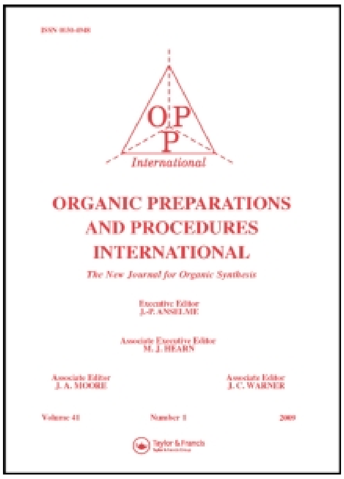


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED PROCEDURE FOR THE PREPARATION OF SOME METHYLENE CYCLOPROPENES

Theophil Eicher[a]; Theodor Pfister[a]; Nils Krüger[a]
[a] Institut für Organische Chemie der Universität Würzburg, West-Germany

To cite this Article Eicher, Theophil , Pfister, Theodor and Krüger, Nils(1974) 'AN IMPROVED PROCEDURE FOR THE PREPARATION OF SOME METHYLENE CYCLOPROPENES', Organic Preparations and Procedures International, 6: 2, 63 — 66

To link to this Article: DOI: 10.1080/00304947409355075

URL: http://dx.doi.org/10.1080/00304947409355075

ORGANIC PREPARATIONS AND PROCEDURES INT. 6(2), 63-66 (1974)

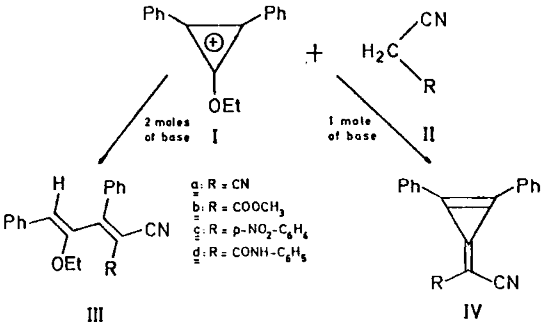
AN IMPROVED PROCEDURE FOR THE PREPARATION OF SOME METHYLENE CYCLOPROPENES

Theophil Eicher, Theodor Pfister und Nils Krüger
Institut für Organische Chemie der Universität Würzburg
West-Germany (BRD)

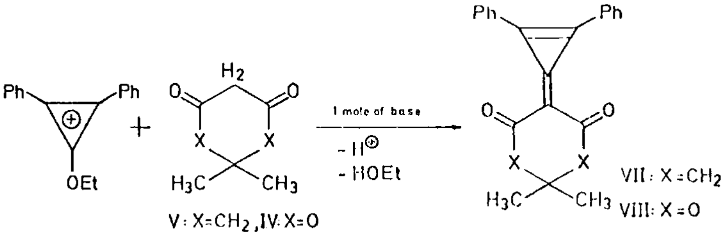
Some years ago, we reported a convenient synthesis of a series of methylene cyclopropene derivatives[1,2] by the reaction of 1,2-diphenyl-3-ethoxy cyclopropenium cation (I) with active methylene species X-CH_2-Y (where X/Y were electron-withdrawing substituents like CN, COOR etc.) in the presence of two moles of ethyldiisopropylamine.

Although this method offered a number of improvements over the synthetic pathways to methylene cyclopropenes hitherto known[3], 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 yield[4].



EXPERIMENTAL

General procedure.- Diphenylcyclopropenone[5] (2.06 g, 10 mmoles) was dissolved in anhydrous 1,2-dichloroethane (20 ml) and alkylated by means of triethyloxonium tetrafluoroborate[6] (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 ethyldiisopropylamine[7] (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 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° (nitromethane) ; IR (KBr, cm^{-1}) 2200, 2180 (C=N), 1860 (methyl ene cyclopropene[2]), 1595 (C=C).

1,2-Diphenyl-3-(cyano-methoxycarbonyl-methylene)cyclopropene (IVb).- 2.35 g (82%), mp 163-164° (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); ^{1}H-NMR ($CDCl_3$, $TMS_{ext.}$, τ) 6.13 (s, 3H, OCH_3), 1.40-2.73 (m, 10 H, phenyl-H).

Anal. Calcd for $C_{19}H_{13}NO_2$ (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° (acetonitrile) ; IR (KBr, cm^{-1}) 2190 (C≡N), 1840 (methylene cyclopropene), 1590 (C=C; UV [acetonitrile, nm (ϵ)] 394 (26700), 269 (25900), 255 (25400); ^{1}H-NMR ($CDCl_3$, $TMS_{ext.}$, τ) 1.85-2.70 (m, aryl-H).

Anal. Calcd for $C_{23}H_{14}N_2O_2$ (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° (acetonitrile ; IR (KBr, cm^{-1}) 2200, 2190

(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); ^{1}H-NMR ($CDCl_3$, $TMS_{ext.}$, τ) 1.70-295 (m, phenyl-H).

Anal. Calcd for $C_{24}H_{16}N_2$) (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-diphenylcyclopropenylidene)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-diphenylcyclopropenylidene)-1,3-dioxane (VIII).[4] - 1.76 g (53%), mp 234-235° (ethanol); IR (KBr, cm^{-1}) 1840 (methylene cyclopropene), 1685, 1640 (C=O)

REFERENCES

1. Th. Eicher and A. Löschner, Z. Naturforsch., 21b, 295 (1966).
2. Th. Eicher and A. Hansen, Chem. Ber., 102, 319 (1969).
3. For a review, see D. Wendisch in "Methoden der organischen Chemie" (Houben-Weyl-Müller), 4. Aufl., Bd. IV/3, p. 753, Thieme Stuttgart.
4. Th. Eicher and A. Löschner, Z. Naturforsch., 21b, 899 (1966).
5. R. Breslow, Th. Eicher, A. Krebs, R. A. Peterson and J. Posner, J. Am. Chem. Soc., 87, 1320 (1965).
6. H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt and E. Pfeil, J. prakt. Chem., 147, 257 (1937).
7. S. Hünig and M. Kiessel, Chem. Ber., 91, 380 (1958).
8. Prepared by S. Andreades, J. Am. Chem. Soc., 87, 3941 (1965), from diphenylcyclopropenone and IIa in acetic anhydride with β-alanine catalyst in 24% yield.

(Received November 2, 1973; in revised form February 8, 1974)