Tetrahedron Letters No. 26, pp. 42-44, 1960. Pergamon Press Ltd. Printed in Great Britain

SOME CYCLOPROPENE REARRANGEMENTS

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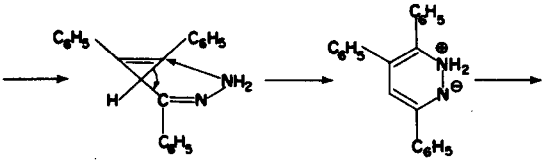
(Received 5 November 1960)

RECENTLY Chandross and Smolinsky reported the rearrangement of triphenylcyclopropenyl azide to triphenyltriazine.[1] As they noted in their paper, we had also observed this interesting reaction, and we wish to report here some other cases in which ring expansion occur by internal attack of a substituent attached to the saturated carbon of a diphenylcyclopropene derivative.

The most closely related example comes from the attempt to prepa the hydrazone of 1,2-diphenyl-3-benzoylcyclopropene. Although an oxime of this compound is easily prepared, reaction of the ketone with hydrazine hydrate in refluxing ethanol led to 3,4,6-triphenyldihydropyridazine, identified by comparison of this compound and its dehydrogenation product with authentic samples.



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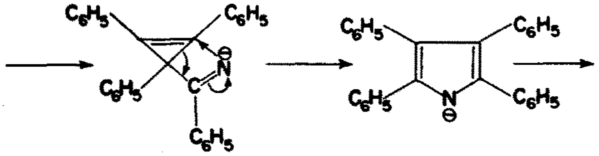
[1] E. Chandross and G. Smolinsky, Tetrahedron Letters, No. 13, 19 (196

A similar rearrangement, in that a nucleophile attacks the double bond and the resulting rearranged anion is resonance stabilized, occurs when triphenylcyclopropenyl cyanide is treated with phenyl lithium. In this case the only product isolated is tetraphenylpyrrole. The reaction is similar to the thermal rearrangement of cyclopropyl imines[2] and ketones[3] to five-membered heterocycles, but in our case it occurs even at -50° C.



Perhaps the most unusual situation occurs in the reaction of diphenylcyclopropenecarboxylic acid chloride with phenyl cadmium reagent in benzene. Addition of the acid chloride at 0° yields only the expected phenyl ketone, but when the addition is carried out at 60° the only isolable product is 2,3,5-triphenylfuran. Under the latter conditions some tarry materials are also formed, but none of the cyclopropene ketone can be detected. Since the ketone is completely unchanged on treatment with the phenyl cadmium in refluxing benzene (and the acid chloride is thermally stable) we feel that the results can be explained only if the intermediate adduct (I) rearranges during the loss of chloride ion. This

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[2] J. Cloke, J. Am. Chem. Soc., 51, 1174 (1929).

[3] C. Wilson, ibid., 69, 3002 (1947).

reaction thus demonstrates the presence of a discreet intermediate such as (I) in a Grignard-type reaction.