Hydrogenation of 24 to 1-Adamantanol.—7-Methylenebicyclo-[3.3.1]nonan-3-one[45] (0.5 g, 3.3 mmol) was hydrogenated, and the product was isolated as described for **3**. 1-Adamantanol (0.5 g, 98% yield) was obtained.

***endo*-3-Methyl-7-hydroxybicyclo[3.3.1]non-2-ene (9).**—A mixture of **3** (0.75 g, 5 mmol), absolute ethanol (150 ml), and sodium borohydride (0.76 g, 20 mmol) was stirred at room temperature overnight. Water was added, and the product was extracted with chloroform. Evaporation of solvent from the dried solution provided **9** (0.4 g, 50% yield by glpc analysis): mp 32.5–33°; ir (CCl_4) 3580, 2950, 1430, 1380, 1350, 1300, 1200, 1110, 1070, 1060, 760, and 930 cm^{-1}; nmr δ 5.85 (indefinite d, 1 H), 3.95 (m, 1 H),[19,20,22,23] 2.9 (s, 1 H, exchangeable with D_2O), 2.5–1.5 (m, 13 H, sharp s at 1.65).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.04; H, 10.47.

1-Methyl-2-oxaadamantane (10). Procedure A.—A product mixture containing **9** (principal component, 0.15 g, 1 mmol) was heated at 100° in formic acid (3 ml) for 8 hr. After the mixture was cooled, ether (20 ml) and water (20 ml) were added. The organic layer was washed with 5% sodium carbonate and then water, dried, and freed of solvent. Glpc analysis indicated that the main product was **10** (0.13 g, 88% yield) whose spectral data were identical with previously reported values.[4]

Procedure B.—Compound **9** (0.288 g, 1.88 mmol) was hydrogenated as described for the hydrogenation of **3**. An 82% yield (0.23 g) of **10** was obtained.

Procedure C.—In an attempt to synthesize the acetyl derivative,[46] a mixture of **9** (2 g), acetic anhydride (25 ml), and zinc chloride (2 g) was heated at 95–105° for 1 hr. The cooled solution was quenched with ice water and extracted with ether. The ether layer, after being stirred overnight with 10% sodium bicarbonate, was separated, washed with water, dried, and freed of solvent. A dark brown liquid (1 g) was obtained which contained **10** as the major component (glpc).

Diazotization of 2.—Diazotization of **2** under various conditions was performed as described in the case of **1**, yielding **5**, **6**, **7**, and **8**. Compounds **5** and **6** were identified by comparison with authentic samples.[4] Compound **7** was identified by comparison with authentic material (*vide infra*). The ir spectra and glpc retention times were essentially identical. However, the nmr spectrum of the diazotization product indicated the presence of an impurity (about 10%, nmr absorption at δ 1.5–1.6). Compound **8** was identified by comparison with authentic material (*vide infra*). The ir spectra and glpc retention times were essentially identical (more thorough investigation was not carried out because of the paucity of material).

3-Hydroxymethylbicyclo[3.3.1]nonane (8) from 6.—Hydroboration[15] of **6** (1.3 g, 9.6 mmol) gave 1.1 g of liquid product. Glpc analysis indicated that **8** (0.91 g, 62% yield) was the principal component: ir (neat) 3420–3350, 2900, 2860, 1460, 1110, 1080, 1040, 1020, and 990 cm^{-1}; nmr δ 3.5 (d, 2 H, J = 4 Hz), 2.3–1.8 (m, 16 H, one exchangeable with D_2O).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.58; H, 12.01.

8 from 7.—Acetate **7**, obtained from diazotization of **2**, was hydrolyzed with 20% sodium hydroxide. The ir spectrum and glpc retention time of the product were essentially identical with those of the alcohol obtained from hydroboration of **6**. However, the nmr spectrum showed the presence of an impurity (about 10%, absorption at δ 1.5–1.6.

3-Acetoxymethylbicyclo[3.3.1]nonane (7) from 8.—A mixture of **8** (0.83 g, 5.4 mmol, obtained from **6**), zinc chloride (1 g, 7.3 mmol), and acetic anhydride (12.5 g) was stirred at 105° for 1 hr, then cooled, quenched with ice water, and extracted with ether.[46] The ether solution was stirred with 5% sodium carbonate for 5 hr at room temperature. After the ether layer was separated, washed with water, dried, and freed of solvent, crude **7** was obtained (1.1 g). Glpc analysis indicated 90% purity (92% yield). Product from glpc collection showed ir (neat) 2950, 2880, 1760, 1470, 1360, 1220, 1110, 1080, 1030, 980, and 885 cm^{-1}; nmr δ 3.9 (d, 2 H, J = 4 Hz), 2.1 (s, 3 H), 2.1–0.9 (m, 15 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.44; H, 10.26. Found: C, 73.67; H, 10.43.

Acknowledgment.—We are grateful to the National Science Foundation and the Graduate School of the University of Wisconsin—Milwaukee for support of this work. We thank Drs. G. B. Gill and W. H. W. Lunn for spectral data on 4-protoadamantanone.

Registry No.—**1**, 34650-78-7; **2**, 37445-20-8; **3**, 38339-46-7; **6**, 19437-17-3; **7**, 41189-05-3; **8**, 19490-36-9; **9**, 41189-07-5; **10**, 6508-22-1; isoamyl nitrite, 110-46-3.

(45) We are grateful to Drs. A. R. Gagneux and K. Scheibli for a sample of this material.

(46) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1962, p 380.

Thermal and Photochemical Reactions of Some Bicyclic Aziridine Enol Ethers[1a]

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Acid–base-catalyzed, thermal, and photochemical rearrangements of some bicyclic aziridine enol ethers are described. For example, 6-phenyl-2,4-bis(benzhydrylidene)-3,5-dioxa-1-azabicyclo[4.1.0]heptane (**3a**), an azirine–ketene adduct, rearranges on alumina to give dioxazepine **4**, which undergoes a further transformation to yield lactone **6**. The latter is converted to the isomeric 1,3 diketone **8** on treatment with alcoholic base. On the other hand, thermolysis of **3a** at 140–150° gives the seven-membered ring diether **15a**, an isomer of **4**, and lactone **16a**, an isomer of **6**. Dioxazepine **15a** rearranges to **16a** on further heating while **15c** leads to the five-membered lactone **19c**. Photolysis of **3a** at 310 nm results in the formation of a mixture of compounds from which **15a** and **16a** are isolated. Further photolysis of **15a** affords **16a**. These results are discussed. The mechanistic pathway for both pyrolysis and photolysis involves R–O cleavage of a cyclic enol ether C=C—O—R followed by O–C or C–C ring closure with rearrangement of R.

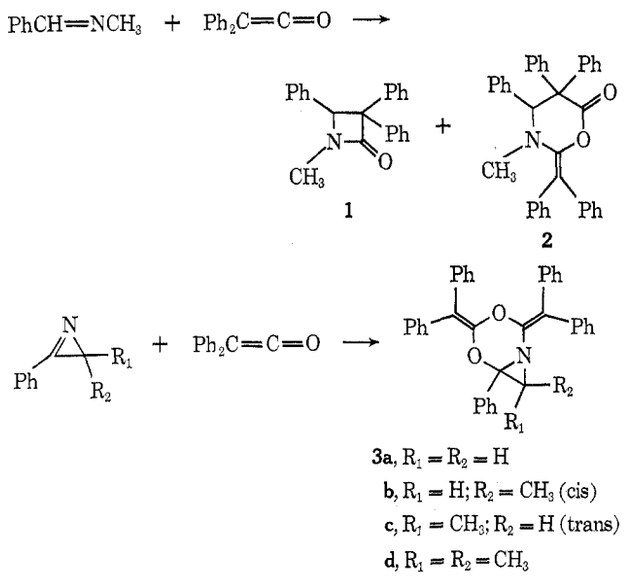
Imines have been shown to react with ketenes to yield 1:1 and/or 1:2 adducts of structures of type **1** and **2**, respectively.[2] In contrast, we have found that a number of 1-azirines react with diphenylketene to give 1:2 cycloadducts that possess the dioxa-1-azabicycloheptane structure **3**.[3]

One interesting feature of this novel heterocyclic system is that it contains a variety of functional groups. Of special interest would be the comparison of the thermal and photolytic behavior of this fused three-

(1) (a) Cycloaddition Reactions. XIV. For paper XIII in this series see A. Hassner and D. J. Anderson, *J. Org. Chem.*, **38**, 2565 (1973). (b) On sabbatical leave from the American University of Beirut, Beirut, Lebanon.

(2) (a) R. Huisgen, B. A. Davis, and M. Morikam, *Angew. Chem., Int. Ed. Engl.*, **1**, 826 (1968); (b) F. Duran and L. Ghosez, *Tetrahedron Lett.*, 245 (1970); (c) J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, Jr., *J. Org. Chem.*, **36**, 2211 (1971); H. B. Kagan and J. L. Luche, *Tetrahedron Lett.*, 3093 (1968), and other papers in the series.

(3) A. Hassner, A. S. Miller, and M. J. Haddadin, *Tetrahedron Lett.*, 1353 (1972).

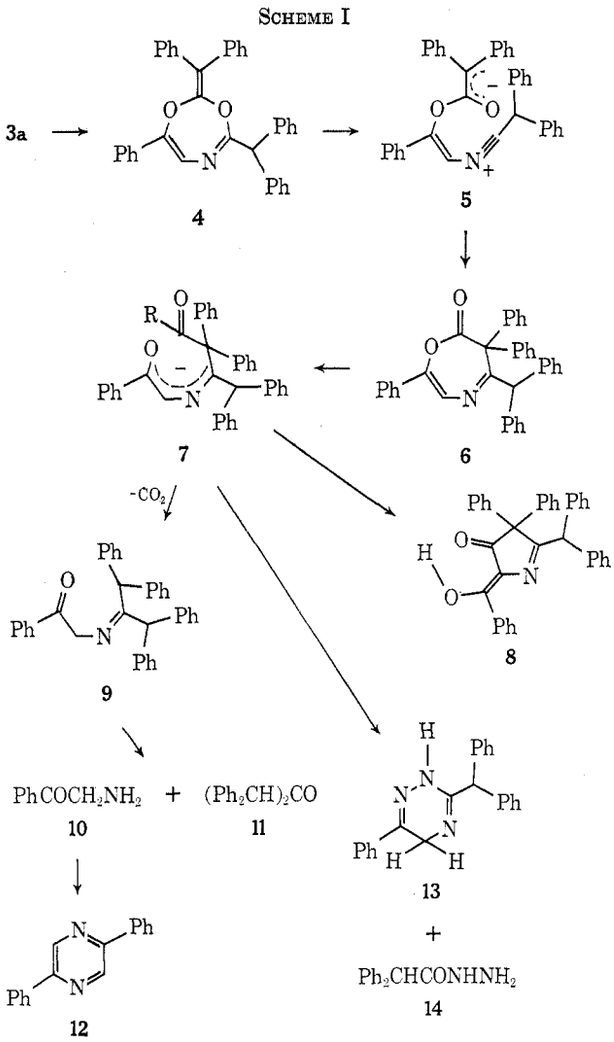


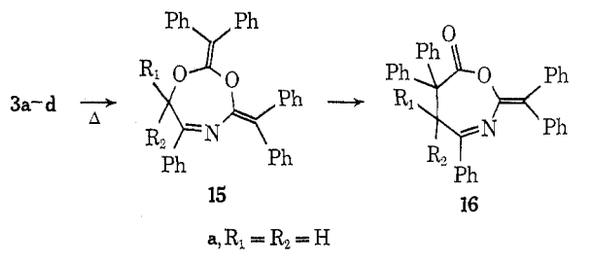
membered ring system with that of simpler aziridines that were studied recently.[4]

Results

Acid–Base Reactions.—Chromatography of dioxazabicycloheptane **3a** on a neutral alumina column or on silica gel resulted in a rearrangement to dioxazepine **4**, the structural proof of which has already been reported.[3] Furthermore, it was found that the fate of aziridine **3a** depended on the duration of contact with alumina. If a concentrated benzene solution of **3a** was left on the chromatography column for 30 min prior to elution, the isolated product was lactone **6** and not dioxazepine **4**. The latter was also converted to lactone **6** on treatment of a benzene solution of **4** with alumina (Scheme I). Lactone **6** showed an infrared carbonyl absorption at 1750 cm^{-1} and a vinyl ester function at 1130 cm^{-1}; its nmr spectrum exhibited a singlet at τ 4.75 (1 H) in addition to the aromatic protons; the mass spectrum gave a strong parent peak at *m/e* 505. Treatment of lactone **6** with methanolic potassium hydroxide transformed it into 1,3 diketone **8** as the major product; 1,1,3,3-tetraphenyl-2-propanone (**11**)[5] and traces of 2,5-diphenylpyrazine (**12**), identified by comparison with an authentic sample, were also isolated. 1,3 diketone **8** gave a blue-green complex with ferric ions, and showed broad infrared carbonyl bands typical of 1,3 diketones (1660–1575 cm^{-1}). Analogous ring contraction reactions are discussed below. The reaction of lactone **6** with hydrazine proceeded to furnish dihydrotriazine **13** and diphenylacethydrazide **14** in good yield. The structure of **13** was established by spectroscopic data, and that of **14** by comparison with an authentic sample.

Thermolysis.—The dioxazabicycloheptanes **3a–d** were found to be thermally labile. When a diglyme solution of **3a** was heated at 140–150° for 3 min, a mixture composed of starting material, dioxazepine **15a**, and oxazepinone **16a** was obtained. The identity of each component was evident from its infrared spectrum. Separation of this mixture was effected by thick layer chromatography, whereby the starting material was isolated as the rearranged dioxazepine **4**. Attempts to effect the rearrangement of **3a** into **15a**, as the only product,





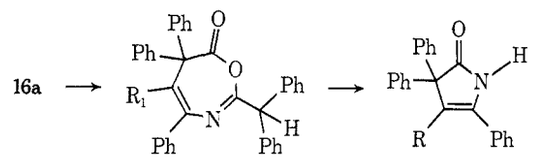
revealed that the reaction did not proceed to a reasonable extent at temperatures below 130°. Furthermore, it was found that **15a** rearranged into **16a** when heated above its melting point (128°). This fact made the isolation of **15a** from **3a** without the formation of **16a** rather difficult. However, the heating of a triglyme solution of **3a** at 180–190[4] yielded oxazepinone **16a**, in 45% yield, as the only isolable product. The structure of dioxazepine **15a** was established by its mass spectrum parent peak at *m/e* 505, infrared absorptions at 1738 (m), 1668 (s), and 1598 cm^{-1} (w) (see Discussion), and nmr singlets at τ 5.1 (1 H),

(4) (a) R. Huisgen and H. Maeder, *J. Amer. Chem. Soc.*, **93**, 1777 (1971); (b) A. Padwa, J. Smolanoff, and S. I. Wetmore, Jr., *Chem. Commun.*, 410 (1972), and references cited therein.

(5) D. C. Dean, W. B. Dickinson, O. R. Quayle, and C. T. Lester, *J. Amer. Chem. Soc.*, **72**, 1740 (1950).

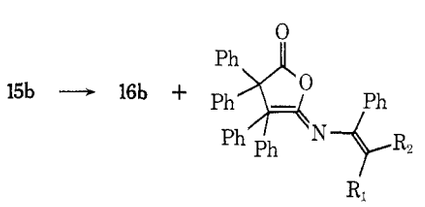
4.75 (1 H), and 2.25–2.82 (m, 25 H). Coupling of the methylene protons in **15a** was not detected on the A-60A nmr instrument.

Oxazepinone **16a** showed a parent peak at *m/e* 505 and $M^+ - CO_2$ at *m/e* 477, vinyl lactone absorptions at 1752 and 1150 cm^{-1} in the infrared, and an nmr singlet at τ 5.9 (broad s, 2 H) in addition to the aromatic protons. Treatment of oxazepinone **16a** with acid effected a 1,5-prototropic shift and gave isomer **17a**, the structure of which was established by spectroscopic data. The reaction of **16a** or **17a** with alcoholic potassium hydroxide afforded enaminoamide **18a**[6] in a quantitative yield and diphenylacetic acid,



both of which were identified by comparison with authentic samples.

The behavior of **3b,c** on heating at 140-150° was analogous to that of **3a**. Dioxazepine **15b** and oxazepinone **16b** were isolated, although in this case **15b** was the major product (15% yield) and **16b** formed only in traces. The heating of dioxazepine **15b** in triglyme at 180–190° for 3 min afforded **16b** as the major product, and a mixture of cis (**19a**) (R_1 = H; R_2 = CH_3) and trans (**19b**) (R_1 = CH_3; R_2 = H)



isomers in a 2:5 ratio (nmr). The structure of **19a,b** was based on a parent peak at *m/e* 519 in the mass spectrum, infrared bands at 1812, 1710, and 690 cm^{-1}, and nmr doublets at τ 8.62 (J = 7 Hz) and 8.3 (J = 7 Hz), a quartet at 4.5, and the aromatic protons at 2.5–2.9 (25 H) (see Discussion). Treatment of **16b** with methanolic base gave enaminoamide **18b** and diphenylacetic acid. Similarly, dioxazabicycloheptane **3d** yielded dioxazepine **15c** on heating at 140–150°. The spectroscopic properties of **15c** were consistent with the assigned structure. Further heating of dioxazepine **15c** at 180–190° gave imino lactone **19c** as the only isolable product in 50% yield. The spectroscopic properties of **19c** were analogous to those of **19b**.

Photolysis.—Irradiation of a benzene solution of bicyclic aziridine **3a–d** with a Rayonet 310-nm lamp gave a mixture of products in each case. Separation by column or thick layer chromatography on neutral alumina or silica gel afforded **15a**, **15b**, **15c**, and oxazepinones **16a** and **16b** from the corresponding bicyclic aziridines. Dioxazepines **15a**, **15b**, and **15c** were the major products of photolysis. Preparatively, photolysis of **3a** constituted a better route to **15a** than the thermal reaction mentioned above. These dioxazepines (**15a** and **15b**) were found to be converted to oxazepinones **16a** and **16b** on further photolysis. Whereas **3d** was rearranged to **15c**, the latter was recovered unchanged. Prolonged photolysis of **15c** (24 hr) resulted in the formation of polymeric material. Unlike thermolysis, photolysis of **3d** or **15c** for 4 hr did not yield any detectable amount (by tlc) of **19c**.

Discussion

Although the bicyclic aziridine systems **3a–d** contain a number of functional groups, it is reasonable to assume that the above rearrangements are initiated at the labile aminal function. This would be especially true in ionic reactions because of the availability of an unshared pair of electrons on either nitrogen or oxygen. For example, the rearrangement of **3a** into dioxazepine **4** is probably initiated by the interaction of alumina with the basic nitrogen in **3a**. Such a reaction pathway is supported by the fact that the rearrangement was reported[7] to proceed in a dry hydrogen chloride–benzene solution, and by the findings that bicyclic aziridines **3b–d** are stable on an alumina chromatography column. Such stability is maintained owing to the steric interaction imposed by the R substituents in **3b–d** toward an incoming electrophile.

The formation of lactone **6** can be postulated to arise from a reverse Ritter-type reaction to yield intermediate **5** (Scheme I), which undergoes a carbon–carbon ring closure to give the thermodynamically stable lactone **6** as compared to **4**. The possibility that lactone **6** is derived from **4** gains support from the fact that dioxazepine **4** on alumina was found to rearrange to **6**.

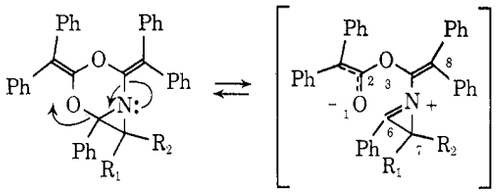
The ring contraction of lactone **6** into 1,3 diketone **8** is envisaged to occur by a methoxide attack on the carbonyl group followed by an intramolecular displacement of the methoxide ion by the enolate carbon [**6** → **7** (R = OCH_3) → **8**]. A possible route to side products **11** and **12** (namely hydrolysis of intermediate **9**) is shown in Scheme I. Furthermore, dihydrotriazine **13** most likely arises through intermediate **7** (R = $NHNH_2$) and subsequent reaction of the protonated **7** with another mole of hydrazine.

It should be noted that the formation of **4** as well as of **6** is the result of that C—N bond cleavage in **3** which marks the original C=N in the azirine. On the other hand, the thermal products **15** and **16** arise from cleavage of what was the original C—N bond in the azirine precursor.

The pyrolysis products **15a**, **15b**, **15c**, **16a**, and **16b** can best be explained to be formed from **3** *via* the common intermediate **20**. An intramolecular attack by enolate anion *via* oxygen upon C_7 gives dioxazepines **15**, while a similar attack of the same anion through carbon leads to oxazepinone **16**. It is interesting to note that **20** is also the postulated intermediate in the formation of **3a–d** from 1-azirines and diphenylketene.[3]

(6) F. R. Japp and F. Klingeman, *J. Chem. Soc.*, **57**, 662 (1890).

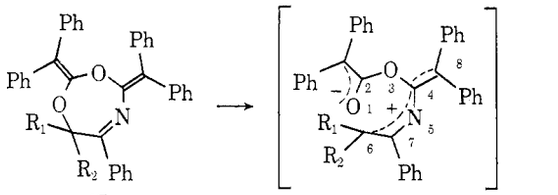
(7) A. S. Miller, Ph.D. Thesis, The University of Colorado, Boulder, Colorado, 1971.



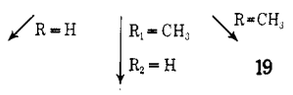
3 20

15 + 16

Moreover, the thermal isomerization of **15** to lactones **16a**, **16b**, and **19a–c** above 140° can be postulated to



15 21



16 19

16 + 19

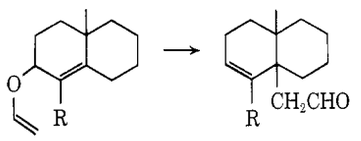
occur through the common intermediate **21**, whereby oxazepinone **16** is the result of an attack of the carbon of the enolate anion on C_7, and product **19** is produced *via* the same attack on C_8.

It is imperative to stipulate at this point that the thermolysis of **3a–d** most likely proceeds *via* diradical intermediates analogous to **20** and **21** and the ionic forms **20** and **21** are merely used here for easier illustration. A free-radical mechanism would be analogous to that involved in the thermal rearrangement of α-alkoxystyrenes into alkyl phenyl ketones,[8] for which Wiberg and coworkers[9] have presented evidence in support of a chain radical process. The thermal isomerizations of **4** to **6** and **15** to **16** further illustrate the preference for C—C *vs* C—O bond formation for the system C—O—C=C → O=C—C—C.

As mentioned above, dioxazepines **15a,b** are rearranged, on heating, into oxazepinones **16a,b**. Whether **15a,b** also are intermediates in the thermal transformation of **3a–c** at 180–190° into **16a,b** cannot be discerned from the above results. However, it seems likely that dioxazepines **15b,c** are intermediates in the formation of imino lactone **19**. Whereast he five-membered ring lactone **19** was found to be the predominant product from either **3d** or **15c** ($R_1 = R_2 = CH_3$), it was only the minor product (**19a,b**) from the monomethyl derivative **15b**, and was not detected at all in the thermolysis of the demethyl system **3a** or **15a**. These facts indicate that so long as the steric bulk at C_7 is not great as in the case of $R_1 = R_2 = H$ or $R = CH_3$ and $R_2 = H$ in intermediate **21**, carbon–carbon bond formation at that site is preferred. However, if two CH_3 substituents are present, positions 6 and 8 become sterically equivalent and ring closure occurs at the site of the most stable radical or carbonium ion, namely C_8, and hence product **19** results.

Much of the evidence in support of the structural assignments of dioxazepines **15a–c** and imino lactones **19a–c** rests on spectroscopic data and mass spectra. The infrared spectra of **15a–c** showed three equally spaced bands at 1735, 1668, and 1600 cm^{-1} which were medium, strong, and weak in intensity, respectively. Although the band at 1735 cm^{-1} is unusually high for an enol ether, cyclic ketene acetals have been recently reported to show intense bands near 1730 cm^{-1},[10] and a similar pattern probably due to coupling or Fermi resonance[10] is found in the ir spectrum of **3** with medium, strong, and weak bands at 1665, 1630, and 1595 cm^{-1}, respectively. The mass spectrum of **19c** showed a host of peaks at *m/e* 333, 332, 331, 330, 329, and 256, 255, 253, 252, and 179, 178, 177. Such peaks can be explained to be due to the ions of the fragment Ph_2CCPh_2, which undergoes two consecutive losses of phenyl groups.

Moreover, the recent report by Dauben and Dietsche[11] on the thermolysis of vinyl ethers of type **22** to yield **23** bears a close analogy to the rearrangement of **15** to **19**.



22 23

The present photochemical investigation was initiated when it was observed that the colorless bicyclic aziridines **3a–c** developed a yellow color on standing in daylight for some weeks. Since these compounds exhibit strong maxima in the ultraviolet in the regions of 310 and 260 nm, we chose to irradiate **3a–d** at the former wavelength. We observed the formation of the same products which were isolated from the thermal reactions of these bicyclic aziridines. These results can be rationalized through biradical or ionic intermediates of type **20** and **21**. It is obvious that such a system (**3a–d**) is rich with photolabile functions, and hence no conclusive mechanistic evidence can be drawn from this preliminary study. Yet, based on the careful work of Baldwin and Walker[12] on the mechanism of the photoreactions of phenylketene acetals (**24** → **25** and **26**), it is reasonable to postulate that a similar homolytic decomposition of the C_1—O bond in the photoexcited **3a–d** initiates the formation of a biradical intermediate (related to **20**) which recombines through a C—O or C—C bond formation to give **15** or **16**.

$$\underset{\mathbf{24}}{PhCH{=}C(OEt)_2} \xrightarrow{h\nu} \underset{\mathbf{25}}{PhCH_2CO_2Et} + \underset{\mathbf{26}}{PhCHEtCO_2Et}$$

Moreover, the phototransformation of **15a,b** into **16a** and **16b**, respectively, can be traced to the homo-

(8) (a) L. Claisen, *Chem. Ber.*, **29**, 2931 (1896); (b) L. Claisen and E. Haase, *ibid.*, **33**, 3778 (1900); (c) F. H. MacDougall, W. M. Lauer, and M. A. Spielman, *J. Amer. Chem. Soc.*, **55**, 4089 (1933).

(9) (a) K. W. Wiberg and K. I. Rowland, *ibid.*, **77**, 1159 (1955); K. W. Wiberg, T. M. Shryne, and R. R. Kintner, *ibid.*, **79**, 3160 (1957); (c) K. W. Wiberg, R. R. Kintner, and M. L. Motell, *ibid.*, **85**, 450 (1963).

(10) W. G. Bentrude, W. D. Johnson, and W. A. Kahn, *ibid.*, **94**, 3058 (1972); K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 19.

(11) W. G. Dauben and T. J. Dietsche, *J. Org. Chem.*, **37**, 1212 (1972). The chemistry of enol ethers has been reviewed by F. Effenberger, *Angew. Chem., Int. Ed. Engl.*, **8**, 295 (1969).

(12) J. E. Baldwin and L. E. Walker, *J. Amer. Chem. Soc.*, **88**, 3769, 4191 (1966).

lytic cleavage of the C—O bisallylic bond in **15** to give diradical (or ion) **21**.

The photochemical behavior of bicyclic aziridines **3a–d** under varied wavelength and solvent conditions should await further investigation. Finally, it is interesting to note that compounds **3a**, **4**, **6**, **8**, **15a**, **16a**, and **17a** are all structural isomers.

Experimental Section[13]

2-Benzhydrylidene-4-diphenylmethyl-7-phenyl-1,3,5-dioxazepine (4).—6-Phenyl-2,4-bis(benzhydrylidene)-3,5-dioxa-1-azabicyclo[4.1.0]heptane[1a] (**3a**) (1 g) was dissolved in benzene (5 ml) and poured onto a neutral alumina column (30 g). Elution with Skellysolve F–benzene (1:1) yielded 2-benzhydrylidene-4-diphenylmethyl-7-phenyl-1,3,5-dioxazepine (**4**), 0.3 g (33% yield), mp 178–180°. The analytical sample (benzene–methanol) melted at 180–181°. The yield of **4** varies with the rate of elution; the longer the starting material is left on the column the lower the yield of **4** and the higher that of product **6** (see below). Further elution with benzene–chloroform gave *N*-phenacyldiphenylacetamide, the identity of which was established by comparison with an authentic sample. **4**: ir 1670, 1600 (w), 1498, 1210, 1150, 1120, 1010, 770, 730, and 705 cm^{-1}; nmr τ 3.35 (s, 1 H), 2.62–3.22 (m, 25 H); mass spectrum M^+ 311, 310, 206, 195, 194, 179, 178, 167, 166, 165, 152, 105, 78, 77.

Anal. Calcd for $C_{36}H_{27}O_2N$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.38; H, 5.35; N, 2.81.

Rearrangement of 3a or 4 into 2,6,6-Triphenyl-5-diphenylmethyl-7*H*-1,4-oxazepin-7-one (6).—1,3,5-Dioxazepine **4** (0.3 g) was dissolved in hot benzene (40 ml). Neutral alumina (20 g) was added and the hot solution was stirred for 1 hr at room temperature. The solution was filtered, and the alumina was washed with dichloromethane (100 ml). The filtrate was evaporated, and the residue was recrystallized from methanol: rocky crystals; 80 mg (27% yield); mp 214–215°; ir 1750, 1670 (w), 1500, 1130, 1030, 910, 770, 750, and 710 cm^{-1}; nmr τ 2.75 (s, 1 H), 2.8 (m, 26 H); mass spectrum M^+ 505, 477, 400, 384, 372, 310, 294, 282, 267, 252, 206, 195, 194, 179, 167, 166, 165, 152, 105, 91, 77.

Anal. Calcd for $C_{36}H_{27}O_2N$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.55; H, 5.50; N, 2.62.

Oxazepinone **6** was directly obtained from **3a** by placing a warm benzene solution of the latter (2.5 g in 40 ml) on a neutral alumina column (60 g) that was prepared in Skellysolve F–benzene (1:1). After the column was left to stand at room temperature for 2 hr, elution with benzene (400 ml) followed by dichloromethane (500 ml) and evaporation of the fractions yielded 0.7 g of oxazepinone **6**.

Rearrangement of Oxazepinone 6 into 2-Benzoyl-4-diphenylmethyl-5,5-diphenyl-3-aza-3-cyclopentenone (8).—Oxazepinone **6** (0.25 g) was placed in 5% methanolic potassium hydroxide (20 ml). The slurry was heated on the steam bath for 15 min, during which the starting material dissolved and the solution turned bright yellow. Dilution with water resulted in the precipitation of a gummy yellow residue which was collected by filtration and treated with hot methanol (10 ml). Acidification of the solution with acetic acid resulted in the formation of a cream-colored solid, which was collected by suction filtration and washed with cold methanol. Recrystallization of this solid from benzene–methanol gave prismatic yellow needles (0.15 g, 60% yield) of 1,3 diketone **8**: mp 212–213°; ir 1660, 1610, 1575, 1495, 1350, 1160, 1100, 820, 750, 730, and 700 cm^{-1}; nmr τ 4.82 (s, 1 H), 2.3–2.8 (m, 24 H), −0.6 (m, 2 H); mass spectrum M^+ 505, 477, 400, 338, 310, 268, 267, 265, 252, 208, 206, 194, 178, 167, 166, 165, 152, 105, 91, 77.

Anal. Calcd for $C_{36}H_{27}O_2N$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.52; H, 5.16; N, 2.71.

Concentration of the mother liquor gave 1,1,3,3-tetraphenylpropanone (20 mg): mp 132° (lit. mp 132°);[5] ir 1710, 1500, 1180, 1160, 740, and 710 cm^{-1}; nmr τ 4.7 (s, 2 H), 2.7 (m, 20 H). Examination of the mother liquor on a thin layer plate showed the presence of 2,5-diphenylpyrazine, the identity of which was established by comparison with an authentic sample.

Reaction of Oxazepinone 6 with Hydrazine.—Oxazepinone **6** (50 mg) was dissolved in hot methanol. A solution of 95% hydrazine (2 ml) was added to the solution, which was heated on the steam bath for 5 min and diluted with water to the incipient point. 2-Diphenylmethyl-5-phenyl-1*H*,4*H*-1,3,6-triazine (**13**) (25 mg, 78% yield) was collected, mp 173–175°. The analytical sample (methanol) melted at 176–177: ir 3200, 1630, 1500, 1350, 1300, 1240, 1090, 1020, 990, 770, 730, and 700 cm^{-1}; nmr τ 5.68 (s, 2 H), 4.82 (s, 1 H), 2.55–2.8 (m, 13 H), 2.2–2.35 (m, 2 H). (the singlet at τ 4.82 was exchanged with D_2O in traces of sodium methoxide); mass spectrum M^+ 325, 324, 310, 234, 220, 194, 193, 166, 164, 152, 104, 103, 77.

Anal. Calcd for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91. Found: C, 81.35; H, 5.92; N, 13.18.

Evaporation of the mother liquor of the above reaction gave a residue which was composed of triazine **13** and diphenylacethydrazide. The identity of the latter was confirmed by comparison with an authentic sample.

Thermal Conversion of Bicyclic Aziridine 3a into Oxazepinone 16a or 16a and 1,3,5-Dioxazepine 15a.—Dioxazabicycloheptane **3a** (2 g) was dissolved in triglyme, and the solution was heated at 180–190° for 3 min. The cold, bright yellow solution was diluted with water, and the resulting yellow gum was isolated by decantation of the solvent followed by treatment with hot methanol. The yellow product was collected and recrystallized from benzene–methanol to afford 0.9 g of oxazepinone **16a**, mp 221–222°. The product was identical with that obtained by the photolysis of **3a**.

The above reaction was performed on 0.5 g of **3a** in diglyme at 140–150°, and the resulting yellowish gum was found, by infrared, to be a mixture of the starting material **3a**, 2,4-bis(benzhydrylidene)-6-phenyl-7*H*-1,3,5-dioxazepin (**15a**), and 2-benzhydrylidene-4,6,6-triphenyl-5*H*,7*H*-1,3-oxazepin-7-one (**16a**). Repeated thin layer chromatography of the above mixture on silica gel gave 1,3,5-dioxazepine **4** (rearrangement product from **3a**), 1,3,5-dioxazepine **15a**, and 1,3-oxazepin-7-one **16a** in very low yields. **15a**, which was prepared in a better yield from the photolysis of **3a**, was rearranged completely into **16a** on heating (in diglyme) at 140–150°.

Rearrangement of Oxazepinone 16a into 2-Diphenylmethyl-4,6,6-triphenyl-7*H*-1,3-oxazepin-7-one (17a).—Oxazepinone **16a** (0.7 g) was dissolved in hot benzene (50 ml) to which acetic acid was added (5 ml). The solution was refluxed on the steam bath for 3 hr. Evaporation of benzene left a yellowish syrup which was washed with water. The gummy product was treated with hot methanol, and the resulting white solid was collected, washed with methanol, and recrystallized from benzene–methanol as rocky white crystals: 0.5 g; mp 176–177°; ir 1768, 1665, 1600 (w), 1495, 1380, 1090, 1080, 770, 740, and 710 cm^{-1}; nmr τ 5.35 (s, 1 H), 3.66 (s, 1 H), 2.5–3.1 (m, 23 H), 2.2–2.45 (m, 2 H); mass spectrum M^+ 505, 477, 461, 384, 358, 311, 310, 295, 294, 283, 282, 269, 268, 267, 265, 253, 252, 207, 194, 191, 179, 178, 169, 168, 167, 165, 152, 132, 105, 91, 78, 77.

Anal. Calcd for $C_{36}H_{27}O_2N$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.31; H, 5.50; N, 2.79.

Conversion of Oxazepinone 16a or Oxazepinone 17a into 2,4,4-Triphenyl-2-pyrrolin-5-one (18a) and Diphenylacetic Acid.—Oxazepinone **16a** (70 mg) was dissolved in 3% methanolic potassium hydroxide (30 ml). The solution was refluxed on the steam bath until it became colorless (20 min). Concentration of the solvent (5 ml) and dilution with water to the incipient point of precipitation gave a white solid (**18a**) which was collected by suction filtration, washed with water, and dried (42 mg), mp 226–228°. The product was identical with an authentic sample of 2,4,4-triphenyl-2-pyrrolin-5-one.[6] Acidification of the mother liquor, extraction with chloroform, and evaporation of the latter gave diphenylacetic acid (18 mg), identified by comparison with a known sample.

Similarly, oxazepinone **17a** (50 mg) was treated with 3% methanolic potassium hydroxide and product **18a** and diphenylacetic acid were isolated.

The same procedure was used in the conversion of oxazepinone **16b** (0.24 g) into 2,4,4-triphenyl-3-methyl-2-pyrrolin-5-one (**18b**, 0.12 g). The product was recrystallized from benzene–acetone: 120 mg; mp 238–240°; ir 3190, 1695, 1500, 1315, 1190, 780, 765, and 705 cm^{-1}; nmr τ 8.18 (5, 3 H), 2.5–2.8 (m, 15 H); mass spectrum M^+ 325, 310, 296, 282, 267, 265, 248, 223, 222, 220, 205, 204, 203, 202, 191, 189, 179, 178, 165, 115, 104, 91, 77.

(13) All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were measured in Nujol on a Perkin-Elmer 451 grating spectrometer. Nmr spectra were taken in deuterated chloroform with TMS as an internal reference using a Varian A-60A spectrometer. Mass spectra were determined on a Varian M.A.T. CH-5 instrument. Elemental analyses were performed at the Galbraith Laboratories, Inc.

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 85.03; H, 5.92; N, 4.15.

Thermal Rearrangement of 3b,c into 2,4-Bis(benzhydrylidene)-6-phenyl-7-methyl-7*H*-1,3-dioxazepine (15b) or 2-Benzhydrylidene-5-methyl-4,6,6-triphenyl-5*H*,7*H*-1,3-oxazepin-7-one (16b).—Dioxazabicycloheptane **3b,c** (1 g of cis–trans 2:1 mixture) was dissolved in diglyme (6 ml) and the solution was refluxed at 140–150° for 2 min. Water was added to the cold solution and the supernatant liquid was decanted. The yellow gum was dissolved in benzene (5 ml) and chromatographed on a column of neutral alumina (20 g) that was prepared in Skellysolve F–benzene (1:1). Elution with the latter solvent mixture and evaporation of the fractions gave dioxazepine **15b** (150 mg). The product was recrystallized from methanol: mp 154°; ir 1735 (m), 1668 (s), 1600 (w), 1495, 1250, 1215, 1155, 1045, 1020, 775, and 700 cm^{-1}; nmr τ 8.3 (d, 3 H, J = 8 Hz), 4.5 (q, 1 H, J = 8 Hz), 2.2–3 (m, 25 H); mass spectrum M^+ 519, 491, 475, 337, 332, 325, 311, 310, 297, 296, 282, 269, 266, 253, 252, 232, 220, 219, 195, 194, 193, 178, 177, 167, 166, 165, 164, 152, 133, 118, 117, 116, 115, 105, 91, 77.

Anal. Calcd for $C_{37}H_{29}O_2N$: C, 85.52; H, 5.63; N, 2.70. Found: C, 85.56; H, 5.72; N, 2.70.

When the above reaction was conducted in triglyme at 180–190° the isolated product was 1,3-oxazepin-7-one **16b**, 46% yield, as yellow, hard needles from benzene–methanol: mp 223–225°; ir 1765, 1600 (w), 1495, 1172, 1165, 1128, 780, 755, 710, and 698 cm^{-1}; nmr τ 8.3 (d, 3 H, J = 8 Hz), 5.3 (q, 1 H, J = 8 Hz), 3.4–3.7 (m, 2 H), 2.5–3.0 (m, 23 H), 2.0–2.28 (m, 2 H); mass spectrum M^+ 519, 491, 475, 327, 325, 309, 297, 296, 283, 282, 281, 280, 268, 267, 266, 265, 221, 195, 194, 193, 178, 168, 167, 165, 117, 105, 91, 77.

Anal. Calcd for $C_{37}H_{29}O_2N$: C, 85.52; H, 5.63; N, 2.70. Found: C, 85.81; H, 5.56; N, 2.79.

Thermal Rearrangement of Dioxazepine 15b into Oxazepinone 16b and Tetraphenyl-*N*-(1-phenylpropene)iminosuccinic Anhydride (19a,b).—Dioxazepine **15b** (150 mg) was heated in triglyme (2 ml) at reflux temperature for 1 min. The solution turned bright yellow, and the cold solution was diluted with water. The resulting curdy yellow solid was collected by filtration. Thin layer chromatography on silica gel, with benzene as the eluent, indicated the formation of two products only, one yellow and the other colorless. The crude product was treated with Skellysolve F and the insoluble yellow solid was found to be oxazepinone **16b** (110 mg, 73% yield). Evaporation of Skellysolve left a whitish residue which upon rubbing with methanol gave a solid that melted at 178–185°, an indication of a mixture. Nmr showed two doublets for the methyl group suggestive of a cis–trans mixture of **19a,b** in a ratio of 2:5: ir 1812 (m), 1710 (s), 1640 (w), 1600 (w), 1495, 1200, 1100, 1080, 970 (s), 960 (s), 760, 720, 712, 710, and 700 cm^{-1}; mass spectrum M^+ 519, 491 (w), 332, 309, 256, 255, 254, 194, 193, 180, 179, 178, 177, 166, 165, 117, 105, 91, 77.

Thermal Rearrangement of 3d into 2,4-Bis(benzhydrylidene)-6-phenyl-7,7-dimethyl-7*H*-1,3,5-dioxazepine (15c) or into 19c.—Dioxazabicycloheptane **3d** (0.5 g) was dissolved in diglyme (3 ml) and the solution was heated at 140–150° for 5 min. The cold solution was diluted with water (5 ml) and the resulting solid was filtered, washed with methanol, and dried, 0.3 g (60% yield) of **15c**. Recrystallization from methanol gave needles that melted at 145°: ir 1738 (m), 1665 (s), 1595 (w), 1490, 1255, 1220, 1210, 1155, 1045, 1021, 960, 920, 770, 750, and 705 cm^{-1}; nmr τ 8.33 (s, 6 H), 2.3–3.1 (m, 25 H); mass spectrum M^+ 533, 351, 339, 324, 323, 195, 194, 166, 165, 131, 129, 116, 105, 91, 77.

Anal. Calcd for $C_{38}H_{31}O_2N$: C, 85.52; H, 5.86; N, 2.62. Found: C, 85.42; H, 5.81; N, 2.51.

Thin layer chromatography of the residue from the mother liquor did not yield any detectable oxazepinone **16c**.

Similarly, the heating of a triglyme solution of 6-phenyl-2,4-bis(benzhydrylidene)-7,7-dimethyl-3,5-dioxa-1-azabicyclo[4.1 0]-heptane (**3d**, 100 mg) at 180–190° gave tetraphenyl-*N*-(1-phenyl-2-methylpropylene)iminosuccinic anhydride (**19c**, 60 mg). Recrystallization of the product from benzene–methanol gave 60 mg of white, hard prisms of **19c**, mp 211–213°. Thin layer chromatography of the residue from the mother liquor did not yield any traceable products other than **19c**: ir 1810 (m), 1705 (s), 1600 (w), 1495, 1225, 1140, 1120, 1110, 1070, 990, 770, and 710 cm^{-1}; nmr τ 8.6 (s, 3 H), 8.33 (s, 3 H), 2.65–3.9 (m, which included three sharp singlets, 25 H); mass spectrum M^+ 533, 505 (w), 489 (w), 350, 339, 333, 332, 331, 330, 329, 324, 323, 311, 256, 255, 254, 253, 252, 240, 239, 238, 234, 195, 194, 181, 180, 179, 178, 177, 166, 165, 152, 131, 119, 116, 115, 105, 104, 103, 91, 77.

Anal. Calcd for $C_{38}H_{31}O_2N$: C, 85.52; H, 5.86; N, 2.62. Found: C, 85.70; H, 6.01; N, 2.50.

Conversion of Dioxazepine 15c into 19c.—Heating of dioxazepine **15c** (40 mg) in triglyme (0.5 ml) at 180–190° for 5 min produced 20 mg of **19c** after crystallization from methanol–acetone.

Thin layer chromatography on silica gel or alumina did not furnish evidence for the formation of oxazepinone **16c**.

Photolysis of **15c** at 310 nm in benzene for 4.5 hr at 15° gave mainly starting material. Further photolysis for 24 hr yielded polymeric material and traces of the starting material.

Photolysis of Dioxazabicycloheptanes 3a–d.—Dioxazabicycloheptane **3a** (1 g) was dissolved in benzene (600 ml) and the solution was irradiated with a 310-nm light for 7 hr at 15°. The resulting bright yellow solution was concentrated to 4 ml and poured onto a neutral alumina (30 g) column that was preprepared in Skellysolve F. Elution with Skellysolve F–benzene (1:1) gave 2,4-bis(benzhydrylidene)-6-phenyl-7*H*-1,3,5-dioxazepine (**15a**). Recrystallization of the product from methanol yielded needles (65 mg) that melted at 127–128°. Further elution with benzene–dichloromethane (2:1, 1:1) gave 2-benzhydrylidene-4,6,6-triphenyl-5*H*,7*H*-1,3-oxazepin-7-one (**16a**), which after recrystallization from benzene–methanol was collected as yellow, short needles (95 mg), mp 221–222°. In some cases, traces of product **16a** were isolated.

Product **15a** had ir 1738 (m), 1668 (s), 1615 (w), 1598 (w), 1495, 1240, 1215, 1160, 1040, 1020, 870, and 710 cm^{-1}; nmr τ 5.1 (s, 1 H), 4.75 (s, 1 H), 2.25–2.82 (m, 25 H); mass spectrum M^+ 505, 477, 461, 311, 310, 296, 295, 294, 284, 283, 268, 267, 266, 254, 253, 252, 224, 208, 207, 206, 195, 194, 193, 192, 181, 180, 179, 167, 166, 165, 103, 77.

Anal. Calcd for $C_{36}H_{27}O_2N$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.48; H, 5.28; N, 2.58.

Product **16a** had ir 1752, 1630 (w), 1600 (w), 1495, 1170, 1150, 770, and 710 cm^{-1}; nmr τ 5.9 (s, 2 H), 3.4–3.52 (m, 2 H), 2.55–3 (m, 21 H), 2.1–2.3 (m, 2 H); mass spectrum M^+ 505, 477, 461, 311, 310, 294, 283, 282, 268, 267, 265, 253, 252, 232, 207, 204, 195, 194, 192, 180, 179, 178, 167, 166, 165, 152, 132, 105, 91, 77.

Anal. Calcd for $C_{36}H_{27}O_2N$: C, 85.52; H, 5.38; N, 2.77. Found: C, 85.70; H, 5.51; N, 2.92.

The above procedure was followed in the photolysis of 6-phenyl-2,4-bis(benzhydrylidene)-7-methyl-3,5-dioxa-1-azabicyclo [4.1.0]heptane (**3b,c**, 0.8 g) which yielded 2,4-bis(benzhydrylidene)-6-phenyl-7-methyl-7*H*-1,3,5-dioxazepine (**15b**, mp 152–154°, 120 mg, 15% yield) and 2-benzhydrylidine-4-phenyl-5-methyl-6,6-diphenyl-5*H*,7*H*-1,3-oxazepin-7-one (**16b**, 10 mg, 1% yield). Both products **15b** and **16b** were identical with those obtained from the thermolysis of **3b,c**.

Similarly, the photolysis of 6-phenyl-2,4-bis(benzhydrylidene)-7,7-dimethyl-3,5-dioxa-1-azabicyclo[4.1.0]heptane (**3d**, 1 g) in benzene gave **15c** (0.25 g, 25% yield). The product was identical with that obtained from the thermolysis of **3d** at 180–190°.

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Registry No.—**3a**, 33893-01-5; **3b**, 37005-08-6; **3c**, 37005-09-7; **3d**, 37005-10-0; **4**, 37005-11-1; **6**, 40711-53-3; **8**, 40711-54-4; **13**, 40711-55-5; **15a**, 40711-56-6; **15b**, 40711-57-7; **15c**, 40711-58-8; **16a**, 40711-59-9; **16b**, 40711-60-2; **17a**, 40711-61-3; **18a**, 28172-27-2; **18b**, 40711-63-5; **19a**, 40742-87-8; **19b**, 40711-13-5; **19c**, 40711-64-6; hydrazine, 302-01-2.