Wieland reaction, on the other hand, proceeds successfully with toluene, benzene, chlorobenzene and ethylbenzoate.

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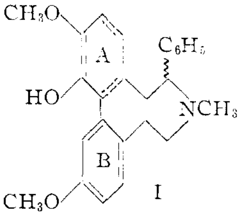
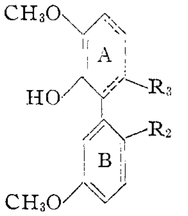
RECEIVED MARCH 18, 1957

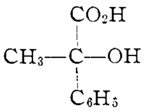
ASYMMETRIC INDUCTION AND ABSOLUTE CONFIGURATION IN THE BIPHENYL SERIES

Sir:

Methylmagnesium iodide converts the phenylglyoxylates of phenyldihydrothebaine (I) and its derivatives (IIa-c) (absolute configurations[1] as shown) to atrolactic esters. Saponification and isolation without optical fractionation give (–)-atrolactic acid (III) (absolute configuration[2] as shown) in optical yields of 70% from I and 91, 89, and 93%, respectively, from IIa-c. These are the highest optical yields known in the reactions of α-ketoesters with Grignard reagents.

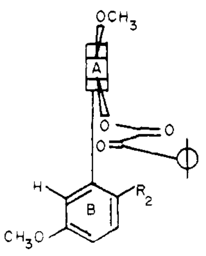

I

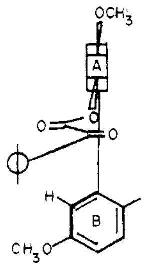



$$\begin{array}{c} CO_2H \\ | \\ CH_3-C-OH \\ | \\ C_6H_5 \end{array}$$
III

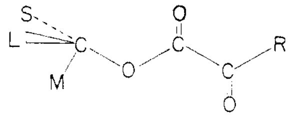
IIa, $R_2 = CH{=}CH_2$; $R_3 = CH_2CH(C_6H_5)N(CH_3)_2$
b, $R_2 = C_2H_5$; $R_3 = CH_2CH(C_6H_5)N(CH_3)_2$
c, $R_2 = CH{=}CH_2$; $R_3 = CH{=}CHC_6H_5$

The formation of III is most reasonably explained on the consideration that most of the product is derived from the two most stable ground state conformations IV and V, in which repulsive interactions are minimized by disposition of the two keto groups coplanar-transoid and the plane of the phenylglyoxylate chain as far away as possible from the ring A methoxyl and ring B, *i.e.*, perpendicular to ring A and at a dihedral angle of 60° with respect to ring B. Approach to the keto carbonyl group in IV and V by the attacking methyl must occur from the direction of ring A, since the underside of the keto group is shielded by ring B. If the rotational barrier between IV and V is high, the major proportion of the product is derived from V, which is more stable than IV because the phenylglyoxylate chain interferes with H instead of R. If the rotational barrier is low compared to the energy of activation for chemical reaction, the product proportions are controlled by the difference in free energy between the transition states derived from IV and V.[3] That from V is the more stable, since in it, the compression of the groups attached to the keto carbonyl as the latter begins to become tetrahedral is against H, whereas in that from IV, this compression is against the large group R. When the effective bulk of R increases (I → II), the stereoselectivity increases. A number of alternative interpretations ascribing special stability to other conformations because of chelate complexing, appear less probable. In particular, the conformation in which each carbonyl group is complexed with a ring methoxyl, and the plane of the phenylglyoxylate residue is perpendicular to ring A and parallel to ring B, would also lead to III. However, in order to explain on this basis the fact that the stereoselectivities with the phenylglyoxylates of IIa-c are 3.5 to 5.8 times greater than with that of I it is necessary to assume that the degree of complexing is less in the latter case. There is no obvious reason why this should be so and, at present, this alternative, while not rigorously excluded, appears unlikely.


IV


V

In elegant studies, McKenzie, Prelog, Turner and their respective co-workers have examined a large number of reactions of the general type R_1-$COCO_2R_a + R_2MgX \rightarrow \rightarrow R_1R_2C(OH)CO_2H$. In eighteen such cases, complete resolution data are available on the product hydroxyacid and, using these, we have now calculated optical yields.[4] For a fixed asymmetric group (R_a), the optical yield is quite insensitive to the size of the incoming group (R_2), but becomes larger as the size of the group (R_1) *already attached* to the keto group increases. This phenomenon requires modification of the previously proposed[5] shielding effect theory of asymmetric induction in α-ketoesters. It is most readily encompassed by the hypothesis that the relative contribution to the total product made by conformation VI diminishes with increasing size of R_1 because of compression effects of the type discussed above.



VI

We are indebted to the National Science Foundation for financial support.

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[1] J. A. Berson, THIS JOURNAL, **78**, 4170 (1956).

[2] *Cf.* J. H. Brewster, *ibid.*, **78**, 4061 (1956).

[3] *Cf.* D. Y. Curtin, *Rec. Chem. Progress*, **15**, 111 (1954); D. Y. Curtin and M. C. Crew, THIS JOURNAL, **77**, 354 (1954).

[4] Complete literature references will be given in a forthcoming publication.

[5] V. Prelog, *Bull. soc. chim.*, 987 (1956), and references cited therein.

DEPARTMENT OF CHEMISTRY
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LOS ANGELES 7, CALIFORNIA MICHAEL A. GREENBAUM

RECEIVED FEBRUARY 9, 1957

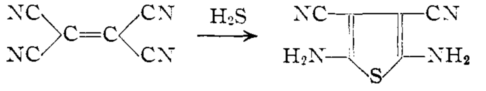
CYANOCARBON CHEMISTRY—SYNTHESIS AND CHEMISTRY OF TETRACYANOETHYLENE

Sir:

Investigation of cyanocarbons, compounds containing only —C≡N groups attached to carbon, and their derivatives has led to the preparation of tetracyanoethylene (I), the first example of a percyanoölefin. This compound has been shown to be exceptionally reactive and readily undergoes a series of addition and substitution reactions.

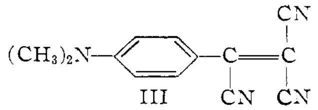
Treatment of dibromomalononitrile–potassium bromide complex[1] with copper powder in benzene under reflux yielded tetracyanoethylene in 65% yield. The product is a white crystalline solid melting at 198–200° in a sealed tube and subliming readily at temperatures above about 120°. (*Anal.* Calcd. for C_6N_4: C, 56.26; N, 43.74; mol. wt., 128. Found: C, 56.42, 56.39; N, 43.23, 43.50; mol. wt., 132.) Tetracyanoethylene is very stable thermally, being unchanged by brief treatment at 600°, and it is resistant to the action of oxygen at moderate temperatures, although it will burn in air.

Tetracyanoethylene is a mild oxidizing agent and converts mercaptans to disulfides, being itself reduced to tetracyanoethane in the process. By treatment with hydrogen sulfide in the presence of pyridine, tetracyanoethylene is converted readily to 2,5-diamino-3,4-dicyanothiophene (II) (92% yield). (*Anal.* Calcd. for $C_6H_4N_4S$: N, 34.13; S, 19.53. Found: N, 34.06, 34.22; S, 19.37.)

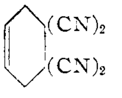


I II

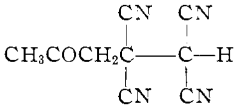
It also reacts with alcohols to give 2,2-dicyanoketene acetals and with N,N-dialkylanilines to give *p*-tricyanovinylaryl amines, a new class of dyes of high tinctorial strength. For example, *p*-tricyanovinyl-N,N-dimethylaniline (III), m.p. 173–175°, has λ_{max} 514 mμ and ϵ_{max} 41,500. (*Anal.* Calcd. for $C_{13}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21. Found: C, 70.31; H, 4.51; N, 25.11.)



Tetracyanoethylene is a very active dienophile, condensing quantitatively with butadiene at 0° to give 4,4,5,5-tetracyanocyclohexene (IV), m.p. 201–202°. (*Anal.* Calcd. for $C_{10}H_6N_4$: C, 65.92; H, 3.32; N, 30.76. Found: C, 65.84, 65.67; H, 3.44, 3.42; N, 30.59, 30.65.)[2] Monoalkylation of ketones having hydrogen alpha to a carbonyl group occurs in the presence of acid catalysts to give α-tetracyanoethyl ketones.[3] For example with acetone in the presence of boron trifluoride at room temperature, 4,4,5,5-tetracyano-2-pentanone (V) is formed in 90% yield; m.p. 118–120° dec. (*Anal.* Calcd. for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.10. Found: C, 58.26, 58.47; H, 3.21, 3.22; N, 30.04, 30.10.)



IV



V

Tetracyanoethylene slowly evolves hydrogen cyanide when exposed to moist air at room temperature.

A large number of other reactions of tetracyanoethylene and of related compounds are under investigation, and detailed reports on this research are being prepared for publication.

CONTRIBUTION NO. 417 FROM
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RECEIVED MARCH 25, 1957

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[1] L. Ramberg and S. Wideqvist, *Arkiv. Kemi, Mineral Geol.*, **12A**, No. 22, 12 pp. (1937); *C. A.*, **32**, 2511 (1938).

[2] R. E. Heckert and N. E. Searle, U. S. Patent 2,781,393 (1957).

[3] W. J. Middleton, U. S. Patent 2,762,837 (1956).

EFFECTS OF RING SIZE ON THE REACTIONS OF CYCLIC OLEFINS: HALOHYDRINS FROM METHYLENECYCLOALKANES[1]

Sir:

As part of a study of the effects of ring size on the orientations of addition reactions with cyclic olefins, we have included additions of hypohalous acids to a series of methylenecycloalkanes (ring sizes C_4 through C_7). Although we observed no orientation effects when hydrogen bromide was the addend,[2] significant differences were obtained with hypohalous acids. Additions of hypohalous acids to acyclic 1-alkenes always occur predominantly or exclusively with "normal" orientation (primary halogen).[3] We have found however that addition of HOCl to methylenecycloalkanes gives mixtures of chlorohydrins, with "abnormal" orientation predominating with the 4- and 6-membered ring compounds,[4] and that addition of HOBr to these olefins gives only "abnormally" oriented bromohydrins.

Freshly distilled aqueous HOCl or HOBr solution[5] was added in portions to a stirred aqueous suspension of an equivalent amount of methylenecycloalkane at 15°. The mixture was stirred for an hour longer and the layers were separated. The infrared spectrum of the dried organic layer was recorded before distillation. The fractions obtained on distillation were identified by comparison with authentic samples previously synthesized. Both the spectrum taken before distillation and the proportions of distillate in the fractions were used in estimating product distributions. These data are summarized in Table I. From isobutylene and HOBr we obtained a 77% yield of addition product which was about 97% 1-bromo-2-methyl-2-propanol.

---

[1] This work was supported in part by Research Corporation and in part by the Petroleum Research Fund of the American Chemical Society.

[2] J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

[3] For example, see P. B. D. la Mare and A. Salama, *J. Chem. Soc.*, 3337 (1956).

[4] Formation of 1-chlorocyclohexylmethanol only from methylenecyclohexane and HOCl has been reported by M. Tiffeneau, P. Weill and B. Tchoubar, *Compt. rend.*, **205**, 144 (1937).

[5] N-Bromosuccinimide could be substituted for HOBr solution without affecting product distributions. See C. O. Guss and R. Rosenthal, THIS JOURNAL, **77**, 2549 (1955).