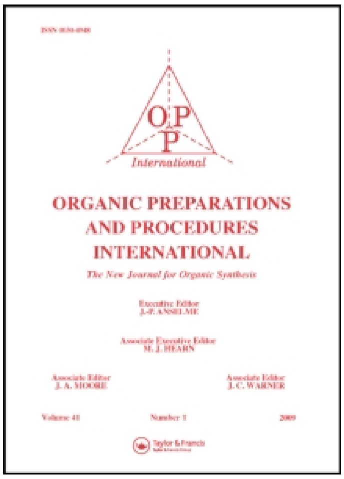

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PHOTOCHEMICAL SYNTHESIS OF BULLVALENEDIONE

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was crystallized from acetone to 6.0 g (46%) of a white solid, mp. 173-174° (lit.[1] 174-176°), identical from IR, NMR and MS comparisons with a sample made by using chloromethyl methyl ether as an alkylating agent.[1]

2,4-Bis (cyanomethyl)-5-methyl-N-acetylbenzylamine (III), mp. 143-144°, was obtained in 97% yield from IIa as described for IIb.[1,6]

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REFERENCES

1. N. G. Kundu, J. A. Wright, K. L. Perlman, W. Hallett and C. Heidelberger, J. Med. Chem., 18, 395 (1975).
2. N. G. Kundu, W. Hallett, and C. Heidelberger, J. Med. Chem., 18, 399 (1975).
3. N. G. Kundu and C. Heidelberger, Biochem. Biophys. Res. Commun., 60, 561 (1974).
4. G. A. Olah, D. A. Beal, S. H. Yu, and J. A. Olah, Synthesis, 560 (1974); G. A. Olah, D. A. Beal and J. A. Olah, 41, 1624 (1976).
5. All reactions should be carried out in a good hood because of the potential toxic nature of the alkylating agents and their decomposition products.
6. The material was identical with an authentic sample made according to reference 1 from IR, NMR and MS comparisons. Crude IIa could be used for the above reaction giving somewhat lower yields (75-85%).

PHOTOCHEMICAL SYNTHESIS OF BULLVALENEDIONE[†]

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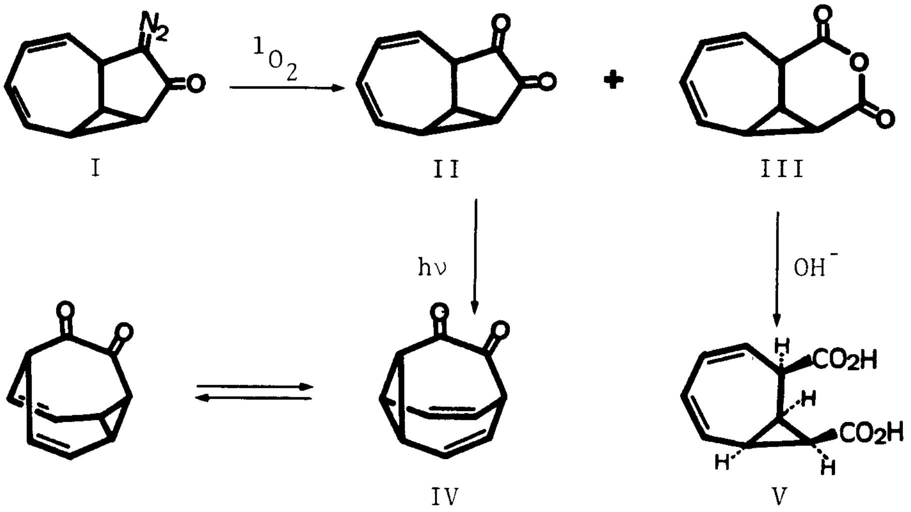
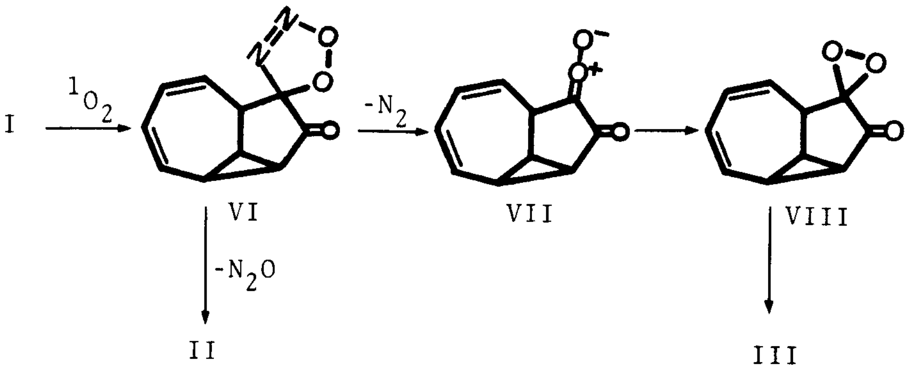
The synthesis of a novel fluxional compound, bullvalenedione IV is of interest, since IV can be directly converted to its semidione which is presumed to serve as a potential intermediate for the intriguing rearrangement of the semidione of bicyclo[4.2.2]deca-2,4,7-triene-9,10-dione to 9,10-dihydronaphthalene-1,2-semiquinone.[1] In order to test this possibility, we carried out the synthesis of IV starting from α-diazoketone I,[2] a versatile precursor for various $C_{11}H_{10}O$ ketones.[3]



When I prepared from tricyclo[5.3.0.0^{2,10}]deca-3,5-dien-9-one,[4] was photooxygenated with singlet oxygen in the presence of methylene blue in CH_2Cl_2, diketone II and acid anhydride III were obtained in 31% and 48% yields, respectively. The mechanism for the formations of fused homotropilidenes II and III can be well rationalized by the mechanism reported previously,[5] where dioxapyrazoline VI and carbonyloxide VII serve as key intermediates. Irradiation of II with 350 nm light in CH_3CN afforded IV



in 48% yield along with bicyclo[3.2.2]nona-3,6,8-trien-2-one (8%)[6] and a mixture of dihydroindenone and indanone (8%). The photochemical transformation of II to IV is noteworthy since either photochemical or thermal transformation of a fused homotropilidene to a bridged homotropilidene is so far unknown. The structure and fluxional property of IV were readily determined by the temperature-dependent ^{1}H NMR analyses. The activation energy, Ea = 12.6 ± 2.5 kcal/mol (log A = 10.8 ± 1.9) (-10° ∿ 28°) was obtained for the degenerate Cope rearrangement.

Acid anhydride III was also shown to be a useful synthetic precursor for the bis-endo-dicarboxylic acid V which cannot be easily prepared by a usual method. Thus, mild hydrolysis of III with sodium carbonate gave a quantitative yield of V.

EXPERIMENTAL SECTION

The ^{1}H NMR spectra were obtained on a Varian EM-390 90 MHz instrument. Chemical shift values are expressed in parts per million downfield from internal $(CH_3)_4Si$. The IR and UV spectra were measured using a Shimadzu IR-27G and a Hitachi 340 spectrometers, respectively. The mass spectra were measured using a Hitachi M-52 mass spectrometer. All melting points are uncorrected.

Tricyclo[5.3.0.0^{2,10}]deca-3,5-diene-8,9-dione (II) and 9-oxatricyclo-[5.4.0.0^{2,11}]dodeca-3,5-diene-8,10-dione (III).- A solution of 2.59 g (17.2 mmol) of I and 120 mg of methylene blue in 430 ml of CH_2Cl_2 was irradiated with six 55W Na lamps under a stream of oxygen for 1.5 hr at 15°. Evaporation of solvent followed by chromatography on silica gel gave on elution with ether 2.35 g of yellow crystals (mp. 93 ∿ 112°) consisting of II and III. Fractional recrystalization twice from CH_2Cl_2-*n*-pentane (1:1) followed by recrystalization from tetrahydrofuran-*n*-pentane gave 948 mg of III as colorless needles, mp. 148 ∿ 150°. The pure diketone II could not be isolated even by several additional recrystalizations of the remaining crystaline mixture of II and III. Flash chromatography on silica gel, however, afforded the pure diketone III. For instance, flash chromatography of 90 mg of the crystaline mixture consisting of 80% of II and 20% of III on silica gel (Merck Kieselgel, 50 g, 200 ∿ 400 mesh) gave on elution with ether-*n*-pentane (6:5) 35 mg of II as yellow needles, mp. 108 ∿ 113° (dec.) and 20 mg of a mixture of II and III. The yields of II and of III were based on ^{1}H NMR analyses of crystaline mixtures of II and III obtained from each fractional recrystalization.

II: IR (KBr): 1756, 1722 cm^{-1}; UV (CH_3CN): λ_{max}, 460 (ε 41), 316 (ε 405), 254 (sh, ε 3250), 235 (ε 3680) nm; m/e (rel intensity): 160 (M^+, 35%), 159 (8%), 132 (44%), 131 (100%), 104 (44%), 103 (42%); ^{1}H NMR ($CDCl_3$): δ 3.08 (C_1-H, ddd, $J_{1,2}$ = 5.5, $J_{1,7}$ = 5.4, $J_{1,10}$ = 5.1 Hz), 2.52 (C_2-H, m, $J_{2,3}$ = 3.3, $J_{2,10}$ = 10.2, $J_{2,7}$ = 2.4 Hz), 5.81 (C_3-H, dd, $J_{3,4}$ = 10.7), 5.67 (C_4-H, dd, $J_{4,5}$ = 5.4 Hz), 6.02 (C_5-H, dd, $J_{5,6}$ = 10.7 Hz), 6.34 (C_6-H, dd, $J_{6,7}$ = 9.1 Hz), 3.39 (C_7-H, ddd), 2.43 (C_{10}-H, dd) ppm.

Anal. Calcd for $C_{10}H_8O$: C, 74.99; H, 5.03 Found: C, 74.42; H, 5.19

III: IR (KBr): 1785, 1760, 1732 cm^{-1}; UV (CH_3CN), λ_{max}, 245 (ε 3960) nm; m/e (rel intensity): 176 (M^+, 17%), 148 (17%), 132 (20%), 131 (92%), 104 (100%), 103 (61%); ^{1}H NMR ($CDCl_3$): δ 2.26 (C_1-H, ddd, $J_{1,2}$ = 2.0, $J_{1,7}$ = 8.1, $J_{1,8}$ = 10.7 Hz), 6.08 (C_2-, C_3-, C_4-H, m), 6.44 (C_5-H, dd, $J_{4,5}$ = 10.8, $J_{5,6}$ = 8.7 Hz), 3.70 (C_6-H, dd, $J_{6,7}$ = 6.5 Hz), 2.49 (C_7-H, ddd, $J_{7,8}$ = 7.2 Hz), 1.95 (C_8-H, dd) ppm.

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58 Found: C, 68.29; H, 4.54

Bullvalenedione (IV).- A solution of 113 mg (0.17 mmol) of II in 30 ml of dry CH_3CN was placed in Pyrex tube and irradiated with RUL-3500 Å lamps using Rayonet Photoreactor for 3 hr. Evaporation of solvent followed by thin layer chromatography (Merck kieselgel RF-254, solvent, *n*-hexane-ether, 1/3) gave 6 mg (8%) of bicyclo[3.2.2]nona-3,6,8-trien-2-one (Rf = 0.9), 6 mg (8%) of a mixture of dihydroindenone and indanone (Rf = 0.7) and 45 mg of yellow crystals, mp. 100 ∿ 113° (Rf = 0.5) which was recrystalized from *n*-hexane to give IV as yellow plates, mp. 115 ∿ 117.5° (31 mg, 35%). 25 mg of II was recovered from the forth band (Rf = 0.35).

IR (KBr): 1717, 1685, 1640 cm^{-1}; UV (CH_3CN): λ_{max}, 404 (ε 60), 297 (ε 543) nm; m/e (rel intensity): 160 (M^+, 2%), 78 (100%); ^{1}H NMR (CD_2Cl_2, at -54°): δ 3.14 (C_1-H, dd, $J_{1,8}$ ($J_{1,2}$) = 9.5, $J_{1,2}$ ($J_{1,8}$) = 8.7 Hz), 2.43 (C_2 (C_8)-H, m, $J_{2,3}$ ($J_{8,7}$) = 8.6 Hz), 6.26 (C_3 (C_7)-H ddd, $J_{3,4}$ ($J_{7,6}$ = 11.0, $J_{3,8}$ ($J_{7,2}$) = 2.4 Hz), 5.83 (C_4 (C_6)-H, dd, $J_{4,5}$ ($J_{6,5}$) = 7.7 Hz), 3.64 (C_5-H, tt, $J_{5,3}$ ($J_{5,7}$) = 1.0 Hz) ppm.

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03 Found: C, 75.17; H, 5.22

Bicyclo[5.1.0]octa-2,4-diene-6,8-*endo*-dicarboxylic acid (V).- A solution of 511 mg (2.90 mmol) of III and 100 mg of Na_2CO_3 in 100 ml of water was heated at 50° for 1 hr. The resulting aqueous solution was acidified with 0.5 N hydrochrolic acid and then subjected to continuous extraction with ether for 7 hr. Evaporation of ether after drying over Na_2SO_4 gave 560 mg of crystals which upon recrystalization from *n*-hexane gave 544 mg (97%) of V as colorless needles, mp. 155 ∿ 157°.

IR (KBr): 3600 ∿ 2300, 1710, 1680 cm^{-1}; UV (CH_3CN), λ_{max}, 270 (ε 3260); m/e (rel. intensity), 194 (M^+, 11%), 131 (100%); ^{1}H NMR of dimethyl ester (CCl_4), δ 1.82 (C_1-H, $J_{1,7}$ = 9.0, $J_{1,8}$ = 10.0 Hz), 5.92 (C_2, C_3, C_4-H, m), 6.28 (C_5-H, dd, $J_{5,4}$ = 10.5, $J_{5,6}$ = 4.8 Hz), 4.18 (C_6-H, dd, $J_{6,7}$ = 9.5 Hz), 2.11 (C_7-H, ddd, $J_{7,8}$ = 7.8 Hz), 1.47 (C_8-H, dd), 3.66 (C_6, C_8-$COOCH_3$).

Anal. Calcd for $C_{10}H_{10}O$: C, 61.85; H, 5.19 Found: C, 61.60; H, 5.24

REFERENCES

†. Organic Photochemistry No. 54; No. 53: T. Miyashi, N. Suto, T. Yamaki, and T. Mukai, Tetrahedron Lett., 4421 (1981).

1. G. A. Russell, R. L. Blankespoor, K. D. Trahanovsky, C. S. C. Chung, P. R. Whittle, J. Mattox, C. L. Myers, R. Penny, T. Ku, Y. Kosugi, and R. S. Givens, J. Am. Chem. Soc., 97, 1906 (1975).
2. T. Miyashi, T. Sugiyama, T. Nakajo, and T. Mukai, Tetrahedron Lett., 3903 (1976).
3. T. Miyashi, T. Nakajo, H. Kawamoto, and T. Mukai, ibid., 151, 155 (1979).
4. W. von E. Doering, B. M. Ferrier, E. T. Forrel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and Saunders, Tetrahedron,

23, 3943 (1967).
5. K. Okada and T. Mukai, Tetrahedron Lett., 359 (1980).
6. M. J. Goldstein and B. G. Odell, J. Am. Chem. Soc., 89, 6356 (1967).

AN IMPROVED SYNTHESIS OF TRIALKYLKETENIMINES

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Ketenimines are valuable substrates in synthetic organic chemistry as they are apt to undergo a variety of photochemical and thermal cycloaddition reactions.[1,2] Ketenimines are readily available by several methods but these are not always applicable to the synthesis of trialkylketenimines. As a matter of fact, only a limited number of trialkylketenimines have been described in the literature. In many cases the rather vigorous reaction conditions have a dramatic influence on the yields of the labile ketenimines.[3]

Recently we reported a facile synthesis of trialkylketenimines 3 by reaction of α-cyanoenamines 1 with methylmagnesium iodide in ether.[4] Ketenimines 3 were isolated in 27-61 % yield but the formation of side-products such as imidoyl cyanides