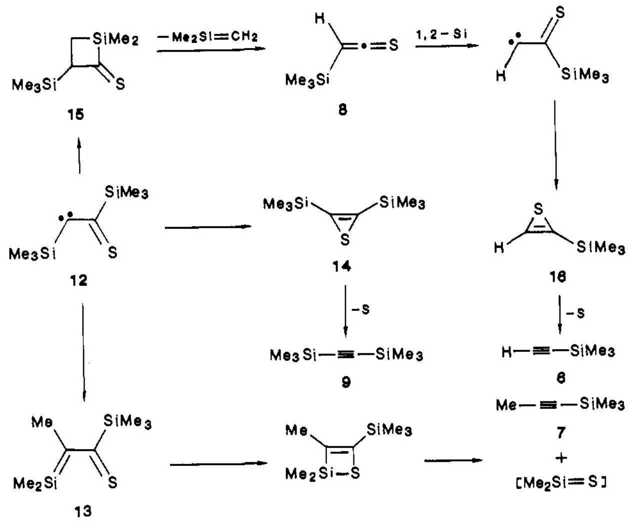
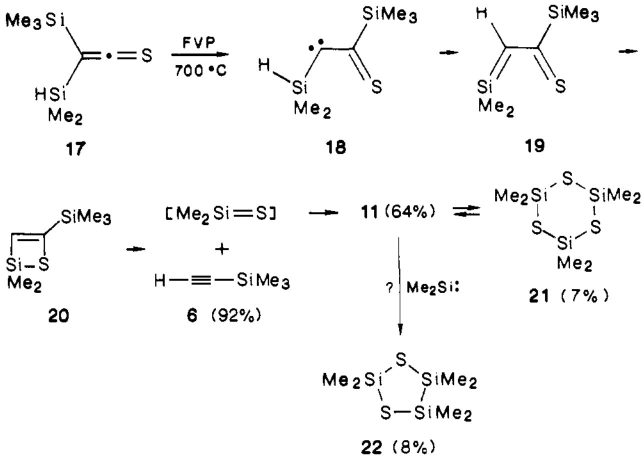
Scheme I



The complexity of the product mixture from **5** is considerably reduced when it is recognized that every one of the products **6–11** can be mechanistically rationalized by processes each initiated by isomerization of **5** to α-thioketocarbene **12** via a 1,2-shift of Me_3Si. Our proposals for the routes to **6–11** all originating from carbene **12** are incorporated into Scheme I. Rearrangement of **12** by 1,2-methyl migration from silicon produces silene **13** which would, in analogy to the mechanism proposed for silylketenes, be expected to close and decompose to acetylene **7** and dimethylsilathione ($Me_2Si{=}S$). Isomerization of **12** to thiirene **14** affords a path to acetylene **9** by extrusion of atomic sulfur. Although we are aware of no precedent for this latter process, MNDO calculations by McKee[5] have directly linked $S(^1D)$ and acetylene to thiirene. Formation of thioketene **8** is explained by intramolecular C–H insertion by carbene **12** to produce silacyclobutane **15** followed by silene extrusion. Thioketene **8** would be expected, by analogy to the **12** → **9** transformation, to isomerize to thiirene **16** and extrude sulfur to afford product **6**. Cyclic products **10** and **11** correspond to reaction of $Me_2Si{=}Si$ with either $Me_2Si{=}CH_2$ or another molecule of silathione. Thus, all products are readily rationalized as arising from a single initial intermediate, carbene **12**.

The apparent complexity of the product mixture arising from thermolysis of **5** is drastically reduced by the simple modification of replacing one methyl group by hydrogen. Thus, FVP of (dimethylsilyl)(trimethylsilyl)thioketene (**17**)[6] at 700 °C (Scheme II) results in 100% conversion of **17** and formation of (trimethylsilyl)acetylene (**6**) in a remarkable 92% yield accompanied by cyclosilathianes **11** and **21** in a combined yield of 71%. Both **11** and **21** are thought to be products of the cyclic oligomerization of dimethylsilathione, $Me_2Si{=}S$,[7] and are known to thermally equilibrate.[8] Thus, once again all major products are easily rationalized as originating from an initial 1,2-silyl migration on the heterocumulenic π-framework.[9] We can only speculate that product **22** arises from Me_2Si: (perhaps from reductive elimination in **17**?) insertion into **11** as has been suggested by Weber.[10]

Scheme II



Both the lower thermal requirements and the higher yield of silathione extrusion products for **17** as opposed to **5** are paralleled in the thermochemistry of the analogous silylketenes[2] and may be explained by the greater migratory aptitude of hydrogen (**18** → **19**, Scheme II) as compared with methyl (**12** → **13**, Scheme I).

Our eventual complete manuscript on the thermochemistry of both silylketenes and silylthioketens will also describe current studies on silathione trapping and kinetic studies on these decompositions.

Acknowledgment. We gratefully acknowledge the National Science Foundation for support of this work.

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[4] All previously reported products were identified by PMR, CMR, exact mass, and comparison with literature values. Because of instability and separation difficulties, **8** was only characterized by the following: PMR δ 3.52 (s 1 H), 0.204 (s, 9 H); CMR δ (−0.032, 49.94, 220.87); MS, relative intensity 130 (M^+, 18), 115 (79), 73 (97), 57 (32), 53 (38), 43 (100), 39 (36), 32 (36); IR (C=C=S, 1744 cm^{-1}). Yields are calculated from calibrated GC measurements.

[5] McKee, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5059.

[6] Synthesized by a method analogous to that in ref 3. Thioketene **17** was characterized by the following: PMR δ 4.24 (sept, 1 H), 0.31 (d, 6 H), 0.23 (s, 9 H); CMR δ (−2.34, 0.17, 49.49, 213.66); exact mass calcd 188.05113, measured 188.05118, and satisfactory elemental analysis for C, H, and S.

[7] Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

[8] Moedritzer, K. *J. Organomet. Chem.* **1970**, *21*, 315.

[9] Other mechanistic possibilities which we do not currently favor have been presented for the analogous silylketene thermolyses.[1]

[10] Soysa, H. S. D.; Jung, I. N.; Weber, W. P. *J. Organomet. Chem.* **1979**, *171*, 177.

Efficient Intramolecular 2 + 2 Photocycloaddition of Styrene Derivatives toward Cyclophanes

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The formation of 1,2-diphenylcyclobutane by the photocyclodimerization of styrene[1] has opposing demands with regard to the styrene concentration: the first dimerization step with a short-lived active species needs high concentration of styrene, whereas the second cyclization step requires dilute conditions to avoid intermolecular side reactions.

In order to overcome this monomer concentration effect by constraining the reactants into a single molecule,[2] α,ω-bis(vinylaryl)alkanes were treated under photoirradiation, which

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[1] (a) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289. (b) Brown, W. G. *J. Am. Chem. Soc.* **1968**, *90*, 1916. (c) Kricka, L. L.; Ledwith, A. *Synthesis* **1974**, 539. (d) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53. (e) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 56. (f) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 608. (g) Asanuma, T.; Gotoh, T.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 485. (h) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1981**, *22*, 2889. (i) Shirota, Y.; Nishikata, A.; Aoyama, T.; Saimatsu, J.; Oh, S.-C.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1984**, 64. (j) Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Perkin Trans. 2* **1986**, 239.

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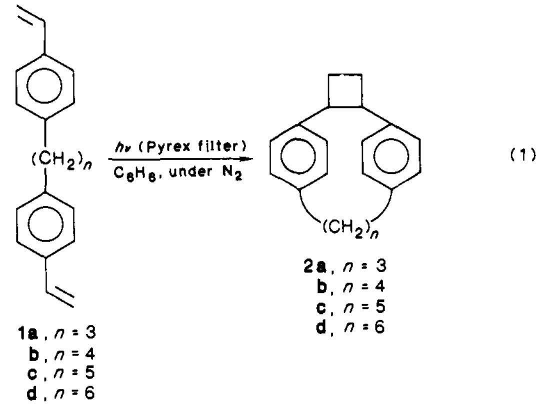
Table I. Preparation of (1,2)Ethano[2.*n*]cyclophanes[a]

entry	monomer (mM)	acceptor[b]	reaction time (h)	product[c]	conv (%)[d]	isolated yield (%)[e]
1	**1a** (5.7)		2	**2a**	25.5	(13.8)
2	**1a** (5.7)	DCNB	2	**2a**	29.4	(9.5)
3	**1b** (5.7)		2	**2b**	40.8	(60.9)
4	**1b** (5.7)		12	**2b**	87.8	(67.8)
5	**1b** (5.7)		38	**2b**		68.9
6	**1b** (5.7)	DCNB	2	**2b**	56.0	50.3)
7	**1c** (5.7)		2	**2c**	40.2	(48.5)
8	**1c** (5.7)	DCNB	2	**2c**	50.8	(23.0)
9	**1d** (5.7)		20	**2d**	53.4	(12.2)
10	**1d** (5.7)	DCNB	2	**2d**	44.3	(28.6)
11	**3a** (10.0)		9	**6a**		35.1
12	**3b** (6.7)		12	**6b**[f]		32.9
13	**4a** (10.0)		9	**7a**[f]		29.3
14	**4b** (6.7)		12	**7b**[f]		38.3
15	**5a** (10.0)		9	**8a**		25.5
16	**5b** (6.7)		12	**8b**		24.4
17	**9a** (1.6)		4	**10a**[g]		95.2
18	**9b** (1.1)		4	**10b**[g]		73.0

[a]Reaction conditions: in benzene through Pyrex filter at 30 °C. For entries 11, 13, and 15, a 200-W medium-pressure mercury lamp was used and for others a 400-W high-pressure mercury lamp. [b]*p*-Dicyanobenzene (DCNB, 10 mol% to monomers) was used as acceptor, if noted by DCNB in this column [c]All products have consistent ^{1}H NMR spectroscopic and analytical data which are available in the Supplementary Material. [d]Obtained by GC (QF-1, 3%, 2 m, 170–250 °C). [e]When yields were determined by GC and corrected on the basis of conversion, they are given in parentheses. [f]Structures were confirmed by NOE experiments. Compounds **6a** and **7a** show 18 and 22% NOE enhancements between a peri-hydrogen and a cyclobutane-methine hydrogen, respectively. NOESY spectra are available in Supplementary Material. [g]See text for the structure.

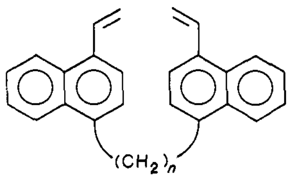
successfully afforded cyclophanes[3] having cis disubstituted cyclobutane ring(s).[4]



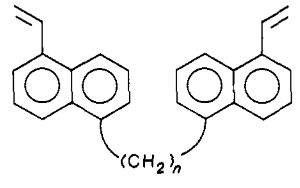
1a, *n* = 3
b, *n* = 4
c, *n* = 5
d, *n* = 6

2a, *n* = 3
b, *n* = 4
c, *n* = 5
d, *n* = 6

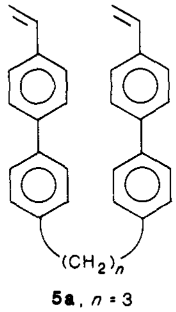
The results are summarized in Table I. *trans*-Cyclophane isomers were not detected either by careful chromatographic or spectroscopic analyses,[5] except for entries 17 and 18 (see Table I and below). Direct irradiation through Pyrex filter gave normally satisfactory results. Irradiation with *p*-dicyanobenzene (10 mol%) improved the yield when the monomers had a longer methylene linkage than pentamethylene ($n = 5$) (see Table I, entries 9 and 10). 1,2-Bis(*p*-vinylphenyl)ethane did not give cyclophane, either by direct irradiation or with the acceptor. Only *exo,cis,syn*-naphthalenophanes were obtained in reaction of **3** or **4** because of the conformational rigidity of the α-vinyl groups.[4d,6]



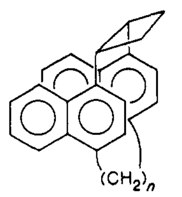
3a, *n* = 3
b, *n* = 4



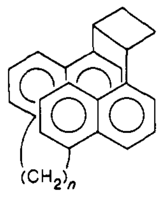
4a, *n* = 3
b, *n* = 4



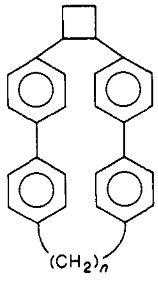
5a, *n* = 3
b, *n* = 4



6a, *n* = 3
b, *n* = 4

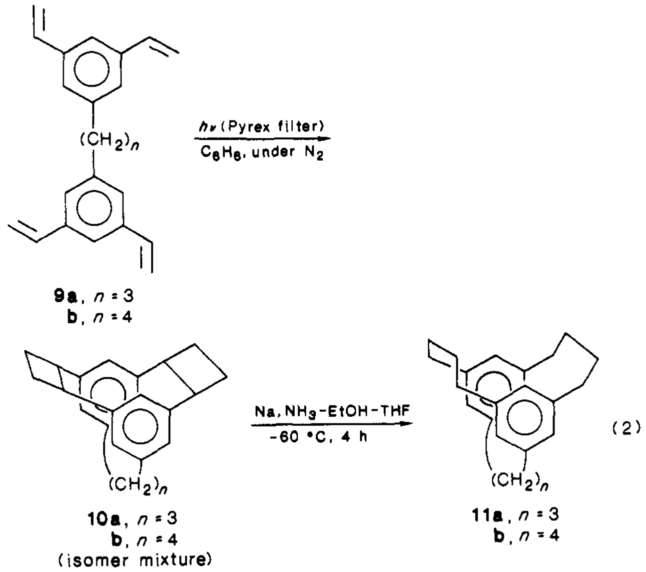


7a, *n* = 3
b, *n* = 4



8a, *n* = 3
b, *n* = 4

Monomer **9** gave an isomeric mixture of three-bridged cyclophanes **10** as beautiful fine needles in surprisingly high yields.[7]



9a, *n* = 3
b, *n* = 4

10a, *n* = 3
b, *n* = 4
(isomer mixture)

11a, *n* = 3
b, *n* = 4

The mixture was treated under Birch reduction conditions (Na in liquid NH$_3$–EtOH–THF) to cleave the cyclobutane rings to the tetramethylene chains.[8] The reaction proceeded very smoothly and gave isomer-free [4.4.*n*](1,3,5)cyclophanes **11** in excellent yields (86.1–95.4%).

Note that the yields of cyclophanes **2** from α,ω-bis(*p*-vinylphenyl)alkanes **1** depend on the methylene chain length (*n*). The length *n* must be greater than two for the cyclization, due to high strain encountered in the transition state. When $n = 4$, the

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(2) The condition can also be fulfilled in *o*-divinylbenzene, but vinyl groups in the molecule and related ones are not so sterically free that their reaction mechanisms seem to be different from the styrene photocyclization. See the following references: (a) Pomerantz, M. *J. Am. Chem. Soc.* **1967**, *89*, 694. (b) Meinwald, J.; Mazzocchi, P. H. *J. Am. Chem. Soc.* **1967**, *89*, 696. (c) Meinwald, J.; Young, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 725.

(3) This is not the first example of this kind of cyclophane, although this is the simplest one. See the following references and ref 2c; (a) Schönberg, A.; Sodtke, U.; Praefcke, K. *Tetrahedron Lett.* **1968**, 3669. (b) Müller, E.; Meier, H.; Sauerbier, M. *Chem. Ber.* **1970**, *103*, 1356. (c) Juriew, J.; Skorochodowa, T.; Merkuschew, J.; Winter, W.; Meier, H. *Angew. Chem.* **1981**, *93*, 285. (d) Mizuno, K.; Kagano, H.; Otsuji, Y. *Tetrahedron Lett.* **1983**, *24*, 3849.

cyclophane yield becomes maximum and decreases as *n* increases, probably because of decreasing entropic advantage.

According to Caldwell's predictor ($\tau(r_c) = 12.1$ for styrene),[9] styrene 2 + 2 photocyclodimerization should occur smoothly. But experimental data of the *inter*molecular reactions under direct irradiation,[1] accumulated so far, seem not to support clearly the prediction, probably due to the side reaction like polymerization. In the present intramolecular reaction, we demonstrated fully that the styrene 2 + 2 photocyclodimerization is indeed a facile process, in which the highly reactive excited intermediate can be trapped intramolecularly and effectively before intermolecular side reactions can compete.

Detailed mechanistic and further synthetic work is now in progress and will be reported elsewhere.

Acknowledgment. This work was supported in part by a special grant from the Ministry of Education, Science, and Culture, Japan (Grant No. 61035038).

Supplementary Material Available: Analytical and ^{1}H NMR spectroscopic data and NOESY spectra (7 pages). Ordering information is given on any current masthead page.

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(4) A typical preparative procedure is as follows: 1,4-bis(*p*-vinylphenyl)butane (**1b**, 637 mg, 2.43 mmol) was irradiated in dry and N_2-degassed benzene (400 mL) under a nitrogen atmosphere by a 400-W high-pressure mercury lamp through Pyrex filter. After 38 h the reaction mixture was concentrated by evaporation and treated with an excess amount of diborane in THF to change the unconsumed monomer to more polar and higher molecular weight materials, from which *cis*-1,2-ethano[2.4]paracyclophane (**2b**) was easily isolated by column chromatography (SiO_2, cyclohexane/benzene). Yield after recrystallization from methanol was 68.9%. For the synthesis of monomers, see the following papers: (a) Nishimura, J.; Ishida, Y.; Hashimoto, K.; Shimizu, Y.; Oku, A.; Yamashita, S. *Polym. J.* **1981**, *13*, 635. (b) Nishimura, J.; Hashimoto, K.; Okuda, T.; Hayami, H.; Mukai, Y.; Oku, A. *J. Am. Chem. Soc.* **1983**, *105*, 4758. (c) Nishimura, J.; Okuda, T.; Mukai, Y.; Hashiba, H.; Oku, A. *Tetrahedron Lett.* **1984**, *25*, 1495. (d) Nishimura J.; Yamada, N.; Okuda, T.; Mukai, Y.; Hashiba, H.; Oku, A. *J. Org. Chem.* **1985**, *50*, 836. (e) Nishimura J.; Yamada, N.; Horiuchi, Y.; Ueda, E.; Ohbayashi, A.; Oku, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2035.

(5) In Supplementary Material.

(6) Staley, S. W.; Dustman, C. K.; Linkowski, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1069.

(7) ^{1}H NMR spectroscopic analysis of the isomer mixture shows at least three components.

(8) Nozaki, H.; Otani, I.; Noyori, R.; Kawanishi, M. *Tetrahedron.* **1968**, *24*, 2183.

(9) Caldwell, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4004.

*Book Reviews**

Advances in Enzymology. Volumes 121, 125, 126, 132, 133, and 134. Series edited by S. F. Colowick and N. O. Kaplan. Academic Press: Orlando. 1986. Volume 121: Edited by J. J. Langone and H. V. Vunakis. xxxiv + 947 pp. $85.00. ISBN 0-12-182021-1. Volume 125: Edited by S. and B. Fleischer. xxx + 788 pp. $85.50. ISBN 0-12-182025-4. Volume 126: Edited by S. and B. Fleischer. xxx + 832 pp. $85.00. ISBN 0-12-182026-2. Volume 132: Edited by G. DiSabato and J. Everse. xxvii + 717 pp. $75.00. ISBN 0-12-182032-7. Volume 133: Edited by M. A. DeLuca and W. D. McElroy. xxvii + 649 pp. $75.00. ISBN 0-12-182033-5. Volume 134: Edited by R. B. Vallee. xxxi + 748 pp. $79.50. ISBN 0-12-182034-3.

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Analytical Applications of Lasers. By Edward H. Piepmeier (Oregon State University). John Wiley & Sons: New York. 1986. xiii + 703 pp. $89.95. ISBN 0471-87023-4

Laser-based methods are having a revolutionary impact in analytical chemistry as well as in many other fields. Although it would be virtually impossible to completely review all of the many applications of lasers in chemical analysis, *Analytical Applications of Lasers* gives remarkably good, up-to-date, and representative coverage of these rapidly progressing and wide-ranging efforts. As Volume 87, it is a fine addition to the series of monographs *Chemical Analysis.*

Written for people with a scientific background, the book was intended to be educational and present some of the most recent advances in the field; in general, it succeeds well. An introductory chapter is intended to acquaint the reader without a background in laser science with the basic principles of laser operation and nonlinear optical phenomena, but otherwise the individual chapters are meant to stand alone. Unfortunately, the introductory chapter is probably too advanced for those who are not already familiar with the concepts which are presented, and too brief to give further insight to others with some knowledge of laser science. It serves the purpose, however, to introduce the reader to terminology and to point out what concepts are important for further study, and while it is lean on references, there is a useful bibliography.

The book chapters are written by experts in each area and are well coordinated; the book has a good index. The editor has not imposed a uniform style on the individual authors, however, and a few of the chapters have suffered thereby, leaning toward being less instructive and more of a listing of comparative characteristics of various techniques or of published results. Examples are Chapter 2 on atomic and ionic fluorescence in flames and plasmas and Chapter 6 on infrared absorption spectroscopy. It is also disappointing that more material was not included on nonlinear methods.

In general, however, the book is an excellent source for scientists with some knowledge of lasers who wish to learn more about particular applications, and the chapters are well referenced. I enjoyed reading the entire volume through, including chapters covering topics outside my own immediate scientific interests. Particularly good were Chapters 3, on laser-enhanced ionization in flames, 4, on detection of small numbers of atoms and molecules; 7, on cryogenic spectrometry; 12, on intracavity-enhanced spectroscopy; 13, on the thermal lens effect; and, although short on applications, 14, on picosecond spectroscopy. The book would be valuable both as part of a personal library and as a reference text for graduate level courses. Its value to students also makes it a book that should be obtained by graduate institutions.

Steven R. Goates, *Brigham Young University*

Thermal Analysis. Third edition. By W. W. Wendlandt (University of Houston). John Wiley and Sons Inc.: New York, NY. 1986. xviii + 814 pp. $89.95. ISBN 0471-88477-4

This book is Volume 19 of the *Chemical Analysis* series of monographs on techniques and applications of analytical chemistry. Thermal analysis (TA) techniques addressed include thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), evolved gas detection and analysis (EGD, EGA), thermophotometry, including reflectance spectroscopy, infrared spectroscopy, thermoluminescence and oxyluminescence, and some of the lesser employed and/or supplementary TA techniques including thermomechanical methods, thermoelectrometry, thermosonimetry, thermomagnetometry, and accelerating rate calorimetry (ARC). In addition, chapters covering computer applications and addressing TA nomenclature are provided.

The general format is to introduce each TA technique, discuss the factors that affect the output or are potential sources of error, and then outline what information can be derived from the technique with specific references to important and/or eloquent adaptations to the "usual" experimental apparatuses. The discussion of each technique is ended with a representative survey of the literature in order to introduce the reader to the spectrum of problems which have been solved by a particular

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