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# 3,7,10,14-TETRASUBSTITUTED 1,8-DIDEHYDRO[14]ANNULENS

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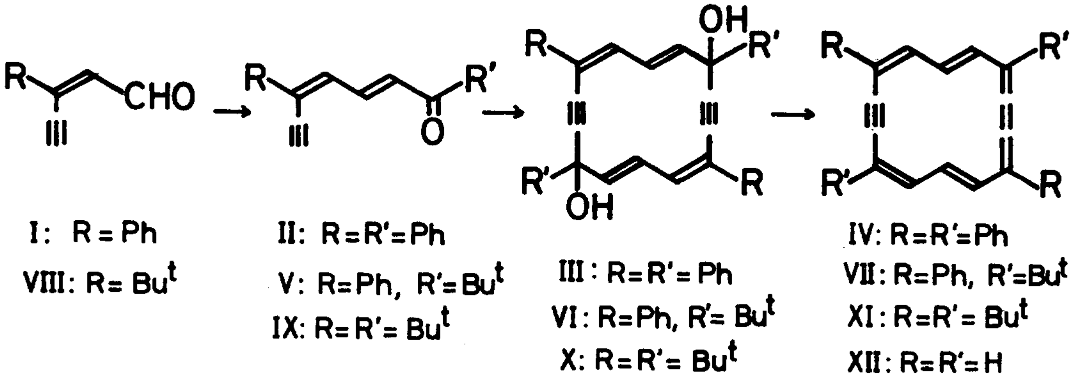
1,8-Didehydro[14]annulene (XII) is an unusually stable and highly aromatic annulene prepared and extensively investigated by F. Sondheimer and his co-workers (1). The dienyne ketones (II and IX) obtained from enyne aldehydes (I and VIII), key intermediates in the syntheses of tetrasubstituted tetradehydro[18]-annulenes (2, 3), appeared to be potential precursors of the present syntheses of tetrasubstituted 1,8-didehydro[14]annulenes. The unsymmetrical dienyne ketones (V, pale yellow crystals, mp 75.5-76.2°C. Found: C, 85.91; H, 7.64%. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61%) was prepared by the condensation of pinacolone with I. After several experimentations, cyclic dimerization of dienyne ketones (II, V and IX) to yield 14-membered cyclic glycols (III, VI and X) could be realized



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under conditions of the Favorskii reaction. A solution of dienyne ketone (II or V or IX) in tetrahydrofuran was added dropwise to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia. After stirring for several hours, the reaction mixture was worked up according to the usual manner. The purification of cyclic glycols (III, VI and X) were found to be rather difficult. However, X could be obtained in a crystalline form which could be separated on chromatography on silica gel in diastereomeric $X_a$ [mp 220-222.2°C (dec.), Found: C, 82.75; H, 10.40%, $M^+$ 436. Calcd. for $C_{30}H_{44}O_2$: C, 82.51; H, 10.16%, Mol. wt., 436.65] and $X_b$ [ mp 230.9-232.4°C (dec.), $M^+$ 436], beside another unidentified by-product [$X_a$: $X_b \approx 10:1$, total yield 69%]. The crude oily glycol (III or VI or X) was mixed with benzene or ether without purification, and the mixture was treated with stannous chloride dihydrate in the presence of hydrochloric acid. Chromatographic purification of the reaction product afforded tetrasubstituted 1,8-didehydro[14]annulene [IV: Found: C, 94.26; H, 5.45%. Calcd. for $C_{38}H_{26}$: C, 94.57; H, 5.43%. VII: Found: C, 91.96; H, 7.70%. Calcd. for $C_{34}H_{34}$: C, 92.26; H, 7.74%. XI: $M^+$ 402. Found: C, 89.42; H, 10.63%. Calcd. for $C_{30}H_{42}$: C, 89.49; H, 10.53%. Mol. wt., 402.7]. The didehydro[14]annulenes (IV, VII and XI) showed no melting points, but underwent color change at > 200°C. The color of crystals, yields based on the dienyne ketones (II, V and IX) and the main absorption maxima of electronic spectra of XI, VII and IV together with those of parent XII are recorded in Table 1.

Table 1. Physical properties of didehydro[14]annulenes

| | Color of crystals | $\lambda_{max}$ in nm ($\varepsilon$) | Yield (%) |
|---|---|---|---|
| XII | red | 309(175,000), 424(23,600), 586(2,900)$^+$ | |
| XI | red | 329(272,000), 452(24,600), 590(922)* | 67 |
| VII | brown violet | 357(195,000), 508(52,600), 623(1,640)* | 29 |
| IV | violet | 388(289,000), 549(53,200), 658(2,520)* | 17 |

+ in isooctane. * in tetrahydrofuran.

3,7,10,14-Tetraphenyl-1,8-didehydro[14]annulene (IV) gave π-complex with 2 moles of trinitrofluorenone [violet crystals, Found: C, 68.87; H, 3.23; N, 7.59%. Calcd. for $C_{38}H_{26}\cdot 2C_{13}H_{5}N_{3}O_{7}$: C, 69.06; H, 3.26; N, 7.55%], whereas 3,10-diphenyl-7,14-di-t-butyldidehydro[14]- and 3,7,10,14-tetra-t-butyltetradehydro[14]-annulenes (VII and XI) formed 1:1 π-complex with the same compound [violet brown crystals, Found: C, 74.27; H, 5.16; N, 5.57%. Calcd. for $C_{34}H_{34}\cdot C_{13}H_{5}N_{3}O_{7}$: C, 74.49; H, 5.19; N, 5.54% and brown crystals, Found: C, 72.19; H, 6.65; N, 5.91%. Calcd. for $C_{30}H_{42}\cdot C_{13}H_{5}N_{3}O_{7}$: C, 71.95; H, 6.60; N, 5.85%, respectively].

The NMR spectroscopic data of tetrasubstituted didehydro[14]annulenes (IV, VII and XI) are summarized in Table 2 together with that of didehydro[14]annulene (XII) (1). The NMR spectra of the tetrasubstituted didehydro[14]annulenes (IV, VII and XI) clearly indicate the presence of induced diamagnetic ring-current reflecting the aromatic nature of the 14 π-electron system. The doublets at $\tau$ 0.12 and 0.47 in the spectrum of diphenyl-di-t-butyldidehydro[14]annulene (VII) can be assigned to the outer protons adjacent to the phenyl and t-butyl groups, respectively. It is to be noted that replacement of hydrogen on the carbon atoms adjacent to acetylenic or cumulenic linkage by substituent group (t-butyl or phenyl) brings about an appreciable down-field shift of the signals of inner protons

Table 2. NMR spectra of didehydro[14]annulenes (60 MHz)

| | XII | XI | VII | IV |
|---|---|---|---|---|
| Solvent | $CDCl_3$ | THF-$d_8$ | THF-$d_8$ | THF-$d_8$ |
| Outer protons | $\tau$ 0.45, dd<br>J=13.3, 8.0 Hz<br>1.57, d<br>J=13.3 Hz | 0.58, d<br>J=13.5 Hz | 0.12, d<br>J=13.5 Hz<br>0.47, d<br>J=13.5 Hz | 0.06, d<br>J=13.5 Hz |
| o-Protons of phenyl | | | 1.2-1.5, m | 1.1-1.5, m |
| m,p-Protons of of phenyl | | | 2.2-2.8, m | 2.1-2.6, m |
| Protons of t-butyl | | 8.10, s | 8.02, s | |
| Inner protons | 15.54, t<br>J=13.3 Hz | 14.39, t<br>J=13.5 Hz | 13.42, t<br>J=13.5 Hz | 12.56, t<br>J=13.5 Hz |

accompanied with a minor shift of peripheral protons (outer protons and protons in the substituents) to the same direction. The same tendency has been observed in tetrasubstituted tetradehydro[18]annulenes (2, 3, 4). It is evident that the substituent groups exert a prominent perturbation on the dehydroannulene system, because, as recorded in Table 1 and Fig. 1, introduction of substituent groups, especially phenyl groups, caused a marked bathochromic shift of the electronic spectra. At first sight, the down-field shift of the signals of inner protons seems to be attributable to a decrease of induced ring-current caused by a perturbation of the substituents. However, this postulation can not explain the minor down-field shift of the signals of peripheral protons. Accumulation of further experimental results seems to be necessary to offer an appropriate interpretation for the interesting NMR behavior.

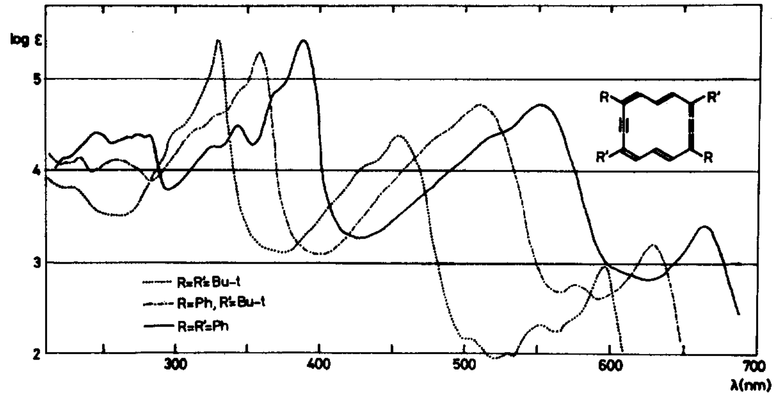

Fig. 1. Electronic spectra of didehydro[14]annulenes in tetrahydrofuran

References

1. F. Sondheimer, Y. Gaoni, L. M. Jackmann, N. A. Bailey, and R. Mason, J. Amer. Chem. Soc., 84, 4595 (1962); Y. Gaoni and F. Sondheimer, ibid., 86, 521 (1964).
2. K. Fukui, T. Okamoto, and M. Nakagawa, Tetrahedron Letters, 1971, 3121.
3. T. Katakami, S. Tomita, K. Fukui, and M. Nakagawa, Chemistry Letters, 1972, 225.
4. J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, Tetrahedron Letters, 1968, 1115.