Transition Metal-catalysed Reactions of Tricyclo[2,1,0,$0^{2,5}$]pentan-3-one Derivatives. Decarbonylation

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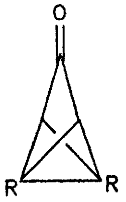
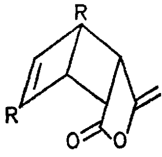
Summary The title compounds are decarbonylated at room temperature by $AgClO_4$ to give, in the presence of trapping agents, the corresponding formal cyclobutadiene adducts.

We have examined the reactivities of the title compounds towards transition metals,[1] in particular, $PdCl_2(C_6H_5CN)_2$ and $AgClO_4$. While the Pd^{II} complex gave a type 2[1a] product of (**1a**) to afford a cyclopentadienone dimer as the final product,[2] the reaction of (**1a**)[1c] and (**1b**)[1c] with Ag^I resulted in evolution of CO (*ca.* 1 equiv.). Although decarbonylation by Rh^I and Pd^{II} complexes is well known,[3] this ready Ag^I-catalysed decarbonylation is unusual[4] and the fate of the remaining $C_4H_2R_2$ fragments of (**1a**) and (**1b**) attracts interest.

Decomposition of (**1a**) in benzene occurred in the presence of $AgClO_4$ at room temperature giving CO (0·90 equiv.) and a mixture of $C_{12}H_{16}$ compounds in low yield as isolable products. Addition of Ag^I to a mixture of (**1a**) and maleic anhydride (2—3 equiv.) gave (**2a**)[5] (>85%). The diphenyl derivative (**1b**) behaved in a similar manner and afforded (**2b**), nearly quantitatively, m.p. 143—145°, the structure of which was assigned on the basis of spectral evidence† and transformation of (**2b**) first into 3,5-diphenyl-1,2-dihydrophthalic anhydride (by heating at 180°) and then to 3,5-diphenylphthalic anhydride, m.p. 174—176° (Pd–C).[6] The rate of decomposition of (**1a**) (0·055—0·186M in benzene) at 35·0 ± 0·1° varied proportionally with the initial Ag^I concentration (0·013—0·193M), being given by the expression, $-d[\mathbf{1a}]/dt = k[\mathbf{1a}] \times [AgClO_4]_0$ with $k = (3·0 \pm 0·6) \times 10\text{M}^{-1}\text{s}^{-1}$. The addition of maleic anhydride to the above solutions did not affect the value of k. This observation requires the existence of an intermediate that is intercepted by the trapping reagent and that the rate-determining step precedes the intermediate. In accord with this inference, the rate (35°) of evolution of CO [$k' = (2·5 \pm 1·0) \times 10\text{M}^{-1}\text{s}^{-1}$] was approximately the same as that of (**1a**) and no n.m.r. signals attributable to unknown species were observed during the course of reaction.



(1)
a; R = Me
b; R = Ph



(2)
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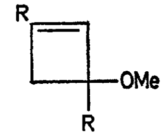

(3)
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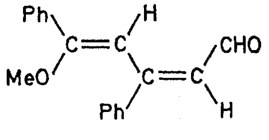
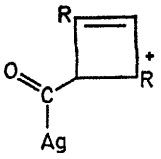
b; R = Ph



(4)



(5)

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†Analytical and spectral data were in accord with the structures proposed.

Treatment of (**1a**) with $\mathrm{Ag^I}$ in methanol[1a] gave (**3a**),† whereas (**3b**) and the aldehyde (**4**)† were the major products obtained from (**1b**).‡ Although these reactions, coupled with several other observations, suggest very strongly that the initial bond cleavage occurs between C(2) and C(3) to provide an intermediate of cation (**5**) or its equivalent, several reactions undoubtedly compete in the ensuing stages, depending upon the substituents of the starting material and upon the solvent employed. Therefore, the course of this reaction remains speculative at present.

It is interesting to compare the above trapping reaction with maleic anhydride with the known chemistry of cyclobutadiene, oxidatively generated from its iron complex.[7] Tricarbonyl-1,3-dimethylcyclobutadieneiron in the presence of maleic anhydride provides (**2a**) upon treatment with ceric ammonium nitrate.[8] Thus 3-ketohomotetrahydranes such as (**1a**) and (**1b**) can be formally regarded as another source of cyclobutadienes.

We thank Mr. A. Clement for the CO measurement and the National Research Council for financial support.

(*Received*, 13*th September* 1972; *Com.* 1577.)

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‡ Control experiments were performed to ascertain that (3a), (**3b**), and (4) were authentic $\mathrm{Ag^I}$-products and were not produced by acid-catalysed reactions.

[1] (a) M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4610; M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, 1971; **93**, 4611; S. Masamune, M. Sakai, and N. Darby, *J.C.S. Chem. Comm.*, 1972, 471; (b) P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, 1972, **94**, 2877 and references therein; W. G. Dauben and A. J. Kielbania, *ibid.*, 1972, **94**, 3669; L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280; (c) S. Masamune, *J. Amer. Chem. Soc.*, 1964, 735; W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 1964, 961.

[2] S. Masamune, H. Ona, and N. Darby, unpublished results. A 1 : 1 mixture of (**1a**) and $PdCl_2(C_6H_5CN)_2$ in benzene or CH_2Cl_2 at room temperature forms a 3,4-dimethylcyclopentadienone–Pd complex (n.m.r.) which apparently releases the ligand relatively slowly to form *endo*-5,6,8,9-tetramethyltricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene-3,10-dione.

[3] *E.g.*, J. Tsuji and K. Ohno, *Synthesis*, 1969, **4**, 157; G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' 3rd edn., vol. II, Methuen and Co., London 1968, ch. 9.

[4] *E.g.*, C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, and J. G. Noles, *Organometallic Chem. Rev. A*, 1970, **5**, 215. G. Bahr and P. Burba in 'Methoden der Organischen Chemie,' (Houben-Weyl) 4th ed., vol. XIII/1, E. Müller, ed., Georg Thieme Verlag, Stuttgart, 1970, pp. 735–799.

[5] H. Ona, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, 1970, **92**, 7495.

[6] A. C. Cope, E. L. Wick, and F. S. Fawcett, *J. Amer. Chem. Soc.*, 1954, **76**, 6158.

[7] L. Watts, J. P. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.

[8] S. Masamune and L. M. Leichter, unpublished results.