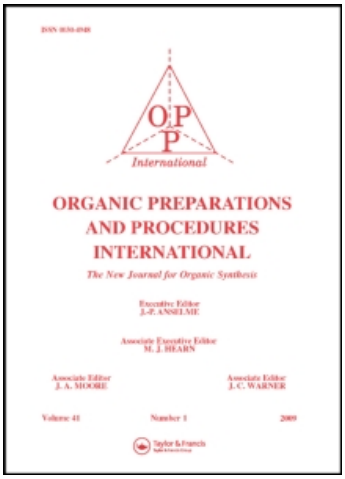

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A NEW SYNTHESIS OF 2,5-DI-*t*-BUTYL-5,6-DICHLORO-1,4-CYCLOHEXENEDIOINE

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A NEW SYNTHESIS OF 2,5-DI-t-BUTYL-5,6-DICHLORO-1,4-CYCLOHEXENEDIONE

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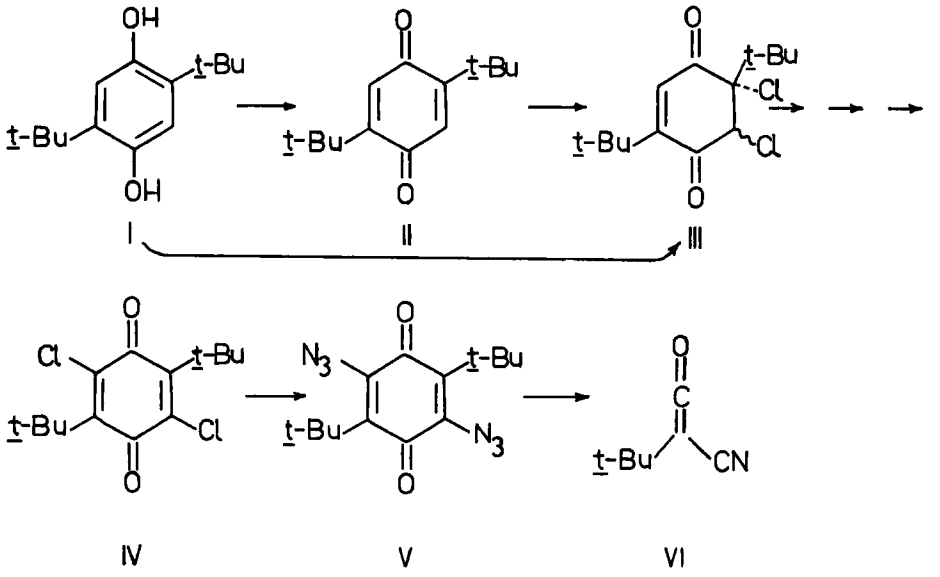
The remarkable reactivity of t-butylcyanoketene (VI) in 2 + 2 cycloadditions prompted us to investigate its reactions with acetylenes[1] and olefins.[2] The starting material for the preparation of VI is compound V, obtained from 2,5-di-t-butylbenzoquinone (II) via alternative chlorination and dehydrochlorination to IV followed by treatment with sodium azide.[3] We now report a modified preparation of interme-



diate III directly from readily accessible 2,5-di-t-butyl-hydroquinone (I), [4] thus avoiding the oxidation step to II.

The title compound (III) was obtained very pure and in high yield (95%) by chlorination in either technical grade or glacial acetic acid, during 3-4 hours, depending on the chlorine flow and the quantity of 2,5-di-t-butylhydroquinone to be chlorinated. Although in this oxidation-addition reaction, hydrogen chloride is evolved, no de-t-butylation occurred, unlike the observation of Moore [5] for related systems but in anhydrous conditions.

To our best knowledge, this conversion of a hydroquinone derivative to a 5,6-dichloro-1,4-cyclohexenedione is the first example reported until now in the literature.

EXPERIMENTAL

2,5-Di-t-butyl-5,6-dichloro-1,4-cyclohexenedione (III). Chlorine was bubbled through a well-stirred suspension of 60 g (0.27 mol) of 2,5-di-t-butylhydroquinone (I) [4] in 450 ml (90-100%) acetic acid at room temperature. After a few minutes, the reaction mixture became yellow, then dark (due to formation of quinhydrone) then pale yellow after 3-4 hours. When the whole suspension had this colour, the reaction was considered completed. The excess of chlorine was removed under reduced pressure with stirring. The suspension filtered, the filtrate poured into 500 ml cold water and refiltered. The combined solid was washed with chilled water, then dried in vacuo. The yield of 2,5-di-t-butyl-5,6-dichloro-1,4-cyclohexenedione (III) was 74.7 g (95%), mp. 127° (crude material, analytically pure), lit. [3] 127-8°.

2,5-DI-t-BUTYL-5,6-DICHLORO-1,4-CYCLOHEXENEDIONE

This compound was converted into 2,5-di-t-butyl-3,6-dichlorobenzoquinone (IV).[3]

REFERENCES

1. M. D. Gheorghiu, L. Stănescu, C. Drăghici and M. Avram, Tetrahedron Letters, 1973, 9.
2. M. D. Gheorghiu, F. Kerek and M. Avram, Rev. Roumaine Chim., 20 (1975), in press.
3. H. W. Moore and W. Weyler, Jr., J. Am. Chem. Soc., 93, 2812 (1971) ; J. Wikholm and H. W. Moore, ibid., 94, 6152 (1972).
4. P. F. Oesper, C. P. Smyth and M. S. Kharash, J. Am. Chem. Soc., 64, 937 (1942).
5. H. W. Moore, D. L. Maurer, D. S. Pearce and M. S. Lee, J. Org. Chem., 37, 1984 (1972).

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