chemical shifts, we assume that they have different configurations. The chemical shift of the proton at C-12 in **41** was about the same as that in **42**, and therefore we assign it the same configuration. That is to say, the hydrogen is assigned exo and the acetate substituent is designated endo.

Registry No.—**5**, 14707-22-3; **6**, 23646-38-0; **7**, 14596-96-4; **8**, 29179-06-4; **9**, 29179-07-5; **10**, 29309-29-3; **11**, 29309-28-2; **12**, 23646-39-1; **13**, 29308-17-6; **14**, 29309-34-0; **15**, 29428-03-3; **16**, 29309-30-6; **17**, 29309-31-7; **18**, 29308-18-7; **19**, 29308-19-8; **20**, 29246-50-2; **21**, 29308-21-2; **22**, 29308-22-3; **23**, 29428-06-6; **24**, 29308-23-4; **25**, 29309-37-3; **26**, 29308-24-5; **27**, 29308-25-6; **28**, 29428-08-8; **29**, 29308-26-7; **30**, 29246-49-9; **31**, 29246-46-6; **32**, 29246-48-8; **33**, 29308-30-3; **34**, 29308-31-4; **36**, 29246-47-7; **37**, 29308-33-6; **38**, 29179-08-6; **39**, 29308-35-8; **40**, 29339-43-3; **41**, 29309-25-9; **42**, 29309-26-0; **44**, 29309-27-1; **45**, 29595-83-3.

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Bridged Polycyclic Compounds. LXIX. Preparation and Structures of the Diketoisojanusenes[1]

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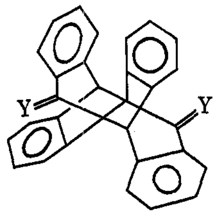
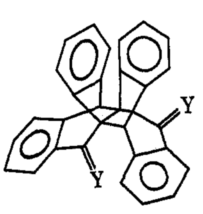
Oxidation of the 6,12-diols of *trans*- and *cis*-isojanusenes led to the isomeric 6,12-diketojanusenes (**1b** and **2b**). The trans diketone **1b** is achiral and X-ray crystallographic data permit the lower melting isomer to be assigned that structure.

In the course of our work[1,2] on the stereochemistry of the rearrangement reactions of derivatives of janusene (5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-*o*-benzenonaphthacene),[3,4] it became necessary to distinguish *trans*-isojanusene (**1a**) and its derivatives from *cis*-isojanusene (**2a**) and its derivatives.[5] To this end we prepared 6,12-diketo-*trans*-isojanusene (**1b**) and 6,12-diketo-*cis*-isojanusene (**2b**) from oxidation of the corresponding alcohols.[2b] Although the pmr spectra and infrared spectra of **1b** and **2b** differed, they could not be used to distinguish between structures **1** and **2**. The lower melting diketone (mp 334–335°) gave a pmr spectrum in chloroform-d_1 with a singlet at τ 4.97 and aromatic proton absorptions at τ 1.94, 2.06, 2.70 and 3.07. The higher melting diketone (mp >360°) gave a pmr spectrum in chloroform-d_1 with a singlet at τ 4.96 and aromatic proton absorptions at τ 2.25, 2.35, 2.72 and 2.99. The infrared spectra were very similar except that the high melting isomer gave strong absorptions at 1248 and 904 cm^{-1} which were absent in the low-melting isomer. The latter, however, gave a medium absorption at 997 cm^{-1} which was not present in the high-melting diketone.



1



2

a, Y = H_2
b, Y = O

Examination of the structures indicated that **1** should be achiral (meso), while **2** should be chiral. Because of the small amounts of compounds **1b** and **2b** on hand, and the difficulties involved in their preparation, we employed X-ray crystallography in order to distinguish between them rather than the usual chemical resolution techniques. We hoped that simple determination of the space group and of the number of molecules per unit cell might be sufficient to assign unequivocally a meso structure to one of the diketones. Fortunately this hope was realized and it has thus been possible to identify the meso compounds on the basis of simple symmetry arguments.

Neither of the two sets of crystals gave a good diffraction pattern. Only the lower melting ones gave a pattern that was adequate for space group determination, and, in this case, no reflections were observed at a Bragg angle greater than about 40° (Cu Kα radiation). All the crystallographic work was carried out on the lower melting isomer. The crystallographic data obtained follow: system, monoclinic; a = 9.09 Å, b = 8.62 Å, c = 14.74 Å, β = 112° 15′; systematic absences, ($0k0$) with k odd; number of molecules/unit cell, 2 (assuming a crystal density of 1.28 g/cc). These data were consistent with either of the space groups $P2_1$ or $P2_1/m$.

This isomer was then identified as the meso isomer since the *dl* isomer can be excluded from either space group as follows. Let us suppose that the isomer is, in fact, the *dl* isomer; then a unit cell containing two molecules must have one *d* enantiomorph and one *l* enantiomorph. If the cell should have space group $P2_1$, these two enantiomorphs would be related by a twofold screw axis, or the molecule itself would have to contain a twofold screw axis. The former alternative is inadmissible

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[1] Previous paper: LXVIII. S. J. Cristol and M. A. Imhoff, *J. Org. Chem.*, **36**, 1861 (1971).

[2] (a) S. J. Cristol and M. A. Imhoff, *ibid.*, **36**, 1849 (1971); (b) S. J. Cristol and M. A. Imhoff, *ibid.*, **36**, 1854 (1971).

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[5] The trivial nomenclature used for these compounds has been described.[2a]

since one diastereoisomer cannot be transformed into the other by the operation of a twofold axis. The second alternative can be excluded since a twofold screw axis cannot be a symmetry element in a nonpolymeric molecule.

If the space group is $P2_1/m$, the symmetry of the cell requires that each of the two molecules in the cell lie on a crystallographic center of symmetry. This requires that the molecules have a center of symmetry, which neither the *d* nor *l* isomer has. Thus the *dl* form cannot crystallize in space group $P2_1/m$.

Since the *dl* isomer cannot be accommodated either in $P2_1$ or $P2_1/m$, with two molecules in the cell, it follows that the isomer with the lower melting point, from crystals of which the diffraction patterns were obtained, must be the meso isomer.

Since the meso isomer itself has a center of symmetry, it is probable that its space group will be $P2_1/m$ with the molecular center of symmetry coinciding with the crystallographic center of symmetry. The space group $P2_1$, however, cannot be entirely ruled out. Fortunately, the above argument does not require an unambiguous space group assignment to the meso form.

Experimental Section

All nuclear magnetic resonance spectra were taken on a Varian A-60A instrument, using saturated solutions in chloroform-d_1 and tetramethylsilane as an internal standard. All chemical shifts are reported in τ units (τ = 10.00 for tetramethylsilane). Infrared spectra were taken on a Beckman IR-5 spectrophotometer in KBr. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were uncorrected.

Preparation of 6,12-Diketo-*trans*-isojanusene (1b).—To a solution of 78 mg (0.19 mmol) of 6,12-dihydroxy-*trans*-isojanusene[2b] in 20 ml of acetone at 0° was added slowly 1 ml of Jones reagent (6.75 g of CrO_3, 5.75 ml of H_2SO_4, 100 ml of water).[6] The reaction mixture was stirred for 2.5 hr at 0° and then poured into 100 ml of ether. The ether solution was washed with three 200-ml portions of water and once with 150 ml of saturated NaCl solution. The ether solution was dried ($MgSO_4$) and filtered and the solvent evaporated under reduced pressure giving 65 mg (83%) of **1b**. Crystallization was from acetone–95% EtOH: mp 334–335° dec; ν_{max} 1705, 1595, 1463, 1283, 1097, 997, 764, 720, 687 cm^{-1} (KBr); pmr ($CDCl_3$) τ 4.97 (s, 2), 1.90–3.10 (m, 16, aromatics).

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.80; H, 4.39. Found: C, 87.58; H, 4.39.

Preparation of 6,12-Diketo-*cis*-isojanusene (2b).—To a solution of 330 mg (0.80 mmol) of 6,12-dihydroxy-*cis*-isojanusene[2b] in 20 ml of acetone at 0° was added slowly 4.9 ml of Jones reagent (6.75 g of CrO_3, 5.75 ml of H_2SO_4, 100 ml of H_2O). The reaction mixture was stirred at 0° for 2 hr and then poured into a mixture of 100 ml of methylene chloride and 100 ml of water. The methylene chloride solution was washed twice with 100-ml portions of water, dried ($MgSO_4$), and filtered, and the solvent evaporated under reduced pressure giving 300 mg (91%) of diketone **2b**. Crystallization was from CH_2Cl_2–acetone: mp >360°; ν_{max} 1690, 1590, 1450, 1248, 904, 778, 746, 693 cm^{-1} (KBr); pmr ($CDCl_3$) τ 4.96 (s, 2), 2.25–3.00 (m, 16, aromatics).

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.80; H, 4.39. Found: C, 87.68; H, 4.34.

Registry No.—**1b**, 29339-42-2; **2b**, 29339-43-3.

Acknowledgment.—The authors are indebted to the National Institute of General Medical Sciences (Public Health Service Grant GM 12139) for support in this work.

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Bridged Polycyclic Compounds. LXX. Rearrangements Accompanying Free-Radical Addition of Thiophenol to 3-Methylenenortricyclene[1]

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The free-radical addition of thiophenol to 3-methylenenortricyclene (**1**) gives the 1,2-addition product, 3-nortricyclylmethyl phenyl thioether (**2**), and a variety of unsaturated thioethers (**7**, **10**, **11**, and **12**) which can be formulated as derivable, under reaction conditions, from the 1,5-homoconjugate addition product, 2-norbornen-2-yl phenyl thioether (**3**). Variation in product compositions with reagent concentrations demonstrates the existence of classical radical intermediates, rather than a single nonclassical free radical.

A considerable degree of attention has been focussed on homoallyl–cyclopropylcarbinyl rearrangements both in ionic and free-radical systems.[2] Bridged polycyclic compounds have been particularly fruitful in elucidating the nature of homoallyl–cyclopropylcarbinyl free-radical intermediates.[3–21] In continuing our research in this area, we undertook a study of thiophenol addition to the symmetrical olefin, 3-methylenenortricyclene (**1**).

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