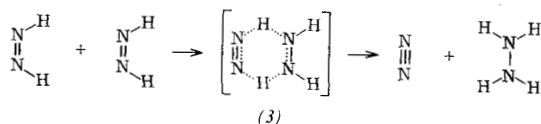


whereas the newly discovered disproportionation according to route B can be regarded as a hydrogenation of an azo double bond [4]. The structure (3) can be considered as a transition state, especially since diimide produced from benzenesulfonylhydrazide hydrogenates added toluene stereospecifically to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



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

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[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).

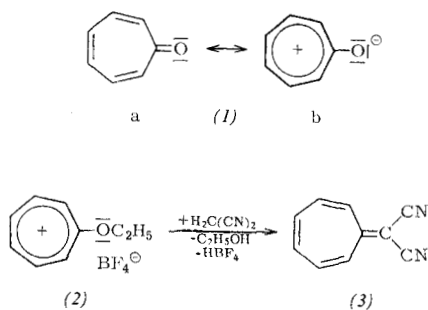
[4] F. Raschig, *Angew. Chem.* 23, 972 (1910).

New Heptafulvene Derivatives

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

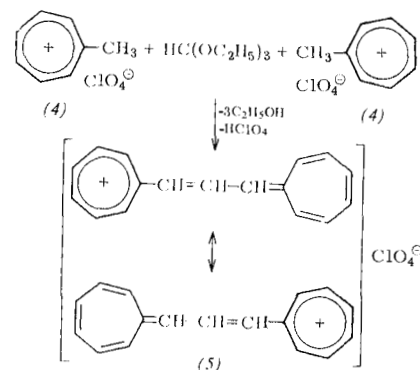
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We have found that the reactivity of the carbonyl group in cycloheptatrienone (1) can be increased by *O*-alkylation. With triethyloxonium fluoroborate [1], (1) gives a quantitative yield of ethoxytropylium fluoroborate (2) (m.p. 40 °C), which reacts 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 $\epsilon = 3.98$), 368 (4.26), 374 (4.27), and 381 (4.27) m μ in *n*-hexane) [2]. Other reactive methylene compounds also react thus with compound (2) to yield heptafulvene derivatives.

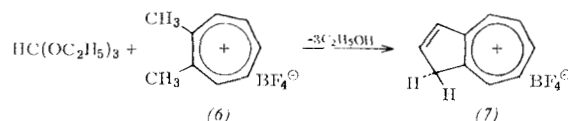


Heptafulvene derivatives also result from condensation of methylated tropylium salts with orthoesters of carboxylic acids or their vinylogs in acetic anhydride [3]. Methyltropylium perchlorate (4) and triethyl orthoformate yield the deep blue [3-(cycloheptatrienylydene)allyl]tropylium perchlorate (5) (decomp. > 200 °C; $\lambda_{\max} = 604$ m μ ; log $\epsilon = 4.1$ 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; $\lambda_{\max} = 632$ m μ ; log $\epsilon = 3.7$ in acetonitrile) and *p*-dimethylaminobenzaldehyde (deep blue crystals, decomp. > 150 °C; $\lambda_{\max} = 657$ m μ ; log $\epsilon = 3.76$ in acetonitrile).



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



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[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).

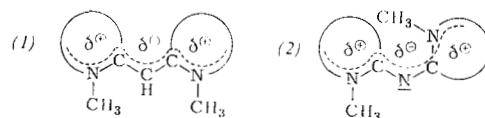
[5] K. Hafner et al., *Liebigs Ann. Chem.* 650, 62 (1961).

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

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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 δ^{\oplus} N-CH₃ group is particularly suitable for determining this configuration and for investigating its geometric isomerism [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 δ^{\oplus} N-CH₃ proton-resonance signal. Two different δ^{\oplus} N-CH₃ 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 δ^{\oplus} N-CH₃ 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.