Tetrahedron. Vol. 34, pp. 1247 to 1250. Pergamon Press 1978. Printed in Great Britain

DIISOPHORONE AND RELATED COMPOUNDS—I

DIMERISATION PRODUCTS OF 3-METHYLCYCLOHEX-2-ENONES

ANTHONY A. ALLEN, C. RICHARD DUFFNER and FREDERICK KURZER*

Royal Free Hospital School of Medicine (University of London), 8 Hunter Street, London WC1N 1BP, England

(*Received UK* 6 *October* 1977; *Accepted for publication* 15 *November* 1977)

Abstract—Depending on the conditions, the self-condensation of 3-methylcyclohex-2-enones produces one or more of several possible dimeric products, including tricyclo[7.3.1.0^{2,7}] tridecane derivatives. Some general structural and spectral features of this class of compounds are discussed, and a simplified method of naming its members is proposed.

We have been concerned for some time with the investigation of products arising in the base catalysed dimerisation of 3-methylcyclohex-2-enones (1).[1] Amongst these, the tricyclic β-ketols of type 3 are of interest for several reasons, especially because their structure includes the bicyclo[1.3.3] nonane skeleton bearing a bridgehead substituent (4), the study of which has recently led to significant progress[2,3] in both the experimental and theoretical sectors. This brief introductory account assembles the information that is relevant to all the work reported in this group of papers. It provides a concise citation of previous results, a proposal for a simplified nomenclature (for 3), and a brief discussion of certain structural and spectral features that are common to all the products to be described.

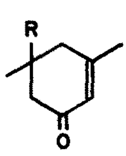
3-Methylcyclohex-2-enones (1) readily undergo base-catalysed self-condensation to a variety of dimeric or more complex products. 3,5-Dimethylcyclohex-2-enone (1, R=H), isophorone (1, R=Me), and piperitone (2) have been studied most closely from this point of view. They are dimerised by sodium or potassium hydroxide,[4-7] preferably under vigorous conditions,[8-10] or by ethanolic sodium ethoxide,[11,12] to the tricyclic β-ketols (3). The action of alkali-free sodamide yields the spiro-diketones (6),[6,10,13] while lithium in ether produces the reduced dimers (7).[10] The mechanism of the dimerisation was considered by Ruzicka[6] in terms of Michael and aldol condensations as early as 1920, but the original formulation[6] of the β-ketols (as 5) has been superseded by 3 as the result of later chemical[9,12] and spectral (NMR) evidence.[10] The dimerisation processes have been elucidated in detail by the investigations of Taylor,[12] Büchi,[13] and especially by Morizur *et al.*,[10] who have critically re-examined the diverging course and the reversibility of the dimerisation under various conditions, and have proposed a unifying mechanism for the interconversions. The photodimerisation of methylcyclohexenones (1) yields, by free radical reactions yet another dimeric structure, viz. the tricyclic diketones (e.g. 8a, b from 1, R=Me, by head-to-head, or head-to-tail condensation, respectively).[14,15]

The action on isophorone (1, R=Me) of alkaline reagents under more severe conditions[9,10,16] leads to trimerisation and simultaneous loss of two molecules of water, resulting in a product $C_{27}H_{38}O$, which also arises from the dimer (3, R=Me) on treatment with aqueous sodium hydroxide at 150°.[9] Its structure (9), recently established by House *et al.*[18] and replacing an earlier tentative formulation,[16,17] is remarkable in that it retains the dimeric tricyclo[7.3.1.0^{2,7}] tridecane structure (3) within its molecular pattern.

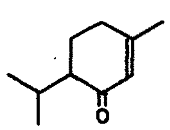
The trivial name "diisophorone" given to the tricyclic dimerisation product (3, R=Me) of isophorone (1, R=Me) is a convenient term when used out of structural context. The systematic names of the dimers (3) are excessively cumbersome: according to Baeyer's system,[19] the dimer (3, R=Me) is derived from the parent hydrocarbon tricyclo[7.3.1.0^{2,7}] tridecane (10), and named 5,5,9,11,11-pentamethyltricyclo[7.3.1.0^{2,7}] tridec-2(7)-en-1-ol-3-one. In the current official (IUPAC) practice, basing names on the fully *unsaturated* parent hydrocarbons,[19,20] 3 (R=Me) stems from benzocyclooctene (11) and is therefore named 5-hydroxy-2,2,7,7,9-pentamethyl-2,3,5,6,7,8,9,10-octahydro-5,9-methanobenzocycloocten-4(1H)-one. This alternative, with minor variations in the numbering, is now adopted for indexing purposes in the abstract literature.[21]

In order to avoid these unwieldy names, we adopt a greatly simplified but unambiguous nomenclature by assigning the generic name *diisophorane* to the parent hydrocarbon (12). The numbering of the Baeyer-system is retained (as in 10), the three cyclohexane rings are designated by letters (as in 12) and functional groups are specified by conventional rules. This proposal, which is not without well established precedents (e.g. norborane, adamantane, etc.), provides a succinct and unique name for each compound of the series. The implied "hidden" inclusion of the five methyl groups in the name of the parent compound (12) is a logical consequence of their origin (from isophorone, 1, R=Me); it is advantageous in shortening the names, and does not preclude the naming of lower homologues. Thus, the dimer 3 (R=H) and its derivatives fit into the scheme as 5,11-bisnordiisophoranes, as do analogous compounds such as 13 (derived from 2). Since the bulk of the existing knowledge relates in fact to derivatives of diisophorone (3, R=Me; i.e. diisophor-2(7)-en-1-ol-3-one), the proposed nomenclature meets the existing requirements most effectively. It is inapplicable, however, to structures incorporating an additional condensed ring (e.g. 9, 14).

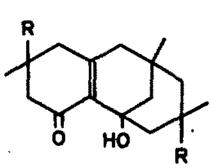
In the elucidation of the structure of diisophorone and its analogues, spectral studies have been of the utmost



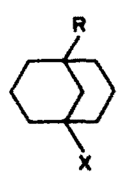
1



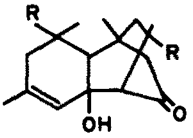
2



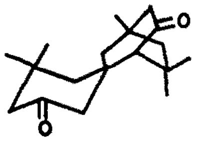
3



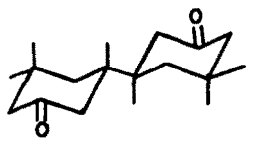
4



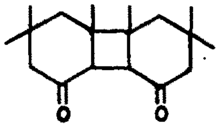
5



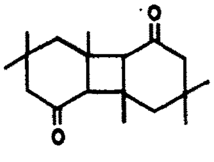
6



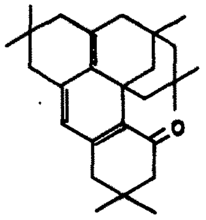
7



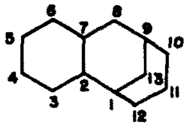
8a



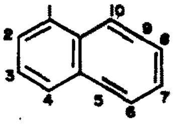
8b



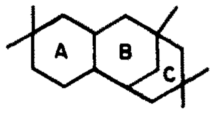
9



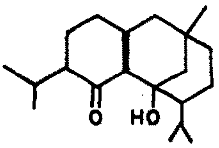
10



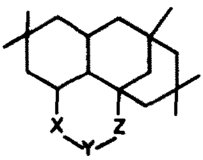
11



12



13



14

importance. The occurrence of hydrogen bonding between the hydroxyl- and keto-groups in "dipiperitone" (13),[11,12] revealed by IR measurements, demonstrated the proximity of these groups to each other, and reduced the number of possible formulations. The study of NMR spectra distinguished decisively between structures 3 and 5 in favour of the former,[10] and provided detailed information on the spatial disposition of the molecule, and the conformation of its subsituents.[22] The IR spectra of diisophorone derivatives display certain absorption characteristics that are common to them all, especially those associated with their cycloalkane framework. Symmetric and antisymmetric stretching of the methyl- and methylene moieties gives rise to a prominent broad band near 2900 cm^{-1}, more intense at the side of higher frequency (*ca.* 2960 cm^{-1}), and slightly less so in its broader part (2900–2860 cm^{-1}). Strong peaks appearing consistently in the 1470–1455 cm^{-1} range are assigned to deformation vibration. The pair of gem-dimethyl-groups in 3 and its derivatives produce, throughout the series, a twin peak at *ca.* 1395 and 1360 cm^{-1}; the latter is nearly always more intense, being presumably enhanced by the C–H symmetric bending peak of the 9-methyl-group which is expected to appear near this frequency; it does in fact persist in the spectra of the 5,11-bisnor-compounds (3, R=H), while the higher frequency band does not. The foregoing assignments have received direct experimental confirmation when the hydrocarbon diisophor-2(7)-ene became accessible;[23] its IR spectrum contains the above, but no other prominent bands. A sharp and intense peak at *ca.* 1040 cm^{-1}, produced by most but not all diisophorone derivatives, has so far not been related to any particular structural feature, but is of occasional diagnostic value. Functional groups in 3 are discernible by their typical absorption bands, and are referred to in the subjoined papers in the appropriate context.

The 3-dimensional[10,22] carbon skeleton of diisophorone is remarkably stable and rigid. Thus, after undergoing a sequence of reactions, a diisophorone derivative may be reconvertible into the initial starting material, showing the absence of structural and steric rearrangement throughout the given series of reactions. The presence in diisophorones (3) of the 1-OH-group allows studies of bridgehead reactivity[24] to be extended to compounds of this series, which may in this connexion be viewed as expanded bicyclo[3.3.1] nonanes. There is, moreover, a formal, if only partial, resemblance between the A–B ring moiety of diisophoranes and that of steroids and triterpenes; it is borne out in the ready applicability of many reactions of common usage in the sterol field. The principal objectives of the present work are the study of replacement reactions at the 1-bridgehead and elsewhere in the diisophorone molecule, the modification or removal of the inert 2(7)-double bond, the degradation of the tricyclic to simpler ring systems, and the attachment of additional condensed rings to the original tricyclic pattern.

Diisophor-2(7)-en-1-ol-3-one (3, R=Me) continues to be the most suitable point of departure experimentally, and has been used most extensively in our work. The lowest homologue of the series, devoid of alkyl groups at C-5 and C-11, is produced from its monomer with some difficulty. The use of the 5,11-bisnor-homologue (e.g. 3, R=H), containing unlike substituents at C-5 and C-11, introduces additional steric uncertainties; these do not arise in diisophorone (3, R=Me), which is, moreover, readily accessible in quantity from commercial isophorone. The 5,11-bisnor-homologue (3, R=H) has been used in supplementary experiments designed to examine the effect of steric hindrance exerted by the 5- and 11-methyl groups, and to confirm the wider applicability of selected reactions. In conclusion, the production of the diisophorones (3, R=H, Me) by methods that have in our experience proved most serviceable,[8] is briefly described, and standard conditions are specified, for reference, for the preparation of ketonic derivatives.

EXPERIMENTAL

General. M.ps are uncorrected. IR spectra were recorded by a Unicam SP 200 instrument, using discs containing the compound (1–2 mg) in KBr (400 mg); the use of Nujol mull or neat liquid is specified when applicable. UV spectra were determined with a Unicam SP 800A spectrophotometer, employing ethanolic solns (0.00005 M or *ca.* 40 mg/1). NMR spectra were recorded at 60 Mc, using a Perkin Elmer R10 spectrometer: solns were *ca.* 0.25 M in $CDCl_3$, and data are reported in ppm (δ) from TMS as internal standard.

Activated alumina used in column chromatography was the Spence H 100–200 mesh grade. TLC was carried out on plates coated with a 250 μ slurry of silica gel G (Merck, after Stahl) and activated by being heated at 100° for 1 hr. The solvent systems were: (A) light petroleum-benzene (1 : 4); (B) ethyl acetate-benzene (1 : 4) or others specified individually. Plates were developed by being sprayed with 50% H_2SO_4, and heated at 100° for 30 min.

Light petroleum had b.p. 40–60°, unless otherwise specified. Pyridine was the pure anhydrous grade. Dimethylformamide was redistilled, and the water-containing fore-run rejected.

The abbreviations vs, s, m, w refer to the intensities (very strong, strong, medium and weak) of the peaks in the IR spectra; d, t, mult and sh denote doublets, triplets, multiplets and shoulders, respectively. Broad peaks (br) are specified.

5,11-*Bisnordiisophor-2(7)-en-1-ol-3-one* 3 (R=H)

3,5-Dimethylcyclohex-2-en-1-one[25] (62 g, 0.5 mole), suspended in a soln of NaOH (120 g, 3 mole) in H_2O (190 ml) was boiled under reflux with stirring for 12 hr (temp. *ca.* 130°; colour initially deep purple). The cooled dark-brown mixture was diluted with H_2O (200 ml), extracted with ether (300 ml), and the deep brown extracts containing some suspended black tarry material successively washed with 3N HCl (3 × 200 ml) and H_2O (4 × 200 ml), the tar being removed with the washings. Evaporation under reduced pressure of the dried (Na_2SO_4) extracts left a viscid orange-brown oil containing a crystalline mass of needles. The whole was redissolved in boiling light petroleum (b.p. 60–80°, 100 ml); the soln deposited on storage pale yellow needles (m.p. 110–112°; 21–26 g, 34–42%) of 3 (R=H) (collected at 0°; rinsed with light petroleum, b.p. 40–60° and 60–80°; 10 : 1). The filtrates deposited a second crop (m.p. 107–109°; 5–6 g, 8–10%); the final mother-liquors therefrom generally contained only intractable oil.

Recrystallisation from light petroleum (b.p. 60–80°; 10 ml per g, recovery 70%) gave 3 (R=H) as pale straw-yellow needles, m.p. 114–115°. Lit. m.p. 120°,[12] 117–118°,[9] 116–118°[10] (Found: C, 77.1; H, 9.75. Calc. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7%).

For further purification, the material (in 1 : 1 benzene-light petroleum, b.p. 60–80°, soln) was filtered through alumina (3 × 12 cm), the column being exhaustively eluted with the same solvent and finally with benzene. The resulting snow-white crystals, m.p. 115–117° (recovery *ca.* 90%) had the following spectral properties:

UV: λ_{max} 248nm (log ϵ 4.00); 320nm (log ϵ 1.89) (*cf* Refs 9, 10, 12). IR: 3470s (OH); 2965, 2925s d, 2880s, 1460s, 1415s, 1375s br (CH_3, CH_2); 1645vs (CO); 1625vs (C=C); 1335ms, 1295s, 1275s, 1155ms, 1125m, 1090ms, 1045s, 1010m, 987s, 920m, 860m, 815mw, 720m, 655m cm^{-1} (*cf* refs 9, 10, 12). NMR: doublet 0.91 δ (3H), J = 6.0 c/s; doublet 1.04 δ (3H), J = 5.2 c/s; 0.98 δ (3H); 5.49 δ (1H). There were no other signals below 2.5 δ (*cf* Ref. 10).

Note. The flask is severely attacked by the concentrated hot alkali and cannot safely be used many times in successive preparations.

Ketonic derivatives of 3 (R=H)

Oxine. A soln of 3 (R=H; 2.48 g, 0.01 mole) and hydroxylamine HCl (0.87 g, 0.0125 mole) in EtOH (40 ml)-anhyd pyridine (6 ml) was boiled under reflux for 2 hr then stirred into ice-water (250 ml). The ppt gave platelets (2.05–2.3 g, 78–88%) of the *oxime*, m.p. 161–163° (from EtOH, 2 ml per g) (Found: C, 72.7; H, 9.6; N, 5.6. $C_{16}H_{25}NO_2$ requires: C, 73.0; H, 9.5; N, 5.3%). IR: 3300–3220vs br mult (OH); 2940–2840vs br, 1460s, 1435, 1425s d, 1380ms br (CH_3, CH_2); 1625ms (C=N); 1290s, 1250m, 1185, 1175ms d, 1145ms, 1125m, 1095m, 1040–1035s br, d; 1025ms, 980s, 935s, 925s, 760ms br, 725ms, 680ms cm^{-1}.

2,4-*Dinitrophenylhydrazone.* A soln of 3 (R=H; 0.5 g, 0.002 mole) and 2,4-dinitrophenylhydrazine (0.60 g, 0.003 mole) in EtOH (20 ml) containing conc. HCl (1 ml) was boiled under reflux for 1 hr. The orange solid which separated on cooling (m.p. 181–182°, 0.73 g, 85%) gave deep-orange felted needles of the derivative, m.p. 180–182° (from EtOAc) Lit. m.p. 191°,[12] 189–190°[9] (Found: C, 61.5; H, 6.9. Calc. for $C_{22}H_{28}N_4O_5$ C, 61.7; H, 6.5%). IR: 3475ms (OH); 3310m (NH); 3100w, 840m, 745m (Ar); 2950s–2850ms, 1435s (CH_3, CH_2); 1618vs (C=N); 1598vs, 1525, 1510s d, 1420s, 1375ms, 1335vs, 1135s, 1105s, 925m cm^{-1}. The 1525–1100 cm^{-1} range closely resembles that of 2,4-dinitrophenylhydrazine.

Semicarbazone. A soln of 3 (R=H; 0.5 g, 0.002 mole) and semicarbazide HCl (0.28 g, 0.0025 mole) in EtOH (10 ml)—pyridine (2 ml) was boiled under reflux during 2 hr. The cooled yellow liquid was stirred into ice-water (50 ml); the resulting ppt gave lustrous microplatelets (0.50 g, 80%) of the *semicarbazone*, m.p. 216–218° (decomp) from EtOH. (Found: C, 66.6; H, 8.9; N, 13.6. $C_{17}H_{27}N_3O_2$ requires: C, 66.9; H, 8.85; N, 13.8%). IR: 3510m (NH, amide); 3340–3280vs br (NH/OH); 2960–2890vs br, 1465–1415s mult, 1380m (CH_3, CH_2); 1690–1675vs mult (CO amide/C=N); 1590vs d, 1290m, 1190m, 1155ms, 1045, 1038m d, 1005mw, 990mw, 930w, 755mw cm^{-1}.

Diisophor-2(7)-en-1-ol-3-one 3 (R=Me) ("Diisophorone")

To a vigorously stirred (PTFE-paddle) soln of isophorone (552 g, 4 mole) in Na-dried benzene (500 ml), finely powdered NaOH (50 g, 1.25 mole; freshly ground in a preheated mortar) was added rapidly, and the stirred mixture boiled under reflux for 5 hr (rapid colour change from yellow to brown to red, slowly turning deep-purple within 45–60 min). The cooled liquid was shaken with 3 N HCl (*ca.* 150 ml, to neutralise the alkali), and washed with warm water (to neutrality). The dried (Na_2SO_4) brown solvent layer was evaporated under reduced pressure, and the residual deep reddish-brown oil dissolved in light petroleum (250 ml). Crystallisation, which usually set in at once, was completed by storage for 1 week, resulting in a deposit of massive sheets of glass-like prisms. The supernatant viscid liquid was decanted and thoroughly drained therefrom, and gave, on more prolonged storage (2–4 weeks), a second crop of equally well-developed large crystals. Crystallisation of the total crude material from light petroleum (*ca.* 150 ml) gave 3 (R=Me), forming two successive main crops of large lustrous prisms, m.p. 79–81° (in *ca.* 45 and 10% yield, respectively; suitable for most synthetic purposes). Further recrystallisation from the same solvent (100 ml per 100 g, recovery 80%) gave colourless refractive prisms, m.p. 82–84°. Lit. m.p. 83.5–84.5°,[8] 86–88°,[9] 84–85°.[10] It had the following spectral properties:

UV: λ_{max} 249nm (log ε 4.12); 318nm (log ε 2.01) (*cf* Ref 10) IR.: 3475s (OH); 2950vs-2850s mult, 1470ms, 1440ms, 1420s (CH_3, CH_2); 1640vs br (CO/C=C); 1385ms, 1370s (·CMe_2); 1305s, 1280ms, 1195, 1180m d, 1160m, 1140ms, 1130mw, 1075mw, 1045s, 1000m, 965m, 915m, 900m, 710m, 650m cm^{-1} (*cf* Refs. 9, 10).

NMR: 0.74 δ (3H); 0.92 δ (3H); 1.01 δ (3H); 1.03 δ (6H); 5.48 δ (1H). There were no other signals below 2.5 δ (*cf* Ref. 10).

Ketonic derivatives of 3 (R=Me)

Oxime. Obtained (82%) by the general method, the derivative formed prisms, m.p. 178–179° (from diethyl-ether) (Found: C, 74.2; H, 10.0; N, 5.0. $C_{18}H_{29}NO_2$ requires: C, 74.2; H, 10.0; N, 4.8%). IR: 3310–3240vs mult (OH); 2940vs–2850vs, 1465s, 1420vs 1195s, 1180s, 1135m, 1100s, 1040vs, 970, 960s d, 930vs, 910s, 1195s, 1180s, 1135m, 1100s, 1040vs, 970, 960s d, 930vsm 910s, 740s br, 720s, 660m cm^{-1}. The spectrum closely resembles that of the oxime of 3 (R=H).

2,4-*Dinitrophenylhydrazone.* Prepared (88%) by the standard method, this formed orange red scales, m.p. 186–188° (from EtOH). Lit. m.p. 188–189°,[9] 198–199°[10] (Found: C, 62.7; H, 7.1; N, 12.3. Calc. for $C_{24}H_{32}N_4O_5$: C, 63.2; H, 7.0; N, 12.3%). IR: 3500mw (OH); 3330w (NH); 3100w, 840mw, 745mw, (Ar); 2960–2840m, 1440ms, 1420ms (CH_3, CH_2); 1620vs (C=N); 1395w, 1375, 1365m d (·CMe_2); 1595vs, 1525, 1510s d, 1340vs, 1315s, 1265ms br, 1135ms, 1110ms, 1090m, 1050m, 920mw cm^{-1}. The spectrum resembles closely that of the DNP of 3 (R=H).

Neither a *p*-nitrophenylhydrazone nor a phenylhydrazone was obtainable by the standard procedure.

Semicarbazone. The crude derivative, obtained (45%) by the standard method, gave on crystallisation from very little EtOH, lustrous platelets of the *solvated semicarbazone*, m.p. 201–204° (decomp) (Found: C, 66.7; H, 9.7. $C_{19}H_{31}N_3O_2\cdot C_2H_5OH$ requires: C, 66.5; H, 9.8%). Keeping the powdered material at 160–170° for 30 min gave the *semicarbazone* as a pale buff powder, m.p. 202–203° (decomp). Lit. m.p. 205–208°[8]; 218–219°[9] (Found: C, 68.7; H, 9.4; N, 12.2. Calc. for $C_{19}H_{31}N_3O_2$: C, 68.5; H, 9.3; N, 12.6%). IR: 3480m (NH, amide), 3360m (OH); 3250m (NH); 2960ms–2880ms br d, 1480–1420s mult (CH_3, CH_2); 1695–1675vs mult (CO amide/C=N); 1390mw, 1365mw (·CMe_2); 1580–1570vs mult, 1340mw, 1305mw, 1195w, 1145w, 1115mw, 1085mw, 1040m, 995w, 760w cm^{-1}. The spectrum resembles closely that of the semicarbazone of 3 (R=H).

Acknowledgements—We are indebted to Bristol Laboratories, of Syracuse, N.Y., for financial support; to Dr. Maxwell Gordon, Vice-president of this Company, and to Prof. J. F. McGhie, of Chelsea College (University of London), for stimulating discussions and continued interest; and to Mr. D. Carter, of the School of Pharmacy, for performing the mass-spectrometric measurements.

REFERENCES

[1] C. R. Duffner and F. Kurzer, *Chem. Indust.* 1642 (1967).

[2] G. L. Buchanan, *Topics in Carbocyclic Chemistry* (Edited by D. Lloyd), p. 199. Logos Press, London (1969).

[3] J. M. Mellor, *Alicyclic Chemistry* (Edited by W. Parker). Specialist Periodical Report, The Chemical Society, London *a* Vol. 1, p. 368 (1973); *b* Vol. 2, p. 362 (1974); *c* Vol. 3, p. 477 (1975); *d* J. Carnduff, Vol. 4, p. 443 (1976); G. B. Gill, Vol. 5, p. 384 (1977).

[4] E. Knoevenagel and E. Reinecke, *Ber. Dtsch. Chem. Ges.* **32**, 418 (1899).

[5] O. Wallach, *Liebigs Ann.* **359**, 263, 279 (1908).

[6] L. Ruzicka, *Helv. Chim. Acta* **3**, 781 (1920).

[7] W. Treibs, *J. Prakt. Chem.* **138**, 299 (1933).

[8] S. A. Ballard and V. E. Haury (to Shell Development Co.), U.S. *Pat.* 2,307,482 (1943); 2,406,652 (1946); *Br. Pat.* 560,598 (1944).

[9] G. Kabas and H. C. Rutz, *Tetrahedron* **22**, 1219 (1966).

[10] J. P. Morizur, B. Furth and J. Kossanyi, *Bull. Soc. Chim. Fr.* 1422 (1967).

[11] L. H. Briggs, C. W. Harland, C. Ralph and H. A. Simmonds, *J. Chem. Soc.* 3788 (1953).

[12] W. I. Taylor, *Chem. Indust.* 252 (1954); W. A. Ayer and W. I. Taylor, *J. Chem. Soc.* 2227 (1955).

[13] G. Büchi, J. H. Hansen, D. Knutson and E. Koller, *J. Am. Chem. Soc.* **80**, 5517 (1958).

[14] W. Treibs, *Ber. Dtsch. Chem. Ges.* **63**, 2738 (1930).

[15] O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker and A. A Griswold, *Rec. Chem. Progr.* **28**, 167 (1967); *Chem. Abstr.* **68**, 68104 (1968).

[16] E. Cyrot, N. Thoai and J. Wiemann, *Tetrahedron Letters* 83 (1970).

[17] Z. W. Wolkowski, *Ibid.* 821 (1971).

[18] J. A. Bertrand, D. Cheung, A. D. Hammerich, H. O. House, W. T. Reichle, D. Vanderveer and E. J. Zaiko, *J. Org. Chem.* **42**, 1600 (1977).

[19] International Union of Pure and Applied Chemistry, *J. Am. Chem. Soc.* **82**, 5545 (1960); *Nomenclature of Organic Chemistry* (3rd Edition) *a* p. 31, *b* p. 35. Butterworth, London (1971).

[20] Chem. Abstracts, Index Guide, Vol. 76–85 (1972–6); Chemical Abstract Service, Columbus p. 1171 et seq. (1977).

[21] *Beilstein's Handbuch der Organischen Chemie* 4th Edn. Vol. 8, 3rd Supplement, p. 569 (1969); *Chem. Abstr.* Collective Index 1962–66, Formula Index p. 3913F (1969).

[22] B. Furth, J. Kossanyi, J. P. Morizur and M. Vandewalle, *Bull. Soc. Chim. Fr.* 1428 (1967).

[23] See Part II, subjoined.

[24] R. C. Fort and P. von R. Schleyer, *Advances in Alicyclic chemistry* (Edited by H. Hart and G. J. Karabatsos) Vol. 1, p. 283. Academic Press, New York (1966).

[25] E. C. Horning, M. O. Denekas and R. E. Field, *J. Org. Chem.* **9**, 548 (1944): *Org. Synth.* Coll. Vol. 3, p. 317 (1955).