

## Cycloaddition Reactions of 1,1-Diphenylethylene Triplets

By THOMAS S. CANTRELL

(Chemistry Department, Rice University, Houston, Texas 77001)

**Summary** Irradiation of 1,1-diphenylethylene in the presence of certain olefins leads to 2 + 2 cycloadducts, sometimes accompanied by products of hydrogen abstraction, by a process apparently involving diphenylethylene excited triplets.

ROSENBERG AND SERVE,<sup>1</sup> have shown that the excited triplet state of 1,1-diphenylethylene has hydrogen-abstracting capability similar to that of the lowest triplet of benzophenone.<sup>2</sup> We now report results on the cycloaddition of excited 1,1-diphenylethylene (**1**) to simple olefins, a process analogous to oxetan formation from benzophenone lowest triplets.<sup>3</sup>

Irradiation (0.02 mol, Corex filter, 450 W medium-pressure mercury arc) of (**1**) in the presence of a 30–50-fold excess of isobutene for 80 h resulted in the isolation, after distillation and preparative g.c., of 1,1-dimethyl-2,2-diphenylcyclobutane (**2**)† in 63% yield, based on unrecovered starting material [33% conversion of (**1**)]. Compound (**2**) was identified by its n.m.r. [ $\tau$  3.0 (10H, narrow m), 7.30 (t,  $J$  7.4, 2H), 8.23 (t,  $J$  7.4, 2H), and 9.00 (s, 6H)] and mass spectral [ $m/e$  236 (rel. intensity 29), 208 (15), 193 (11), 180 (100), 165 (53), and 115 (30)] data.

Irradiation of (**1**) in cyclopentene (32 h) gave 56% of a mixture of (**3**), 3-(1,1-diphenylethyl)cyclopentene, [n.m.r.  $\tau$  3.04 (m, 10H), 4.3–4.8 (2H, br m), 7.8–8.7 (4H, m) 8.48 (3H, s);  $m/e$  248 (20) 180 (100), 171 (73)] and (**4**), 7,7-diphenylbicyclo[3,2,0]heptane,† [ $\tau$  2.9 (10H, m) and 7.8–8.5 (10H, m);  $m/e$  248] in a 3:1 ratio, separable by g.c. on SE-30.

From irradiation through Corex for 32 h of a mixture of

† All compounds so designated give acceptable analytical data.

<sup>1</sup> H. M. Rosenberg and P. Servé, *J. Amer. Chem. Soc.*, 1970, **92**, 4746.

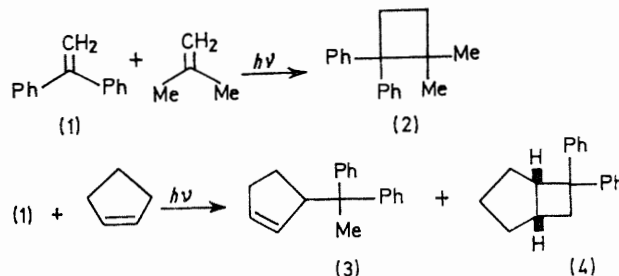
<sup>2</sup> P. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 99.

<sup>3</sup> D. R. Arnold, *Adv. Photochem.*, 1969, **6**, 301.

<sup>4</sup> Compare data for 3,3-diphenylcyclobutene: M. Pomerantz, *J. Amer. Chem. Soc.*, 1966, **88**, 5349.

H. M. Rosenberg, P. Servé, and R. Rondeau, *Canad. J. Chem.*, 1969, **47**, 4295.

(**1**) and 1,2-dichloroethylene, followed by treatment of the reaction mixture with zinc dust, there was obtained, in addition to much recovered (**1**), small amounts ( $\leq 10\%$ ) of 3,3-diphenylcyclobutene identified by its spectral properties.<sup>4</sup> Other olefins tried as substrates (2-methylbut-2-ene



and tetramethylethylene) only gave hydrogen abstraction products analogous to (**3**). Irradiation of (**1**) in isobutene in the presence of sufficient xanthone to absorb  $>99\%$  of the incident light resulted in formation of (**2**), at a slower rate. The addition of (**1**) (0.2M) to isobutene was completely quenched by piperylene (0.4M). The additions must therefore proceed *via* an excited triplet. The similarities in chemical behaviour of triplet (**1**) and benzophenone thus include the 2 + 2 cycloaddition to olefins, as well as hydrogen abstraction<sup>1,5</sup>

*Added in proof.* Addition of triplet (**1**) to furan gives 55% of a 1:1 adduct, m.p. 83–84°.

(Received, September 9th, 1970; Com. 1532.)