesses a high reactivity in thermal [2 + 2] cycloadditions, reacting with alkenes ^{1,2} and 1,2-cyclononadiene ².

Our interest in the synthesis of four-membered rings bearing bulky groups ³ as potential precursors of sterically hindered cyclobutadienes prompted us to investigate the reaction of 1 with various acetylenes. The resulting cyclobutenones would be a close step to our goal.

The cycloadditions were performed either in boiling benzene when 1 was generated in situ from 2,5-diazido-3,6-di-*t*-butyl-1,4-benzoquinone (2) in the presence of an acetylene, or at room temperature by adding a solution of acetylene in benzene to a solution of 1 in the same solvent. Phenylacetylene, *t*-butylacetylene, *t*-butylphenylacetylene and diphenylacetylene gave in a 40-80% yield the cyclobutenones 3a (m.p. 88°), 4a (liquid ⁴), 5a (m.p. 119.5°) and 6 (m.p. 136.8-137.5°).

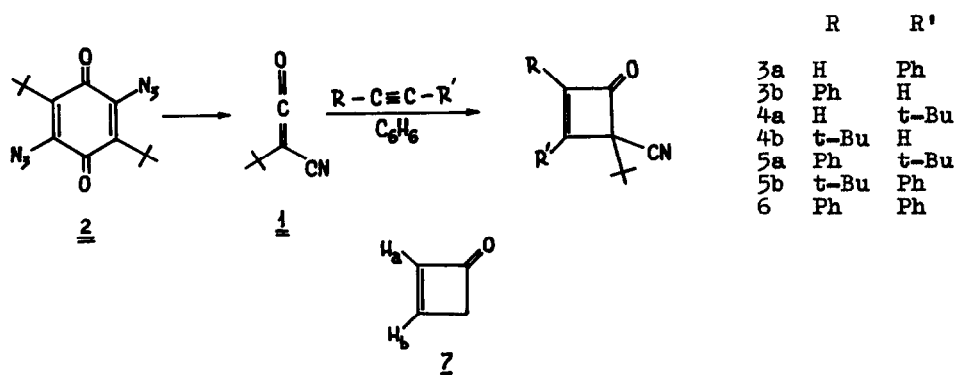


Table 1. Spectroscopic data on cyclobutenones ⁵.

Compd.	IR (cm ⁻¹)	UV λ_{max} ^{EtOH} nm(1gℓ)	NMR δ (^{CCl₄}) TMS int
<u>3a</u>	1768, 2235	290 (4.09)	1.19 (9H); 6.65 (1H); 7.17-7.78 (9H)
<u>4a</u>	1782, 2232	228 (3.75)	1.22 (9H); 1.38 (9H); 6.25 (1H)
<u>5a</u>	1767, 2230	278 (4.03)	1.02 (9H); 1.25 (9H); 7.49 (5H)
<u>6</u>	1775, 2230	230 (4.26); 315 (4.08)	1.15 (9H); 7.28-7.94 (10H)

Since there are two possible relative orientations of the reacting molecules in the cycloaddition, but only one isomer is always formed, the cycloaddition is regiospecific. While the structure of the cyclobutenone 6 is straightforward from the spectroscopic data, the structure of cyclobutenones 3a, 4a and 5a resulted from unsymmetrical acetylenes had to be proved as distinguished from the isomeric structures 3b, 4b and 5b. The structural assignments are based on (i) NMR, (ii) Eu(DPM)₃ shift reagent NMR ⁶ and (iii) UV spectroscopy.

(i) The chemical shifts of protons H_a and H_b in the parent cyclobutenone (7) are very different: $\delta_{\text{H}_a} = 6.17$ ppm, while $\delta_{\text{H}_b} = 8.35$ ppm ⁷. Therefore the actual hydrogen chemical shift can distinguish unambiguously which isomer is formed in the cycloaddition reaction when monosubstituted acetylenes were used. Indeed, since the chemical shift observed was $\delta = 6.65$ ppm and $\delta = 6.25$ ppm respectively, the structures of compounds obtained from the cycloaddition of 1 with Ph-C≡CH and t-Bu-C≡CH, are 3a and 4a respectively.

(ii) The position of t-butyl groups as in 4a and 5a is confirmed by Eu(DPM)₃ shift reagent experiments. Each compound has two t-Bu groups, one attached to a double bond, t-Bu_a, the other bonded to a saturated carbon, t-Bu_b. Usually $\delta_{\text{t-Bu}_a} > \delta_{\text{t-Bu}_b}$ ⁸. Assuming that Eu(III) is coordinated mainly at the oxygen atom, and negligibly at the nitrogen, substituents in positions 2 and 4 will experience a higher pseudocontact shift than a substituent in position 3.

In the NMR spectrum of 4a and 5a in the presence of Eu(DPM)₃, it was

observed that the protons of $t\text{-Bu}_a$ have smaller gradient (see fig. 1, A and B) than those of $t\text{-Bu}_b$ which are vicinal to the $>\text{C}=\text{O}$ group. One concludes that according to these findings the reaction products of 1 with $t\text{-Bu-C}\equiv\text{C-OH}$ or $t\text{-Bu-C}\equiv\text{C-Ph}$ are indeed 4a and 5a.

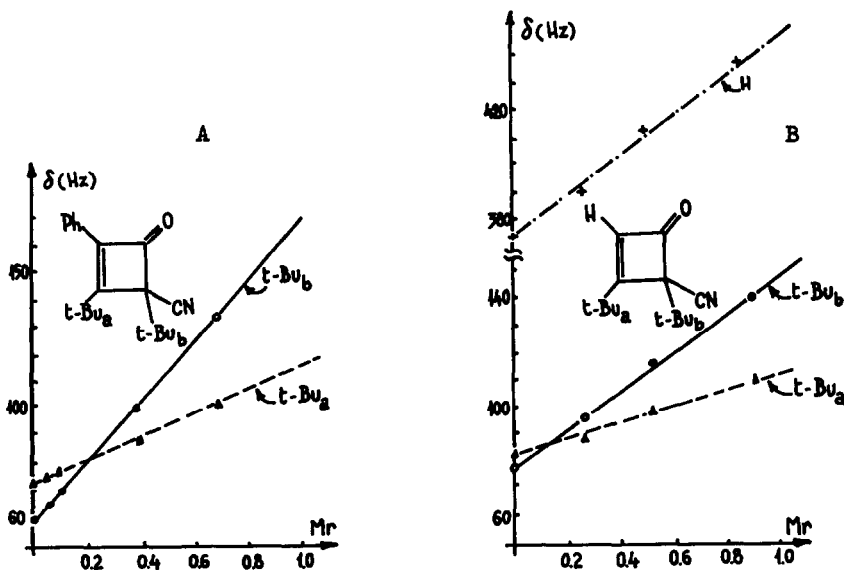


Fig. 1. Dependence of chemical shift
versus molar ratio (Mr) : $\text{Eu(DPM)}_3/\text{substrate}$

(iii) In compound 3a the phenyl group is conjugated, while in 5a, the phenyl group is cross-conjugated with the α, β -unsaturated system of cyclobutenone. This fact is evidenced in the UV spectrum; thus for 3a the maximum is displaced bathochromically by 12 nm relative to 5a, consistent in direction and magnitude with literature data for similar structures ⁹.

Further work concerning other reactions of 1 with acetylenes and chemical properties of cyclobutenones is now in progress.

Acknowledgements. We are most grateful to M. Elian for suggesting the experiments with Eu(DPM)_3 and to Miss E. Sliam and Mrs. V. Daniel for microanalyses.

REFERENCES AND NOTES

1. H.W. Moore and W. Weyler, Jr., J.Amer.Chem.Soc., 92, 4132 (1970) ; ibid., 93, 2812 (1971).
2. W. Weyler, Jr., L.R. Byrd, M.W. Moore, J.Amer.Chem.Soc., 94, 1027 (1972).
3. M. Avram, D. Constantinescu, I.G. Dinulescu and C.D. Nenitzescu, Tetrahedron Letters, 1960, 5215 ; M. Avram, D. Constantinescu, I.G. Dinulescu, O. Constantinescu-Simon, G.D. Mateescu and C.D. Nenitzescu, Rev. Roumaine Chim., 15, 1097 (1970) ; M. Avram, E. Avram, I.G. Dinulescu, N. Stefan, F. Chiraleu, M. Elian and C.D. Nenitzescu, Chem.Ber., 105, 2375 (1972).
4. Compound 4a was isolated by glc on a Carlo-Erba Model GV Chromatograph using a 4m x 6 mm stainless steel column packed with 20% methylphenyl-silicone OV-7 on silanized Chromosorb W support, with hydrogen as carrier gas 140 ml/min. The temperature was programmed 2°/min between 80-200°.
5. All newly synthesized compounds gave satisfactory elemental analysis.
6. $\text{Eu}(\text{DPM})_3$ stands for tris-(dipivaloylmethanato)europium(III). For leading references of its use in NMR spectroscopy see J.K.M. Sanders and D.H. Williams, J.Amer.Chem.Soc., 93, 641 (1970) ; R. v. Ammon and R.D. Fischer, Angew.Chem., 84, 737 (1972).
7. J.B. Sieja, J.Amer.Chem.Soc., 93, 2481 (1971).
8. For correlation of δ t-Bu versus type of hybridization of atom to which it is bonded see R.S. Macomber, J.Org.Chem., 37, 1205 (1972).
9. E.V. Dehmlow, Chem.Ber., 100, 3829 (1967) ; M.C. Caserio, H.E. Simmons Jr., E. Johnson and J.D. Roberts, J.Amer.Chem.Soc., 82, 3102 (1960) ; S.L. Manatt, M. Vogel, D. Knutson and J.D. Roberts, ibid., 86, 2645 (1964).