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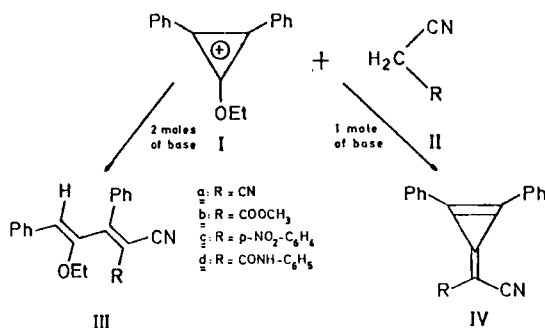
AN IMPROVED PROCEDURE FOR THE PREPARATION
OF SOME METHYLENE CYCLOPROPENES

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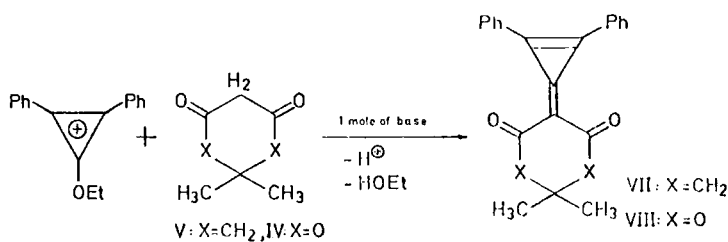
Some years ago, we reported a convenient synthesis of a series of methylene cyclopropene derivatives^{1,2} by the reaction of 1,2-diphenyl-3-ethoxy cyclopropenium cation (I) with active methylene species X-CH₂-Y (where X/Y were electron-withdrawing substituents like CN, COOR etc.) in the presence of two moles of ethyldiisopropylamine.

Although this method offered a number of improvements over the synthetic pathways to methylene cyclopropenes hitherto known³, it completely failed when malononitrile, methyl cyanoacetate and p-nitrophenyl acetonitrile (IIa-c) were reacted. Instead of methylene cyclopropenes (IVa-c), 2-ethoxy-butadienes (IIIa-c) were formed as a result of a ring opening reaction.

We now found that the ring opening reaction does not take place when I and II are reacted in the presence of one mole of base and the desired methylene cyclopropene derivatives IVa-d are obtained in good yield and in high degree of purity.



Similarly, the procedure can be extended to cyclic β -dicarbonyl compounds (V and VI) to yield methylene cyclopropenes (VII and VIII) previously obtained only in moderate yield⁴.



EXPERIMENTAL

General procedure.— Diphenylcyclopropenone⁵ (2.06 g, 10 mmoles) was dissolved in anhydrous 1,2-dichloroethane (20 ml) and alkylated by means of triethyloxonium tetrafluoroborate⁶ (1.90 g, 10 mmoles). After 15 min., a solution of II (10 mmoles) in 20 ml of solvent (1,2-dichloroethane or acetonitrile) was added; then a solution of ethyldiisopropylamine⁷ (1.30 g, 10 mmoles) in 1,2-dichloroethane (20 ml) was added dropwise over a period of 90 min. with efficient stirring. When the addition was complete, the

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resulting solution was stirred for another 3 min. and the solvent evaporated in vacuo. The residue was triturated with benzene (40 ml) and the precipitated amine hydrofluoroborate salt was filtered. The benzene solution on evaporation of the solvent yielded the main portion of crude product (IV, VII, VIII); a second (minor) crop was obtained as insoluble material when the hydrofluoroborate salt was dissolved in water. Both fractions were combined and recrystallized.

1,2-Diphenyl-3-dicyanomethylene cyclopropene (IVa)⁸.- 2.15 g (85%), mp 290-291^o (nitromethane); IR (KBr, cm⁻¹) 2200, 2180 (C≡N), 1860 (methylene cyclopropene²), 1595 (C=C).

1,2-Diphenyl-3-(cyano-methoxycarbonyl-methylene)cyclopropene (IVb).- 2.35 g (82%), mp 163-164^o (acetonitrile); IR (KBr, cm⁻¹) 2200 (C≡N), 1845 (methylene cyclopropene), 1690 (C=O); UV [acetonitrile, nm (ε)] 350 (10900), 304 (27900), 293 (28600), 268 (20800); ¹H-NMR (CDCl₃, TMS_{ext.}, τ) 6.13 (s, 3H, OCH₃), 1.40-2.73 (m, 10 H, phenyl-H).

Anal. Calcd for C₁₉H₁₃NO₂ (287.3): C 79.43 H 4.56 N 4.87
 Found : C 79.36 H 4.39 N 5.03

1,2-Diphenyl-3-(cyano-p-nitrophenyl-methylene)cyclopropene (IVc).- 2.05 g (58%), mp 236-237^o (acetonitrile); IR (KBr, cm⁻¹) 2190 (C≡N), 1840 (methylene cyclopropene), 1590 (C=C); UV [acetonitrile, nm (ε)] 394 (26700), 269 (25900), 255 (25400); ¹H-NMR (CDCl₃, TMS_{ext.}, τ) 1.85-2.70 (m, aryl-H).

Anal. Calcd for C₂₃H₁₄N₂O₂ (350.4): C 78.85 H 4.03 N 8.00
 Found : C 79.16 H 4.08 N 7.92

1,2-Diphenyl-3-(cyano-phenylcarbamoyl-methylene)cyclopropene (IVd).- 1.84 g (53%), mp 210-211^o (acetonitrile); IR (KBr, cm⁻¹) 2200, 2190

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(C=N), 1835 (methylene cyclopropene), 1665 (C=O), 1595 (C≡C); UV [acetonitrile, nm (ε)] 354 (9900), 305 (sh), 290 (23900), 256 (21200), 237 (22200); ¹H-NMR (CDCl₃, TMS_{ext.}, τ) 1.70-2.95 (m, phenyl-H).

Anal. Calcd for C₂₄H₁₆N₂ (348.4): C 82.74 H 4.63 N 8.04
Found : C 82.81 H 4.82 N 8.06

1,3-Diketo-5,5-dimethyl-2-(1,2-diphenylcyclopropenylydene)cyclohexane
(VII).⁴ - 2.10 g (64%), mp 198-199° (ethanol); IR (KBr, cm⁻¹) 1825 (methylene cyclopropene), 1650, 1610 (C=O).

4,6-Diketo-2-dimethyl-5-(1,2-diphenylcyclopropenylydene)-1,3-dioxane
(VIII).⁴ - 1.76 g (53%), mp 234-235° (ethanol); IR (KBr, cm⁻¹) 1840 (methylene cyclopropene), 1685, 1640 (C=O)

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