

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

THE NITRATION OF DIPHENYLCYCLOPROPENONE

C. W. Bird^a; A. F. Harmer^a

^a Department of Chemistry, Queen Elizabeth College, London

To cite this Article Bird, C. W. and Harmer, A. F.(1970) 'THE NITRATION OF DIPHENYLCYCLOPROPENONE', *Organic Preparations and Procedures International*, 2: 2, 79 – 81

To link to this Article: DOI: 10.1080/00304947009458607

URL: <http://dx.doi.org/10.1080/00304947009458607>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

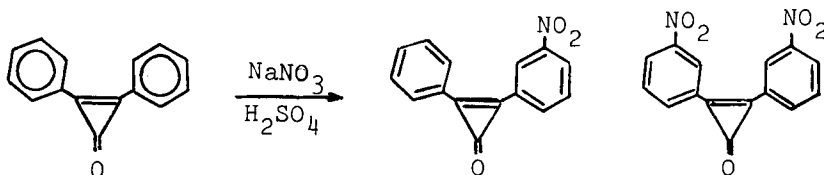
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE NITRATION OF DIPHENYLCYCLOPROPENONE

C. W. Bird and A. F. Harmer
 Department of Chemistry
 Queen Elizabeth College, London, W. 8

Two methods have been employed for the preparation of arylphenylcyclopropenones. One entails the reaction of the appropriate acetylene with phenyl (bromodichloromethyl)mercury¹ and the other reaction of phenylketene dimethylacetal with an arylidene chloride in the presence of potassium *t*-butoxide.² Since the latter reaction failed with nitrobenzylidene chlorides, it occurred to us that direct nitration of the readily available diphenylcyclopropenone³ might provide an alternative route.

Nitration was effected by addition of a molar equivalent of sodium nitrate to a solution of diphenylcyclopropenone in sulphuric acid. As diphenylcyclopropenone is completely protonated in this medium, it was anticipated that the mononitro product would be *meta*-orientated. This was confirmed by photochemical decarbonylation⁴ to 3-nitrodiphenylacetylene, an authentic sample of which was prepared from *m*-iodonitrobenzene and cuprous phenylacetylde.⁵



C.W. BIRD AND A.F. HARMER

Similarly the use of two molar equivalents of sodium nitrate gave a dinitrodiphenylcyclopropenone, which is presumably the 3,3'-isomer.

Experimental

3-Nitrodiphenylcyclopropenone. To a solution of 2 g. (.01 mole) diphenylcyclopropenone in 30 ml. of conc. sulphuric acid was added 0.8 g. (.01 mole) of sodium nitrate. The solution was allowed to stand at r.t. for 1 hr., then heated for a further hour on the steam-bath and poured onto ice. The sticky precipitate was washed with water. Crystallization from ethyl acetate gave 1.2 g. (49%) of 3-nitrodiphenylcyclopropenone, m.p. 171-172°.

Anal. Calcd. for $C_{15}H_9NO_3$: N, 5.58. Found: N, 5.60.

3,3'-Dinitrodiphenylcyclopropenone. An identical procedure to the above was employed except that 1.6 g. of sodium nitrate was added. The 3,3'-dinitrodiphenylcyclopropenone (1 g., 35%) had m.p. 179° dec. (from ethyl acetate).

Anal. Calcd, for $C_{15}H_8N_2O_5$: N, 9.46. Found: N, 9.47.

3-Nitrodiphenylacetylene. (a) This compound, m.p. 70-71° (from 40-60° petroleum ether) was prepared from m-iodonitrobenzene and cuprous phenylacetylde.⁵

Anal. Calcd. for $C_{14}H_9NO_2$: N, 6.28. Found: N, 6.17.

(b) A solution of 3-nitrodiphenylcyclopropenone (0.5 g.) in ethyl acetate (200 ml.) in a pyrex flask under a nitrogen atmosphere was irradiated with ultraviolet light, or sunlight, until the characteristic infrared bands of the cyclopropenone at 1850 and 1630 cm^{-1} had disappeared. The

NITRATION OF DIPHENYLCYCLOPROPENONE

solution was evaporated and the residue recrystallized from 40-60° petroleum ether, yielding 3-nitrodiphenylacetylene identical with the above sample.

References

1. D. Seyferth and R. Damrauer, J. Org. Chem., 31, 1660 (1966).
2. C. W. Bird and A. F. Harmer, J. Chem. Soc.(C), 959 (1969).
3. R. Breslow and J. Posner, Organic Syntheses, 47, 62 (1967).
4. C. W. Bird and J. Hudec, Chem. and Ind., 570 (1959).
5. R. D. Stephens and C. E. Castro, J. Org. Chem., 28, 3313 (1963).

(Received July 7, 1969)