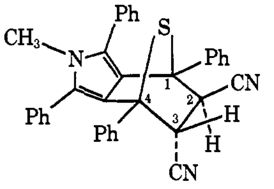
treatment of **5** with sodium methoxide in methanol at room temperature.

In contrast to the above addition across the thiocarbonyl ylide system, reaction of **4** with fumaronitrile in refluxing benzene gave an exclusive 1:1 cycloadduct **7** as colorless irregular prisms, mp 231–234° (dec), in which addition had occurred across the azomethine ylide system ($\lambda_{max}^{CHCl_3}$ 288 nm, log ϵ 4.27; ν_{CN} 2245 cm^{-1}; nmr (CF$_3$COOD) τ 7.07 (s, 3, NCH$_3$), 5.20 (d, 1, J = 3.7 Hz, H$_3$), 4.53 (d, 1, J = 3.7 Hz, H$_2$), 3.17–2.27 (m, 20, aromatic)). On attempted dissolution in warm solvents, the adduct **7** underwent a ready retro-Diels–Alder type reaction, also observed in the mass spectrometer. This thermal instability allowed the conversion of **7** into **6** (60%) with trace amounts of **5** by refluxing in xylene (14 hr). These data show the greater reactivity of the azomethine ylide over the thiocarbonyl ylide dipole and the greater thermodynamic stability of the cycloadducts from the latter.

As was shown earlier[2] with dimethyl acetylenedicarboxylate, dibenzoylacetylene in refluxing benzene (15 hr) gave a cycloadduct **8** (R = COPh) in which addition had occurred across the azomethine ylide system. Formed in 66% yield, it crystallized from acetonitrile as pale yellow needles, mp 247–249° (dec) ($\lambda_{max}^{CHCl_3}$ 264 nm (log ϵ 4.54), 273 sh (4.48), 284 sh (4.45); ν_{CO} 1670, 1650 cm^{-1}; nmr (CDCl$_3$) τ 7.98 (s, 3, NCH$_3$), 3.20–2.30 (m, 30, aromatic); M$\cdot^+$ 675 (1)). This adduct could be oxidized to the benzo[*c*]thiophene derivative **9** (R = COPh) with *m*-chloroperbenzoic acid.[2,7] In refluxing xylene (48 hr) addition also occurred across the azomethine ylide system giving **8** in 31% yield along with a 17% yield of **9**. It is thought that **9** resulted from the slow oxidation of **8** rather than from the elimination of methyl nitrene and that the insensitivity of the acetylene cycloadditions to temperature is due to the stability of the azomethine ylide cycloadducts.



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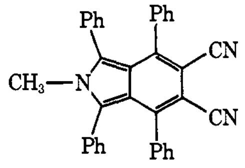

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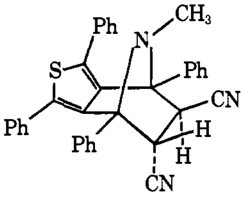

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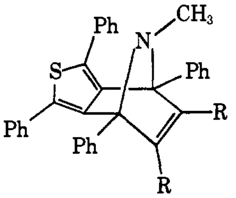

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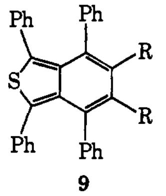

9

The above manifestations of ylide chemistry were observed with a variety of olefinic dipolarophiles and these results will be described in the full publication.

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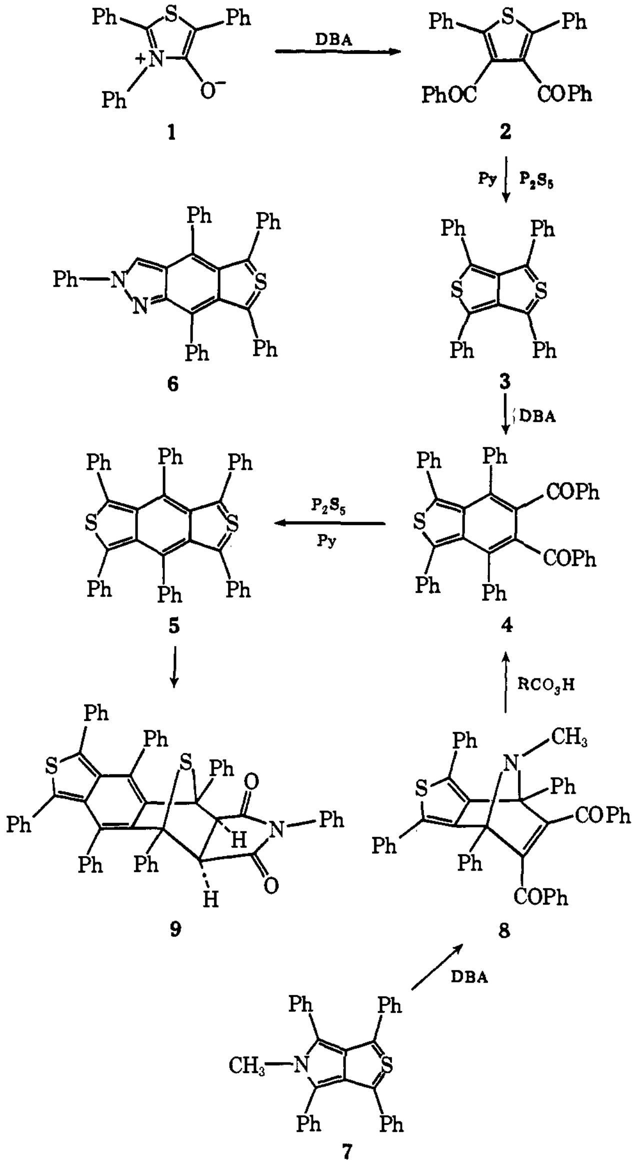
[7] K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **95**, 2750 (1973).

The Thieno[3,4-*f*]benzo[*c*]thiophene System, a Nonclassical 14π-Electron Heterocycle

Sir:

The thieno[3,4-*c*]thiophene ring system (**3**), first reported[1] in 1967, was the initial bicyclic heterocycle containing 10 π electrons and a "tetravalent sulfur" atom. Other representatives of this class of compound have since been described,[2] but the original system still re-

Scheme I



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(2) (a) R. H. Schlessinger and J. D. Bower, *ibid.*, **91**, 6891 (1969); (b) M. P. Cava and M. A. Sprecker, *ibid.*, **94**, 6215 (1972); (c) K. T. Potts and D. McKeough, *ibid.*, **94**, 6215 (1972).

tains its interest especially as a recent X-ray study[3] has shown that the four phenyl substituents are not coplanar with the ring system.

Cycloaddition reactions utilizing the "masked" 1,3-dipole of mesoionic ring systems[4] provide a convenient synthetic route not only to **3** but also to its benzolog, the thieno[3,4-*f*]benzo[*c*]thiophene system (**5**). The latter is another example of a stable tricyclic 14π-electron system containing a "tetravalent sulfur" in a five-membered ring, the properties of 2,4,5,7,8-pentaphenylthieno[3,4-*f*]benzo[*c*]pyrazole (**6**) being described earlier,[2c] the other known example of this type of system being unstable.[2a] Other examples, however, are known where the sulfur atom is in a six-membered ring, as in the naphtho[1,8-*cd*]thiapyran[5] and acenaphtho[5,6-*cd*]thiapyran[6] ring systems.

Condensation of anhydro-4-hydroxy-2,3,5-triphenylthiazolium hydroxide (**1**) with dibenzoylacetylene (DBA) in refluxing benzene over 30 hr gave,[7] in 42% yield, yellow irregular prisms (from ethanol) of 3,4-dibenzoyl-2,5-diphenylthiophene (**2**), mp 139–141° (ν_{CO} 1660, 1640 cm^{-1}; M$\cdot^+$ 444 (100); $\lambda_{max}^{CH_3OH}$ 198 nm (log ϵ 4.81), 262 (4.66)). Treatment of **2** with P_2S_5 in refluxing pyridine for 90 min, followed by quenching the reaction in ice–water, gave purple needles (from acetic anhydride) of 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (**3**), mp 245–247° (83%) ($\lambda_{max}^{CHCl_3}$ 258 nm (log ϵ 4.30), 262 sh (4.27), 292 (4.15), 551 (3.92); M$\cdot^+$ 444 (100), M^{2+} 222 (10)), in agreement with the physical constants reported previously.[1] Although **3** and dibenzoylacetylene gave 5,6-dibenzoyl-1,3,4,7-tetraphenylbenzo[*c*]thiophene (**4**), it was more readily available from **8**, prepared from 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (**7**) and dibenzoylacetylene in refluxing benzene over 15 hr.[8] Oxidation of **8** with *m*-chloroperbenzoic acid in methylene chloride resulted in a 90% yield of **4**, obtained as yellow irregular prisms from acetic anhydride, mp 299–300° (ν_{CO} 1670 cm^{-1}; M$\cdot^+$ 646 (100)).

1,3,4,5,7,8-Hexaphenylthieno[3,4-*f*]benzo[*c*]thiophene (**5**) was obtained in 74% yield from **4** and P_2S_5 in refluxing pyridine over 5 hr and working up the reaction by pouring it into 10% sodium hydroxide solution. The highly insoluble greenish blue product was purified by digestion with hot dioxane, finally being obtained as finely matted, blue needles, mp 348–350° ($\lambda_{max}^{CHCl_3}$ 245 nm (log ϵ 4.59), 259 sh (4.50), 316 (4.38), 370 sh (3.48), 793 (4.06), 877 (3.25)). The most intense ion in the mass spectrum was the molecular ion, *m/e* 646, the only other significant ions being M^{2+} 323 (18) and $PhC{\equiv}S^+$, *m/e* 121 (27). Additional evidence in support of structure **5** comes from the formation of a 1:1 cycloadduct with *N*-phenylmaleimide in refluxing xylene over 9 hr. This adduct, obtained as yellow, irregular prisms (from chloroform–hexane) in 82% yield, mp 373–375° (dec) ($\lambda_{max}^{CHCl_3}$ 287 nm (log ϵ 4.39), 371 (4.03); ν_{CO} 1710 cm^{-1}), was assigned the exo configuration (**9**) on the basis of the chemical shifts of the protons α to the imide carbonyl groups [τ 5.20 (s, 2)]. No endo isomer was detected under these reaction conditions.

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(7) All products described here gave satisfactory analytical data.

(8) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **95**, 2749 (1973).

(9) Sterling–Winthrop Fellow, 1971–1973.

Book Reviews

Molecular Evolution and the Origin of Life. By S. W. Fox (Institute of Molecular Evolution, University of Miami) and K. Dose (Johannes Gutenberg University). W. H. Freeman and Co., San Francisco, Calif. 1972. xi + 359 pp. $16.00.

The book contains a foreword by A. Oparin, eleven chapters, an appendix, and an index. Chapters are titled: (1) History of Concepts (15 pp), (2) Cosmology (17 pp), (3) Geological Conditions on the Primitive Earth (31 pp), (4) Micromolecules (68 pp), (5) Macromolecules (60 pp), (6) Self-assembly of Polyamino Acids and Other Substances into Microsystems (40 pp), (7) Interpretations of Experiments with Proteinoid Microsystems (24 pp), (8) Origin and Evolution of Optical Activity (7 pp), (9) Perspectives on Molecular Evolution in Organisms (14 pp), (10) Organisms and Molecular Fossils in Ancient Sediments (30 pp), (11) Extraterrestrial Molecular Evolutions (28 pp). An appendix contains directions for preparations in the laboratory and suggestions for investigations (3 pp). A general index takes up eleven pages; author and compound indexes have unfortunately been omitted.

The authors offer an analysis of the evolution of carbon compounds from their cosmic origin through the stages of Darwinian selections followed by speculations on extraterrestrial evolution. Data have been gathered from astronomy, biology, chemistry, geology, and physics to support the authors' viewpoint of constructionism, which is defined as "the science of synthesis of molecules and assembly of systems from those molecules."

There is no scarcity of books, essays, reviews, publications, and other treatments on different aspects of the orgin of life. "Molecular Evolution and the Origin of Life," along with many others, introduces the general reader not only to the background information but also to current theories and investigations in the several scientific disciplines.

The specialist may be critical of a lack of rigor in the handling of data from his own field. Sometimes for lack of critical evaluation of material presented, the nonspecialist reader will be unable to separate speculation from fact. For example, chemists will be critical of the recognition of aminocyanocarbene ($H_2N\ddot{C}CN$) for the