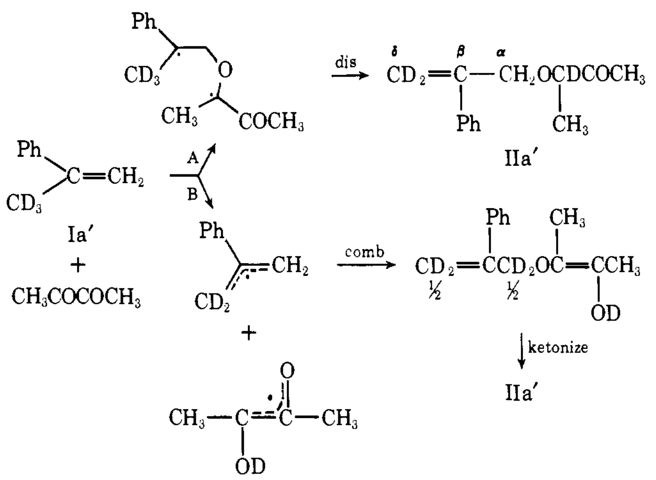
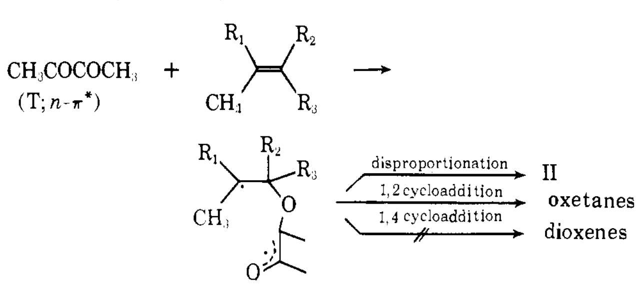


This result demonstrates that II is produced through path A, since path B would introduce deuterium equally into positions C_α and C_δ. With regard to the photoreactions of carbonyl compounds with olefins, this is conclusive evidence in support of a biradical intermediate.

In order to identify the excited state of biacetyl which is involved in these reactions, the emission of biacetyl (0.05 *M*) in the presence of Id (1.0 *M*) was examined in degassed benzene at room temperature. The phosphorescence of biacetyl was completely quenched but the fluorescence was unaffected,[14] which indicates that the reactions are derived from the $n-\pi^*$ triplet of biacetyl.

In the most reasonable mechanism which satisfies the above results, attack of the carbonyl oxygen of excited biacetyl (T; $n-\pi^*$) on olefins produces a biradical intermediate which either cyclizes to form oxetanes or disproportionates intramolecularly to give II. Table I shows that the ratio of cyclization to disproportionation varies with the type of olefin. Though further evidence might be necessary to explain these phenomena clearly, the decrease in cyclization for Ic and Id may be caused by steric hindrance,[15] mainly 1,3-diaxial interactions which have been reported to decrease the formation of cyclobutanes from the biradical intermediate formed upon δ-hydrogen abstraction by the carbonyl excited state.[16]

The occurrence of II and the absence of 1,4 cycloadducts (dioxenes)[4] in these reactions indicate unambiguously that the photochemical behavior of biacetyl toward olefins is different from that of monoketones or *o*-quinones such as phenanthrenequinones. Further studies will resolve these problems. The generality of this reaction and the nature of the biradical intermediate are under current investigation.



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and the recovered olefin were deuterated the same per cent as the starting olefin (87% D), and no scrambling occurred in them.

(14) The emission of biacetyl in the presence of olefin was compared with that in the absence of it taken under similar conditions.

(15) It is well known that the free energy of activation for cyclization is governed mainly by a strain factor and by the probability of the two active centers meeting each other: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 198.

(16) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970).

Monodehydro[26]annulene. The Demonstration of a Diamagnetic Ring Current in a 26-Membered Macrocycle[1]

Sir:

The question of the exact limit for aromaticity in [4*n* + 2]annulenes is an interesting one. It has been calculated that the limit lies between the 22- and the 26-membered rings.[2] In agreement with this is the finding that [22]annulene[3] and monodehydro[22]annulene[4] show a diamagnetic ring current in the nmr spectra, but tridehydro[26]annulene[5] (the only previously known [26]annulene derivative) shows no ring current.

Of course, the possibility existed that the lack of a diamagnetic ring current in tridehydro[26]annulene is due to the perturbation of the three acetylenic linkages, which causes the nondelocalized alternate bond structure to be energetically preferred to the delocalized system. This perturbation is likely to become of importance in rings of this size, since the difference in energy between the two forms is predicted to be small.[2] In order to test this possibility, it was desirable to synthesize [26]annulene itself, or a dehydro[26]annulene containing fewer acetylenes than the tridehydro compound. We have now succeeded in synthesizing monodehydro[26]annulenes (*e.g.*, **5**), containing only one acetylenic bond. This substance was indeed found to possess a diamagnetic ring current, and it is, therefore, presumably aromatic. This is the largest macrocycle for which a ring current has been observed,[6,7] and the limit for aromaticity in [4*n* + 2]annulenes appears to lie above the 26-membered ring.

Reaction of *trans,trans*-1,6-dibromo-2,4-hexadiene (**1**)[4] with an excess of ethynylmagnesium bromide[8] in tetrahydrofuran in the presence of cuprous chloride[9]

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(1) Unsaturated Macrocyclic Compounds. LXXXV. For part LXXXIV, see P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *Chem. Commun.*, 947 (1971).

(2) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965). See also H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc., Ser. A*, **251**, 172 (1959); **257**, 445 (1960); C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).

(3) R. M. McQuilkin, B. W. Metcalf, and F. Sondheimer, *Chem. Commun.*, 338 (1971).

(4) R. M. McQuilkin and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 6341 (1970).

(5) C. C. Leznoff and F. Sondheimer, *ibid.*, **89**, 4247 (1967).

(6) See R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 105 (1971).

(7) Evidence for a diamagnetic ring current in the dianion of 1,3,7,9,13,15,19,21-octadehydro[24]annulene, a 26-π-electron system, has been obtained previously (R. M. McQuilkin, P. J. Garratt, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 6682 (1970)).

(8) E. R. H. Jones, L. Skattebøl, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); *Org. Syn.*, **39**, 56 (1959).

(9) See J. P. Danehy, D. B. Killian, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **58**, 611 (1936).

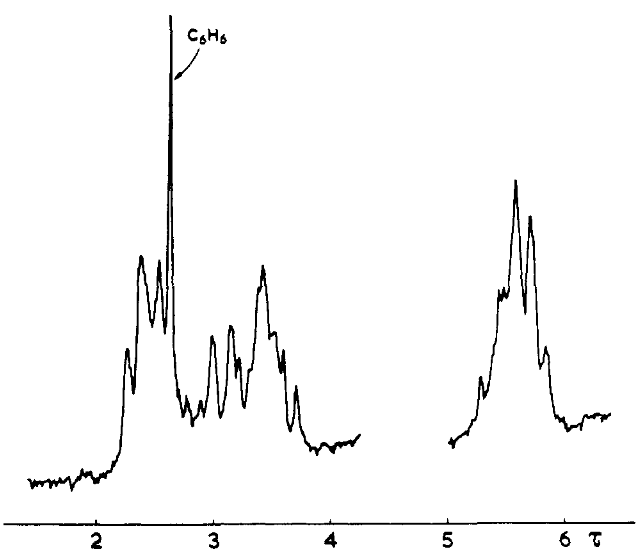
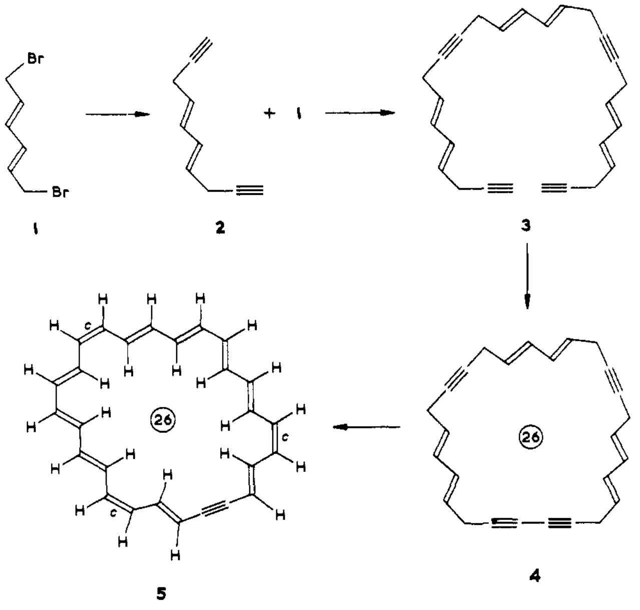


Figure 1. The 100-MHz spectrum of monodehydro[26]annulene (*e.g.*, **5**), measured in CD_2Cl_2 at $-90°$, using a time-averaged computer (internal standard, TMS).

yielded 65% of *trans,trans*-deca-4,6-diene-1,9-diyne (**2**) (see Scheme I): bp 51–53° (0.3 mm); mp 31–32°; mass spectrum *m/e* 130; λ_{max}^{EtOH} 220 sh (ϵ 27,200), 227 (29,700), and 234 sh nm (23,300); nmr ($CDCl_3$, 60 MHz) τ 3.40–4.60 (m, 4, olefinic), 6.80–7.10 (m, 4, methylene), and 7.87 (t, 2, acetylenic). The diene-diyne **2** was treated with 1.1 mol equiv of ethylmagnesium bromide in tetrahydrofuran at room temperature, and then with 0.5 mol equiv of **1** in the presence of cuprous chloride[9] (boiling 1 hr). Chromatography on silica gel led to 10% of the C_{26} hexaenetetrayne **3**: mp 99–100°; nmr spectrum ($CDCl_3$, 60 MHz) τ 3.40–4.75 (m, 12, olefinic), 6.85–7.25 (m, 12, methylene), and 7.95 (t, 2, acetylenic). Substance **3** was very unstable and no mass spectrum could be obtained. The structure is based on the nmr spectrum and the fact that catalytic hydrogenation in tetrahydrofuran over platinum gave hexacosane (mass spectrum *m/e* 366).

Scheme I



Oxidative coupling of **3**, by dropwise addition of a solution in pyridine and tetrahydrofuran during 3.5 hr to cupric acetate monohydrate in pyridine at 72°,[4] gave ~2%[10] of the cyclic "monomer" **4** after chromatography on silica gel. The structure of **4** is based on the absence of terminal acetylene protons (nmr, ir) and the fact that catalytic hydrogenation as previously led to cyclohexacosane (mass spectrum *m/e* 364). Compound **4** was immediately subjected to rearrangement with a saturated solution of potassium *tert*-butoxide in *tert*-butyl alcohol (25°, 3 min). Chromatography on alumina (activity III) and then on silical gel gave monodehydro[26]annulene (*e.g.*, **5**) in ~3% yield as the sole highly colored substance. The compound formed dark purple rhombs from benzene–pentane (dark red in concentrated solution), which decomposed on attempted melting point determination: mass spectrum *m/e* 336.189 (calcd for $^{12}C_{26}{}^{1}H_{24}$: 336.188); λ_{max}^{ether} 291 (ϵ 42,800), 370 (131,000), 386 (152,000), 439 (14,900), and 460 nm (15,900).[11] The monodehydro[26]annulene appeared to be homogeneous; *e.g.*, no separation occurred by chromatography on silica gel impregnated with 0.5% silver nitrate.[3] The monocyclic nature of the substance was confirmed by catalytic hydrogenation in tetrahydrofuran over platinum, which again led to cyclohexacosane (mass spectrum *m/e* 364).

The nmr spectrum of the monodehydro[26]annulene at $-90°$ (Figure 1) consisted of complex multiplets at τ 2.1–3.8 and 5.2–6.0, the integrated areas being ~15:9.[12] The integration shows these bands to be due to the outer and inner protons, respectively, and indicates that the molecule contains 15 outer and 9 inner protons, as in **5**. However, the exact stereochemistry is unknown, and **5** is one of many possibilities. The fact that the inner protons resonate at considerably higher field than the outer protons clearly demonstrates the existence of a diamagnetic ring current, although this effect is less than in the lower homolog, monodehydro[22]annulene (outer protons, τ 1.55–3.75; inner protons, τ 6.55–9.30, at room temperature).[4]

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(10) This yield could not be improved by varying the conditions. It may be noted that *all-trans*-4,10,16,22-hexacosatetraene-1,7,13,19,25-pentayne, an isomer of **3**, could not be oxidized to the corresponding cyclic "monomer" (Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 4940 (1968)).

(11) The ϵ values are minimum ones, since the substance could not be dried thoroughly in view of its instability.

(12) The spectrum determined at room temperature was similar (τ 2.4–4.1 and 4.9–5.6), but was less well resolved.

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Syntheses and Photochemistry of 1,2,3-Trisilacycloheptane Derivatives. Precursors for Tailor-Made Organosilylenes

Sir:

Recently, considerable attention has been devoted to the chemistry of divalent silicon compounds (sily-