[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

# Syntheses for 6-Substituted-1,2,3,4-tetraphenylfulvenes[1]

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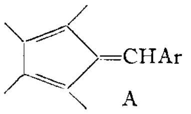
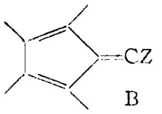
*p*-Nitro- and *p*-chlorobenzaldehydes, cinnamaldehyde *p*-dimethylaminocinnamaldehyde, 1-naphthaldehyde, furfural, quinoline-2-, quinoline-4- and quinoline-6-aldehydes, and benzothiazole-2-aldehyde have been condensed with 1,2,3,4-tetraphenylcyclopentadiene to give the corresponding 6-substituted fulvenes. 2-Methylmercapto-3-ethylbenzothiazolinium, 3-ethyl-2-(β-acetanilidovinyl)-benzoxazolium, -benzothiazolium and -benzoselenazolium and 1-ethyl-2-(β-acetanilidovinyl)-quinolinium iodides have been condensed with the same hydrocarbon to give the corresponding 6,6-disubstituted fulvenes.

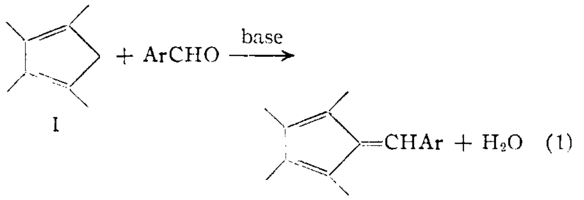
In connection with studies of the ultraviolet spectra of cross-conjugated systems and the relationship of structure to photoconductive behavior of organic compounds, it was of interest to prepare a series of 6-substituted fulvenes A and B, where Ar is an aryl ring and Z is a heterocyclic system. The general preparative methods have been reviewed.[5] In this investigation compounds of type A have been prepared by the base-catalyzed condensation of tetraphenylcyclopentadiene (I) with aldehydes (equation 1); compounds of type B have been synthesized by the alkoxide-catalyzed condensation of I with quaternized heterocyclic compounds containing a potential aldehyde group (equation 2).



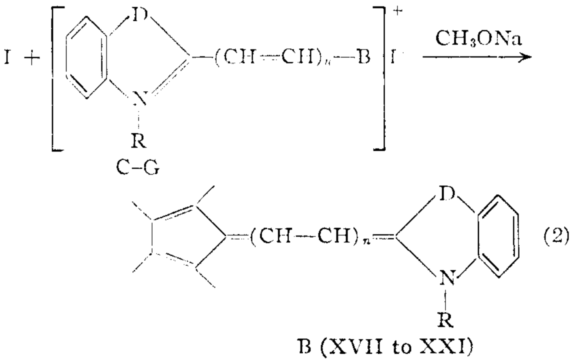
A



B



(1)



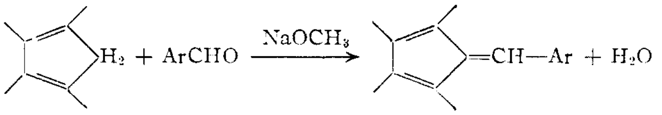
(2)

B (XVII to XXI)

The base-catalyzed condensation of I with aromatic aldehydes has been described by Dilthey and Huchtemann.[6] With a more extended series of aldehydes than those used previously, no particular difficulty was encountered. Table I summarizes the results. In an entirely similar fashion a number of heterocyclic aldehydes were found to give the corresponding compounds (see Table II). XII and

TABLE I

6-ARYL-SUBSTITUTED FULVENES



| Cmpd. no. | Ar– | Quant. taken,[a] g. | Reflux time, hours[b] | Solv. for recrystn. | M.p., °C., dec. | Yield, % | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| II | $C_6H_5$– | 2.0 | 4.0 | | 203–204[c] | 73 | | | | | | |
| III | *p*-$CH_3OC_6H_4$– | 0.5 | 2.0 | Petroleum ether[d] | 199–199.5[e] | 88 | | | | | | |
| IV | *p*-$(CH_3)_2NC_6H_4$– | 2.0 | 3.0 | Petroleum ether[d] | 253–255[f] | 74 | 90.98 | 90.94 | 6.23 | 6.31 | 2.79 | 2.76 |
| V | *p*-$NO_2C_6H_4$– | 1.0 | 2.0 | Benz.-pet. eth.[d] | 227–228 | 32 | 85.86 | 86.33 | 5.00 | 5.00 | 2.78 | 2.86 |
| VI | *p*-$ClC_6H_4$– | 1.5 | 2.0 | Petroleum ether[d] | 176–177 | 50 | 87.69 | 87.48 | 5.11 | 5.21 | | |
| VII | $C_6H_5CH{=}CH$– | 1.0 | 2.0 | Methanol | 193–194 | 37 | 94.18 | 94.43 | 5.82 | 5.98 | | |
| VIII | *p*-$(CH_3)_2NC_6H_4CH{=}CH$[g] | 0.76 | 4.0 | Benz.-pet. eth.[d] | 229–231 | 16 | 91.05 | 90.72 | 6.70 | 6.56 | 2.65 | 2.90 |
| IX | 1-Naphthyl- | 1.15 | 4.0 | Acetic acid | 209–211 | 49 | 94.45 | 94.41 | 5.55 | 5.51 | | |

[a] One gram of the diene was taken. [b] In methanol. [c] Footnote 6 reported m.p. 200–201°. [d] B.p. 90–100°. [e] Footnote 6 reported 197–198°. [f] Footnote 6 reported 208–210°. [g] This aldehyde was prepared according to the procedure of footnote 7, modifying that of footnote 8.

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(1) This work was supported by the Photographic Branch of the Signal Corps Engineering Laboratories of the U. S. Army, Contract W36-039 SC44483, Signal Corps Project No. 39-195B, Dept. of the Army Project No. 3-99-04-052 and Contract DA 36-039 SC-15326, Signal Corps Project No. 36-1958-0(036401.1), Dept. of the Army Project No. 3-99-04-052. It was reported in part in the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950, Abstracts, p. 71 N.

(2) Taken from a portion of the Dissertation presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the degree of Doctor of Philosophy, 1953.

(3) Deceased, January 7, 1950.

(4) To whom inquiries should be sent.

(5) J. H. Day, *Chem. Revs.*, **53**, 167 (1953).

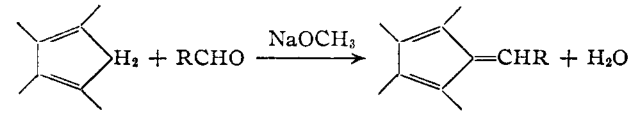
(6) W. Dilthey and P. Huchtemann, *J. prakt. Chem.*, **154**, 238 (1940).

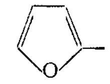
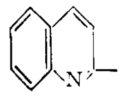
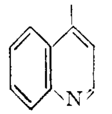
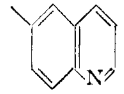
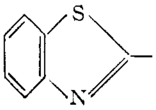
(7) S. Gister, M.S. Thesis, Polytechnic Institute of Brooklyn, 1950.

(8) W Köuig, W. Schramek and G. Rosch, *Ber.*, **61**, 2074 (1928).

TABLE II

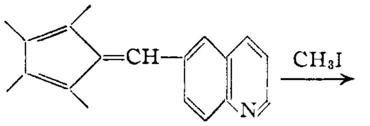
6-HETEROCYCLE-SUBSTITUTED FULVENES



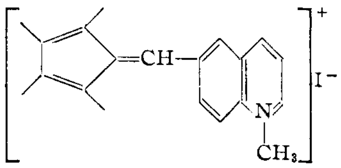
| Cmpd. no. | R– | Quant. taken, g. Aldehyde | Quant. taken, g. Diene | Reflux hr. (in MeOH) | Solv. for recrystn. | M.p., °C., dec. | Yield, % | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X |  | 1.47[a] | 1.0 | 4.0 | Petrol. eth.[b] | 187–188 | 55.6 | 91.04 | 91.13 | 5.37 | 5.66 | | |
| XI |  | 0.60 | 1.0[a] | 1.75 | Methanol | 242–243 | 85 | 91.91 | 91.96 | 5.34 | 5.41 | 2.75 | 2.71 |
| XII |  | .50 | 1.18 | 0.75 | Bz.-pet. eth.[b] | 226.5–227.5 | 79.7 | 91.91 | 92.06 | 5.34 | 5.42 | 2.75 | 2.73 |
| XIII |  | .30 | 0.70 | 3.0 | Bz.-pet. eth.[b] | 210–210.5 | 41 | 91.91 | 91.92 | 5.34 | 5.51 | 2.75 | 2.66 |
| XIV |  | .50 | 1.15 | 0.5 | Bz.-pet. eth.[b] | 229.5–230 | 72.3 | 86.18 | 85.68 | 4.89 | 5.22 | 2.72 | 2.84[c] |

[a] This aldehyde was prepared by N. Picus. [b] B.p. 90–100°. [c] Calcd. for $C_{37}H_{25}NS$: S, 6.22. Found: S, 6.19

XIII were quaternized with methyl iodide to give the corresponding ionic compounds XV and XVI.



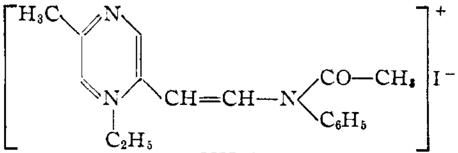
XIII



XV

It is noteworthy that attempts to prepare fulvenes by the condensation of tetracyclone with active methyl or active methylene groups were unsuccessful. The only reported reactions of this carbonyl group are those of organometallic reagents,[9–12] *p*-nitrophenylhydrazine,[13] 2,4-dinitrophenylhydrazine[14] and certain reducing agents.[13] The unsuccessful attempts to effect a condensation with tetracyclone were with (1) 3-ethyl-2-methylbenzothiazolium iodide (a) in acetic anhydride at reflux for five minutes or for one hour, (b) as in (a) with added potassium acetate, (c) in ethanol with piperidine or a mixture of piperidine and pyridine, (d) in dioxane with concentrated sulfuric acid, (e) in acetic anhydride at 175° for 15 hours; with (2) 2-methylbenzothiazole and zinc chloride at 225° for one-half hour or for eight hours. The low reactivity of the carbonyl group in tetracyclone may find an explanation in the distribution of the positive charge of the carbon of the carbonyl group over the rest of the molecule[15,16] or in steric hindrance due to the 2- and 5-phenyl groups.

Both Kendall[17,18] and Piggott and Rodd[19,20] have described the condensation of β-acetanilidovinyl compounds with compounds having active methyl groups. Kendall[17] also has described the condensation of quaternized methylmercapto (or seleno) heterocycles with active methylene compounds to give substituted fulvenes. Each of these procedures was applied successfully to tetraphenylcyclopentadiene to give heterocyclic-containing fulvenes. Thus, 3-methyl-2-methylmercaptobenzothiazolium iodide (C) and the β-acetanilidovinyl compounds (D-G, respectively) from 3-ethyl-2-methylbenzoxazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methylbenzoselenazolium and 1-ethyl-2-methylquinolinum iodides reacted with I to give



XXII

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[9] K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

[10] A. Löwenbein and G. Ulich, *Ber.*, **58**, 2662 (1925).

[11] E. C. Schreiber and E. I. Becker, THIS JOURNAL, **76**, 3354 (1954).

[12] A. G. Bonagura, M. B. Meyers, S. J. Storfer and E. I. Becker, *ibid.*, **76**, 6122 (1954).

[13] N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, *ibid.*, **75**, 2283 (1953).

[14] W. Josten, *Ber.*, **71B**, 2230 (1938).

[15] S. B. Coan, D. E. Trucker and E. I. Becker, THIS JOURNAL, **75**, 900 (1953).

[16] A. Di Giacomo and C. P. Smyth, *ibid.*, **74**, 4411 (1952).

[17] J. D. Kendall (to Ilford Ltd.), U. S. Patent 2,153,927, April 11, 1939.

[18] J. D. Kendall (to Ilford Ltd.), U. S. Patent 2,265,174, December 9, 1941.

[19] Imperial Chemical Industries, H. A. Piggott and E. H. Rodd, British Patent 344,409, March 4, 1931.

[20] Imperial Chemical Industries, H. A. Piggott and E. H. Rodd, British Patent 354,898, August 20, 1931.

the corresponding fulvenes XVII to XXI. Several attempts to condense I with 2-(β-acetanilidovinyl)-1-ethyl-2-methylpyrazinium iodide (XXII) were unsuccessful.

The colors of the fulvenes obtained ranged from orange-red to brown.

## Experimental[21]

**General.**—Most of the aldehydes and acetanilidovinyl compounds employed here were prepared according to literature procedures and are given here with a melting point and the literature reference. Where discrepancies were apparent, analytical data are given here. A typical condensation reaction to give a fulvene also is described.

TABLE III

QUATERNARY NITROGEN BASES (C–G) UTILIZED IN PREPARATION OF HETEROCYCLIC FULVENES (B)

| | R | B | D | *n* |
|---|---|---|---|---|
| C | $-CH_3$ | $-SCH_3$ | S | 0 |
| D | $-C_2H_5$ | $-N(C_6H_5)COCH_3$ | O | 1 |
| E | $-C_2H_5$ | $-N(C_6H_5)COCH_3$ | S | 1 |
| F | $-C_2H_5$ | $-N(C_6H_5)COCH_3$ | Se | 1 |
| G | $-C_2H_5$ | $-N(C_6H_5)COCH_3$ | —CH=CH— | 1 |

TABLE IV

6-HETEROCYCLIC-SUBSTITUTED FULVENES

| | Starting materials | | | | Products | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Prod. no. | Hetero-cyclic base[a] | Quant. taken, g. | Reflux time, hr.[b] | Solv. for recrystn. | M.p., °C., dec. | Yield, % | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
| XVII[c] | C[d] | 4.0 | 16 | Pet. eth. (90–100°)-bz. | 346–350 | 77.5 | 85.84 | 85.87 | 5.26 | 5.33 | 2.71 | 2.64 |
| XVIII | D[e] | 0.87 | 7.25[g] | Methanol-bz.[f] | 244.5–255.5 | 9.3 | 88.69 | 88.49 | 5.77 | 5.74 | 2.59 | 2.43 |
| XIX | E[e] | .90 | 1 | Pet. eth. (90–100°)-bz. | 277–279 | 56 | 86.14 | 86.20 | 5.60 | 5.69 | 2.51 | 2.68 |
| XX | F[e] | .97 | 1 | Washed with methanol | 278–279 | 50 | 79.45 | 79.36 | 5.17 | 5.31 | 2.32 | 2.42 |
| XXI | G[e] | .89 | 3 | Pet. eth. (90-100°)-bz. | 283–285 | .. | 91.43 | 91.32 | 6.03 | 5.92 | 2.54 | 2.66 |

[a] Refer to Table III for structure. [b] Methanol solvent except where indicated. [c] Prepared by D. E. Trucker. [d] Diene taken, 1.8 g. [e] Diene taken, 0.74 g. [f] Chromatographed on Alcoa F-20 activated alumina (benzene as solvent and developer) prior to recrystallization. [g] Dry isopropyl alcohol.

**Starting materials:** tetraphenylcyclopentadiene had m.p. 179–180°[9]; *p*-dimethylaminocinnamaldehyde, m.p. 133–137.5° (reported m.p. 133–140°,[7,22] m.p. 141°[8]). Quinoline-2-carboxaldehyde was prepared both by the selenium dioxide oxidation of quinaldine[23,24] and *via* 2-quinolyltribromomethane,[25–27] m.p. 71° (reported m.p. 69–70°,[28] m.p. 70–71°[29]). Quinoline-4-carboxaldehyde had m.p. 51–52°[23,24]; quinoline-6-carboxaldehyde, m.p. 75–76°.[30] 3-Ethyl-2-methylbenzoselenazolium iodide was prepared by quaternizing 2-methylbenzoselenazole[31] with ethyl iodide in a sealed tube for one hour at 130°.[32]

**Benzothiazole-2-carboxaldehyde** was prepared from directions for the selenium dioxide oxidation of 2-methylbenzothiazole as taken from the literature[33]; m.p. 75–77° (reported m.p. 65°[33]).

*Anal.* Calcd. for $C_8H_5NOS$: C, 58.88; H, 3.09; N, 8.58; S, 19.65. Found: C, 59.05; H, 2.96; N, 8.70; S, 19.76.

**Condensation of Aldehydes with I.**—The procedure was standardized for each aldehyde and the results are given in Tables I and II. As a typical example the preparation of III follows: A solution of 0.50 g. (1.35 mmoles) of tetraphenylcyclopentadiene and 1.0 g. (7.3 mmoles) of *p*-anisaldehyde in 25 ml. of dry methanol was refluxed under a calcium chloride guard tube while 50 ml. of a 4% methanolic solution of sodium methoxide was added dropwise during ten minutes. After two hours additional refluxing the solution was cooled, filtered and washed with dry methanol until the washings were almost colorless. The brown-red solid was recrystallized from petroleum ether (b.p. 90–100°) to give 0.60 g. (1.2 mmoles, 88%) of product, m.p. 199–199.5°.

**Quaternization of Basic Fulvenes. XVI.**—A solution of 0.30 g. (0.59 mmole) of XII in 7 ml. of methyl iodide was allowed to stand at room temperature for two days and then refluxed for one-half hour. Ether was added to the cooled solution precipitating the product, which was recrystallized from ethanol to give 0.35 g. (0.54 mmole, 91%) of dark orange product, m.p. 264–265° dec.

*Anal.* Calcd. for $C_{40}H_{30}IN$: C, 73.73; H, 4.64; N, 2.15. Found: C, 74.14; H, 4.88; N, 2.22.

**Quaternization of Basic Fulvenes. XV.**—A solution of 0.070 g. (0.137 mmole) of XIII in 4 ml. of methyl iodide was refluxed for 2.5 hours and then allowed to stand at room temperature for two days. Ether was added precipitating the product, which was recrystallized from methanol to give a mixture of dark, wine-colored plates and golden-brown needles, 0.050 g. (0.077 mmole, 56%). The melting points of the differently colored crystals were the same and they may thus be polymorphic forms.

*Anal.* Calcd. for $C_{40}H_{30}IN$: C, 73.73; H, 4.64; N, 2.15. Found: C, 73.07; H, 4.58; N, 2.12.

**Condensation of I with Quaternized Heterocyclic Compounds.**—The conditions for each reaction are given in Table IV. The general procedure for isolation of the products was the same as that used for the condensations of I with aldehydes.

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[21] Analyses by Drs. Weiler and Strauss, 164 Banbury Road, Oxford, England, and Dr. K. Ritter, Postfach, Basel 2, Switzerland.

[22] This wide melting point may be due to either a *cis–trans* mixture or to a mixture of polymorphic forms. In any case on remelting, the melting point rises to the higher value.

[23] C. E. Kwartler and H. G. Lindwall, THIS JOURNAL, **59**, 524 (1937).

[24] H. Kaplan, *ibid.*, **63**, 2654 (1941).

[25] D. L. Hammick, *J. Chem. Soc.*, 2882 (1923).

[26] D. L. Hammick, *ibid.*, 1302 (1926).

[27] We are happy to express our thanks to Mr. C. V. Clemency who prepared a sample according to this procedure.

[28] C. A. Buehler and J. O. Harris, THIS JOURNAL, **72**, 5015 (1950).

[29] W. v. Miller and J. Spady, *Ber.*, **18**, 3402 (1885).

[30] V. M. Rodionov and M. A. Berkengeim, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 330 (1944); *C. A.*, **39**, $4077^1$ (1945).

[31] H. Bauer, *Ber.*, **46**, 92 (1913).

[32] We express our thanks to Dr. S. Beinfest for the specific directions and for certain modifications of the procedure of footnote 31.

[33] W. Borsche and W. Doeller, *Ann.*, **537**, 53 (1939). No reason for the discrepancy in the melting points was apparent.