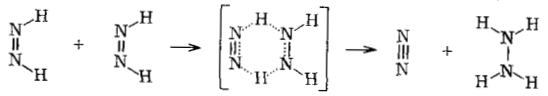
whereas the newly discovered disproportionation according to route B can be regarded as a hydrogenation of an azo double bond [4]. The structure *(3)* can be considered as a transition state, especially since diimide produced from benzenesulfonylhydrazide hydrogenates added tolane stereospecifically to give *cis*-stilbene in at least 95 % yield, according to infrared analysis.



*(3)*

The consequences of this auto-hydrogenation are currently being investigated.

Received, February 13th, 1963 [Z 449/279 IE]

[1] *S. Hünig* and *H. R. Müller*, Ph. D. thesis, Universität Würzburg 1962.

[2] *S. Hünig* and *W. Thier*, Diplom thesis, Universität Würzburg 1963.

[3] *S. Hünig* et al., Tetrahedron Letters *11*, 353 (1961); *E. J. Corey* et al., *ibid. 11*, 347 (1961); *E. E. van Tamelen* et al., J. Amer. chem. Soc. *83*, 3725 (1961).

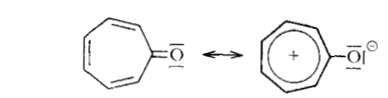
[4] *F. Raschig*, Angew. Chem. *23*, 972 (1910).

## New Heptafulvene Derivatives

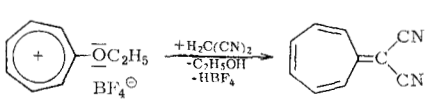
By Prof. Dr. K. Hafner, Dr. H. W. Riedel, and Dipl.-Chem. M. Danielisz

Chemisches Institut der Universität Marburg (Germany)

We have found that the reactivity of the carbonyl group in cycloheptatrienone *(1)* can be increased by *O*-alkylation. With triethyloxonium fluoroborate [1], *(1)* gives a quantitative yield of ethoxytropylium fluoroborate *(2)* (m.p. 40 °C), which reacts smoothly with malonic dinitrile in the presence of bases to form thermostable orange 8,8-dicyano-, heptafulvene *(3)* (m.p. 200 °C; $\lambda_{max}$ = 252 (log ε = 3.98). 368 (4.26), 374 (4.27), and 381 (4.27) mμ in n-hexane) [2]. Other reactive methylene compounds also react thus with compound *(2)* to yield heptafulvene derivatives.



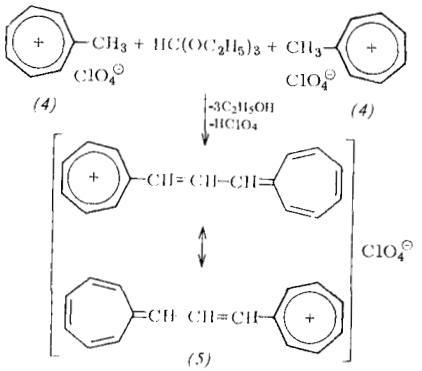
a *(1)* b



*(2)* *(3)*

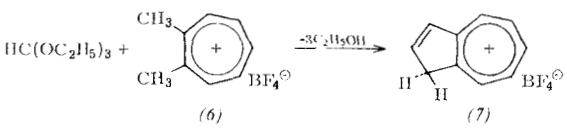
Heptafulvene derivatives also result from condensation of methylated tropylium salts with orthoesters of carboxylic acids or their vinylogs in acetic anhydride [3]. Methyltropylium perchlorate *(4)* and triethyl orthoformate yield the deep blue [3-(cycloheptatrienylidene)allyl]tropylium perchlorate *(5)* (decomp. > 200 °C; $\lambda_{max}$ = 604 mμ; log ε = 4.1 in acetonitrile), a non-benzenoid isomer of the diarylpolymethine-carbonium salts [4].

Analogous colored salts are formed from compound *(4)* and azulene-1-aldehyde (deep blue crystals, decomp. > 150 °C; $\lambda_{max}$ = 632 mμ; log ε = 3.7 in acetonitrile) and *p*-dimethylaminobenzaldehyde (deep blue crystals, decomp. > 150 °C; $\lambda_{max}$ = 657 mμ; log ε = 3.76 in acetonitrile).



*(4)* *(4)* *(5)*

1,2-Dimethyltropylium fluoroborate *(6)* reacts with ethyl orthoformate in acetic anhydride to give the known azulenium fluoroborate *(7)* [5].



*(6)* *(7)*

Received, February 13th, 1963 [Z 448/278 IE]

[1] Cf. *H. Meerwein* et al., Liebigs Ann. Chem. *641*, 1 (1961).

[2] Compound *(3)* has also been prepared by another route by *T. Nozoe* et al., see *J. W. Cook*, Progr. org. Chemistry *5*, 159 (1961).

[3] *K. Hafner* et al., Liebigs Ann. Chem. *624*, 37 (1959); *650*, 80 (1961); Angew. Chem. *71*, 378 (1959).

[4] *K. Hafner* and *H. Pelster*, Angew. Chem. *73*, 342 (1961).

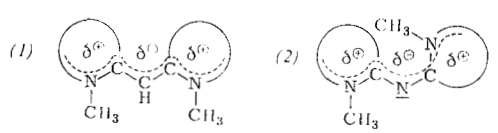
[5] *K. Hafner* et al., Liebigs Ann. Chem. *650*, 62 (1961).

## Investigations of Cyanine Dyes by P.M.R. Spectroscopy

By Dr. H. J. Friedrich

Chemisches Institut der Universität Würzburg (Germany)

Cyanine dyestuffs of type *(1)* can occur in geometrically isomeric forms and for steric reasons mostly exist in one fixed configuration under normal conditions [1]. Proton resonance of the $\delta^{\oplus}\rangle N-CH_3$ group is particularly suitable for determining this configuration and for investigating its geometric isomerism [2].



*(1)* *(2)*

Symmetrical methinecyanines with a planar structure and an all-*trans*-configuration [1] *e.g. N,N'*-dimethylpseudoisocyanine or *N,N'*-dimethyl-dibenzoxazolo-monomethinecyanine, give a single $\delta^{\oplus}\rangle N-CH_3$ proton-resonance signal. Two different $\delta^{\oplus}\rangle N-CH_3$ resonance signals are observed with formally symmetrical, but for steric reasons non-planar derivatives, *e.g. meso*-substituted *N,N'*-dimethyldibenzthiazolomonomethinecyanines. Similarly, formally symmetrical planar cyanines with a mono-*cis*-configuration [1], *e.g. N,N'*-dimethyldipyridomonomethinecyanine, give two different $\delta^{\oplus}\rangle N-CH_3$ signals.

The P.M.R. spectra show that all the azacyanines so far investigated exist (for an as yet unknown reason) in the mono-*cis*-form *(2)*, *e.g.* the *N,N'*-dimethylmono-azacyanines containing pyridine, quinoline, and benzthiazole rings. This surprising result is supported even further by ultraviolet and infrared spectroscopic findings.



Hafner, Klaus: New Heptafulvene Derivatives aus Angewandte Chemie international Edition 2, Jahrgang 1963, Nr. 4
Copyright © 1963 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim